

# APPLICATION OF THE METHOD OF PROJECTIVE REPRESENTATIONS TO THE ANALYSIS OF SECOND-ORDER RAMAN SCATTERING SPECTRA IN ENANTIOMORPHOUS TETRAGONAL CRYSTALS

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We propose a method to determine the selection rules for two-phonon transitions and zero-slope points in the Brillouin zone with the use of irreducible projective representations. The appropriate calculations are carried out for points  $\Gamma$ ,  $Z$ ,  $A$ ,  $M$ ,  $X$ , and  $R$  of the first Brillouin zone of tetragonal enantiomorphous crystals that are described by the space symmetry groups  $P4_12_12$  and  $P4_32_12$ . The results of these calculations are applied to the analysis of the spectra of two-phonon Raman scattering (RS) in the crystals of zinc and cadmium diphosphides,  $\alpha$ -ZnP<sub>2</sub> and CdP<sub>2</sub>, and paratellurite TeO<sub>2</sub>.

## 1. Introduction

Upon the study of phonons with wave vectors  $\vec{k}$  considerably exceeding the wave vectors of optical photons participating in the scattering, in particular phonons near the boundary of the first Brillouin zone, within the method of RS, informative are the spectra of RS with the simultaneous participation of two phonons (second-order spectra). As distinct from the first-order spectra (with the participation of one phonon) which can be analyzed with the use of representations of the corresponding point group of symmetry defining the crystal class (the factor-groups of a space symmetry group), one should use the space symmetry group to find the selection rules for second-order spectra.

In the present work, we describe a method for both the calculation of the selection rules for two-phonon RS spectra and the determination of points suspicious as for an extremum with the use of projective representations. As an example, we consider tetragonal enantiomorphous crystals, whose symmetry is described by space groups  $P4_12_12$  and  $P4_32_12$ . The method of projective representations was earlier used for the classification of one-phonon spectra of tetragonal crystals of zinc and cadmium diphosphides

[1]. The crystal structures described by the mentioned space groups are of special interest, because they have the highest symmetry among anisotropic and simultaneously gyrotropic crystals. This fact makes them to be convenient models for the approbation of the general methods of group-theoretic analysis of energy states in crystals.

The results of calculations are applied to the analysis of the second-order RS spectra of tetragonal crystals of zinc and cadmium diphosphides<sup>1</sup> derived in this work and those of paratellurite. Crystals of  $\alpha$ -ZnP<sub>2</sub> and CdP<sub>2</sub> are isostructural indirect-gap semiconductors [4, 5], whereas crystals of TeO<sub>2</sub> are a dielectric, whose structure [6] is significantly different from that of diphosphides.

## 2. Selection Rules and Zero-slope Points

By analyzing the second-order spectra, we consider the vibrations, which correspond to arbitrary points of the Brillouin zone (in particular, such that belong to the zone boundary) and whose wave vectors  $\vec{k}_1$  and  $\vec{k}_2$  satisfy the condition  $\vec{k}_1 + \vec{k}_2 = \vec{k}_{\text{phot}}$ . For tetragonal crystals, points  $\Gamma$ ,  $Z$ ,  $A$ ,  $M$ ,  $X$ , and  $R$  are of special interest, because these points are characterized by a high symmetry. For the determination of the selection rules of two-phonon transitions at these points and for the elucidation whether the mentioned points are zero-slope points, it is necessary to use the irreducible representations of the groups of wave vectors which define, in turn, the representations of the full space group [7]. The irreducible representations of the group of a wave vector can be constructed within the method of projective representations. Work [1] presents a method of construction of the irreducible projective

<sup>1</sup>Second-order RS spectra of crystals of  $\alpha$ -ZnP<sub>2</sub> and CdP<sub>2</sub> were earlier derived in [2, 3].

representations of groups  $P4_12_12$  and  $P4_32_12$  for points  $\Gamma$  and  $Z$ . By using this method, we determined the characters of the irreducible projective representations of these groups for the remaining points which are given in Appendix (Tables 1A-8A). Phonon states are described by the representations  $\Gamma_1 \div \Gamma_5$ ,  $Z_6$ ,  $Z_7$ ,  $(A_6 + A_7)$ ,  $(M_1 + M_4)$ ,  $(M_2 + M_3)$ ,  $M_5, X_5$ ,  $(R_1 + R_4)$ , and  $(R_2 + R_3)$ , where parentheses stand for the morganing of complex conjugate representations, which is conditioned by the account of the invariance of energy states with respect to the time inversion. In Tables 1A–8A, the double parentheses mean the doubling of representations upon the account of the invariance of states with respect to the time inversion. The morganing of representations and their doubling are caused by the degeneration on the Brillouin zone boundary in the absence of external magnetic and electric fields, and the appearance of this union is defined by the Herring criterion [7].

The selection rules for the processes of scattering with the creation of two phonons can be briefly written as

$$[D^2] \supset [V^2]_\alpha \quad \text{— for overtones,} \quad (1)$$

$$D_1 \times D_2 \supset [V^2]_\alpha \quad \text{— for combined tones.} \quad (2)$$

where  $D, D_1, D_2$  are the physically irreducible projective representations of vibrational wave functions, and  $[V^2]_\alpha$  are the irreducible representations of the second-order symmetrized tensor. That is, the symmetrized square  $[D^2]$  or the direct product of physically irreducible projective representations  $D_1 \times D_2$  of phonons participating in the act of scattering must contain an irreducible representation of the second-order symmetrized tensor.

In this case, the vectors  $\vec{k}_i$  and  $-\vec{k}_i$  of the star  $\{\vec{k}\}$  are equivalent. Therefore, according to [6], a formula for the determination of the selection rules for overtones takes the following form:

$$N_0^{\text{ovt}} = \frac{1}{2h} \sum_{g \in G_{\vec{k}}} \chi(g) \left[ \chi_{\vec{k}, \mu}^2(g) + K^2 f \chi_{\vec{k}, \mu}(g^2) \right], \quad (3)$$

where  $K^2 = +1$  — for the representations describing the states with integral spin,  $-1$  — for the representations describing the states with half-integral spin.  $f = 1$  — if the operator is even with respect to the time inversion,  $-1$ ,  $f$  the operator is odd with respect and  $\chi(g)$  is the character of the representation, by which the tensor of RS is transformed. For the determination of selection rules in the case of combined tones, we use the formula

$$N_0^{\text{combt}} = \frac{1}{h} \sum_{g \in G_{\vec{k}}} \chi(g) \chi_{\vec{k}, \nu}(g) \chi_{\vec{k}, \mu}(g). \quad (4)$$

In the absence of external magnetic fields, one should substitute the characters of morganed representations in all the formulas defining the selection rules. The selection rules derived in such a manner are presented in Table 1. For example, the combined tone  $Z_6 \times Z_6$  can be observed in the spectrum, whose polarization corresponds to modes  $\Gamma_1$  and  $\Gamma_5$ .

In order that the vibrational transition allowed by the selection rules for a certain point  $\vec{k}_0$  of the Brillouin zone be observed in the RS spectrum, this point should be also a point with high density of states. That is, the condition  $\left. \frac{dE(\vec{k})}{d\vec{k}_\alpha} \right|_{\vec{k}_0} = 0$  must be satisfied (in this case, the point  $\vec{k}_0$  is a zero-slope point of the dispersion curve of phonon states along the direction parallel to the wave vector  $\vec{k}_\alpha$ ). By using the  $\vec{k}\vec{p}$ -method [7], we studied whether the studied points are zero-slope points (the results are given in Table 2). For example, the dispersion curve corresponding to the representation  $\Gamma_5$  has zero slope in the plane normal to the  $z$  axis, whereas the curve corresponding to the same representation has nonzero slope along the  $z$  axis.

### 3. Experimental Results

We performed the measurements at room temperature with spectrometers DFS-24 and Coderg T-800 with a resolution of less than  $1 \text{ cm}^{-1}$  at  $\lambda=550 \text{ nm}$ . RS was induced by the emission of a one-mode He–Ne-laser LGN-222 ( $\lambda = 632.8 \text{ nm}$ ) with a power of 40 mW in the crystals of zinc and cadmium diphosphides and by the emission of an argon laser ILA ( $\lambda = 488 \text{ nm}$ ) with a power of 300 mW in the crystal of paratellurite (the derived spectra are presented in Figs. 1–5). The first-order RS spectra of the crystals of zinc and cadmium diphosphides (Fig. 1) and paratellurite (Fig. 2) are given for the same polarizations, at which we can observe the lines corresponding to overtones in second-order spectra. In the two-phonon RS spectra of the tetragonal crystals of  $\text{ZnP}_2$  and  $\text{CdP}_2$ , we can separate two regions: the high-frequency ( $500\text{--}1000 \text{ cm}^{-1}$ ) region for both crystals and the low-frequency one ( $150\text{--}270 \text{ cm}^{-1}$  for the crystal of  $\alpha\text{-ZnP}_2$  and  $100\text{--}230 \text{ cm}^{-1}$  for the crystal of  $\text{CdP}_2$ ).

In Fig. 3, we present the second-order RS spectra for the low-frequency regions of the crystals  $\text{ZnP}_2$  and  $\text{CdP}_2$ . It is worth noting that the spectra are observed only at the polarization, where the modes  $\Gamma_1$  are active.

**Table 1. Group-theoretic selection rules for two-phonon RS spectra for the tetragonal crystals of ZnP<sub>2</sub>, CdP<sub>2</sub> and TeO<sub>2</sub>**

| Point Brillouin zone | Overtones   | Combined tones   |
|----------------------|---|--|
| $\Gamma$             | $\Gamma_1 \subset [\Gamma_1^2], [\Gamma_2^2], [\Gamma_3^2], [\Gamma_4^2], [\Gamma_5^2]$<br>$\Gamma_3 \subset [\Gamma_5^2]$<br>$\Gamma_4 \subset [\Gamma_5^2]$<br>$\Gamma_5 \subset 0$                 | $\Gamma_1 \subset \Gamma_1 \times \Gamma_1, \Gamma_2 \times \Gamma_2, \Gamma_3 \times \Gamma_3, \Gamma_4 \times \Gamma_4, \Gamma_5 \times \Gamma_5$<br>$\Gamma_3 \subset \Gamma_5 \times \Gamma_5, \Gamma_1 \times \Gamma_3, \Gamma_2 \times \Gamma_4$<br>$\Gamma_4 \subset \Gamma_5 \times \Gamma_5, \Gamma_1 \times \Gamma_4, \Gamma_2 \times \Gamma_3$<br>$\Gamma_5 \subset \Gamma_1 \times \Gamma_5, \Gamma_2 \times \Gamma_5, \Gamma_3 \times \Gamma_5, \Gamma_4 \times \Gamma_5$ |
| $Z$                  | $\Gamma_1 \subset [Z_6]^2, [Z_7]^2$<br>$\Gamma_3 \subset 0$<br>$\Gamma_4 \subset 0$<br>$\Gamma_5 \subset [Z_6]^2, [Z_7]^2$  | $\Gamma_1 \subset Z_6 \times Z_6, Z_7 \times Z_7$<br>$\Gamma_3 \subset Z_6 \times Z_7$<br>$\Gamma_4 \subset Z_6 \times Z_7$<br>$\Gamma_5 \subset Z_6 \times Z_6, Z_7 \times Z_7, Z_6 \times Z_7$   |
| $A$                  | $\Gamma_1 \subset [(A_6 + A_7)^2]$<br>$\Gamma_3 \subset 0$<br>$\Gamma_4 \subset [(A_6 + A_7)^2]$<br>$\Gamma_5 \subset [(A_6 + A_7)^2]$  | $\Gamma_1 \subset (A_6 + A_7) \times A_6 + A_7$<br>$\Gamma_3 \subset (A_6 + A_7) \times A_6 + A_7$<br>$\Gamma_4 \subset (A_6 + A_7) \times (A_6 + A_7)$<br>$\Gamma_5 \subset (A_6 + A_7) \times (A_6 + A_7)$   |
| $M$                  | $\Gamma_1 \subset [(M_1 + M_4)^2], [(M_2 + M_3)^2]$<br>$\Gamma_3 \subset 0$<br>$\Gamma_4 \subset [(M_1 + M_4)^2], [(M_2 + M_3)^2]$<br>$\Gamma_5 \subset 0$  | $\Gamma_1 \subset (M_1 + M_4) \times (M_1 + M_4)$<br>$\Gamma_3 \subset (M_1 + M_4) \times (M_2 + M_3), M_5 \times M_5$<br>$\Gamma_4 \subset (M_1 + M_4) \times (M_1 + M_4)$<br>$\Gamma_5 \subset (M_1 + M_4) \times M_5, (M_2 + M_3) \times M_5$   |
| $X$ and $X'$         | $\Gamma_1 \subset [X_5^2]$<br>$\Gamma_3 \subset [X_5^2]$<br>$\Gamma_4 \subset [X_5^2]$<br>$\Gamma_5 \subset [X_5^2]$  | $\Gamma_1 \subset X_5 \times X_5$<br>$\Gamma_3 \subset X_5 \times X_5$<br>$\Gamma_4 \subset X_5 \times X_5$<br>$\Gamma_5 \subset X_5 \times X_5$   |
| $R$                  | $\Gamma_1 \subset [(R_1 + R_4)^2], [(R_2 + R_3)^2]$<br>$\Gamma_3 \subset [(R_1 + R_4)^2], [(R_2 + R_3)^2]$<br>$\Gamma_4 \subset 0$<br>$\Gamma_5 \subset [(R_1 + R_4)^2], [(R_2 + R_3)^2]$             | $\Gamma_1 \subset (R_1 + R_4) \times (R_1 + R_4), (R_2 + R_3) \times (R_2 + R_3)$<br>$\Gamma_3 \subset (R_1 + R_4) \times (R_1 + R_4), (R_2 + R_3) \times (R_2 + R_3)$<br>$\Gamma_4 \subset (R_1 + R_4) \times (R_2 + R_3)$<br>$\Gamma_5 \subset R_1 + R_4) \times (R_1 + R_4), (R_2 + R_3) \times (R_2 + R_3)$  |
| $R'$                 | $\Gamma_1 \subset [(R'_1 + R'_3)^2], [(R'_2 + R'_4)^2]$<br>$\Gamma_3 \subset [(R'_1 + R'_3)^2], [(R'_2 + R'_4)^2]$<br>$\Gamma_4 \subset 0$<br>$\Gamma_5 \subset [(R'_1 + R'_3)^2], [(R'_2 + R'_4)^2]$ | $\Gamma_1 \subset (R'_1 + R'_3) \times (R'_1 + R'_3)$<br>$\Gamma_3 \subset (R'_1 + R'_3) \times (R'_1 + R'_3)$<br>$\Gamma_4 \subset (R'_1 + R'_3) \times (R'_2 + R'_4)$<br>$\Gamma_5 \subset (R'_1 + R'_3) \times (R'_1 + R'_3)$   |

**Table 2. Zero-slope points of the energy dispersion curves of phonon states for groups P4<sub>1</sub>2<sub>1</sub>2 and P4<sub>3</sub>2<sub>1</sub>2**

| Representations of an appropriate point of the Brillouin zone | Number of components $\left. \frac{dE(\vec{k})}{dk_\alpha} \right _{\vec{k}_0} \neq 0$ |                               |                               |
|---|--|-------------------------------|-------------------------------|
|   | Along the $z$ axis   | Along the $x$ axis            | Along the $y$ axis            |
| $\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4$                      | 0  |                               | 0                             |
| $\Gamma_5$  | 1  |                               | 0                             |
| $Z_6, Z_7$  | 0  |                               | 0                             |
| $A_6, A_7$  | 1 — diagonal; 0 — nondiagonal  |                               | 1 — diagonal; 0 — nondiagonal |
| $M_1, M_2, M_3, M_4$  | 0 — diagonal; 0 — nondiagonal  |                               | 0 — diagonal; 0 — nondiagonal |
| $M_5$   | 0  |                               | 0                             |
|   | Along the $z$ axis   | Along the $x$ axis            | Along the $y$ axis            |
| $X_5$   | 0  | 1                             | 0                             |
| $R_1, R_2, R_3, R_4$  | 0 — diagonal; 0 — nondiagonal  | 0 — diagonal; 0 — nondiagonal | 0 — diagonal; 0 — nondiagonal |

The high-frequency region of the two-phonon spectra of diphosphides (Fig. 2) significantly differs from the low-frequency one. The spectra are observed at different polarizations and have intensities of the same order. Therefore, the assertion about the domination of modes  $\Gamma_1$  in this case [4] has no foundations, and the comparatively narrow lines (566.7; 718.9; 728.9; 858.6; 863.4; 902.3; 951.7; and 958.2 cm<sup>-1</sup> in the spectrum of the crystal of ZnP<sub>2</sub> and 511.2; 664.8; 835.0; 838.1; 887.1; and 937.4 cm<sup>-1</sup> in the spectrum of the crystal of CdP<sub>2</sub>) correspond, probably,

to vibrations of sufficiently long phosphorus chains [8]. The two-phonon spectrum of the crystal of paratellurite, as distinct from that of the crystals of ZnP<sub>2</sub> and CdP<sub>2</sub>, contains only the high-frequency region (Fig. 3) which is similar by its form to the high-frequency regions of the spectra of the crystals of zinc and cadmium diphosphides, though the crystal of TeO<sub>2</sub> has no substructural elements such as layered packets or sufficiently long chains, to whom we would refer the lines of 1435.6; 1472.8; 1513.3; 1555.6; and 1593.3 cm<sup>-1</sup>.

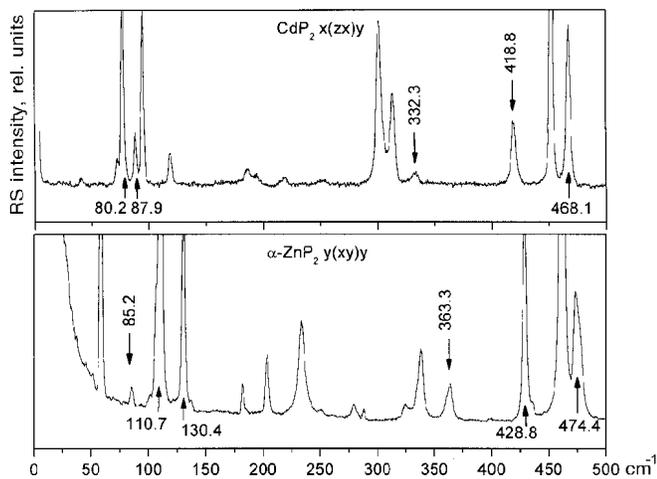


Fig. 1. First-order RS spectra in the crystals of  $\alpha$ -ZnP<sub>2</sub> and CdP<sub>2</sub>,  $T = 293$  K (it is practically impossible to observe the 80.2-cm<sup>-1</sup> line at the given polarization as distinct from the other lines shown in the figure)

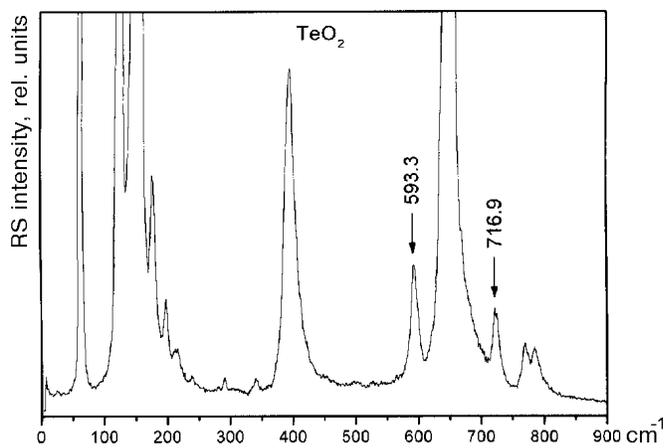


Fig. 2. First-order RS spectrum in the crystals of TeO<sub>2</sub>,  $T = 293$  K

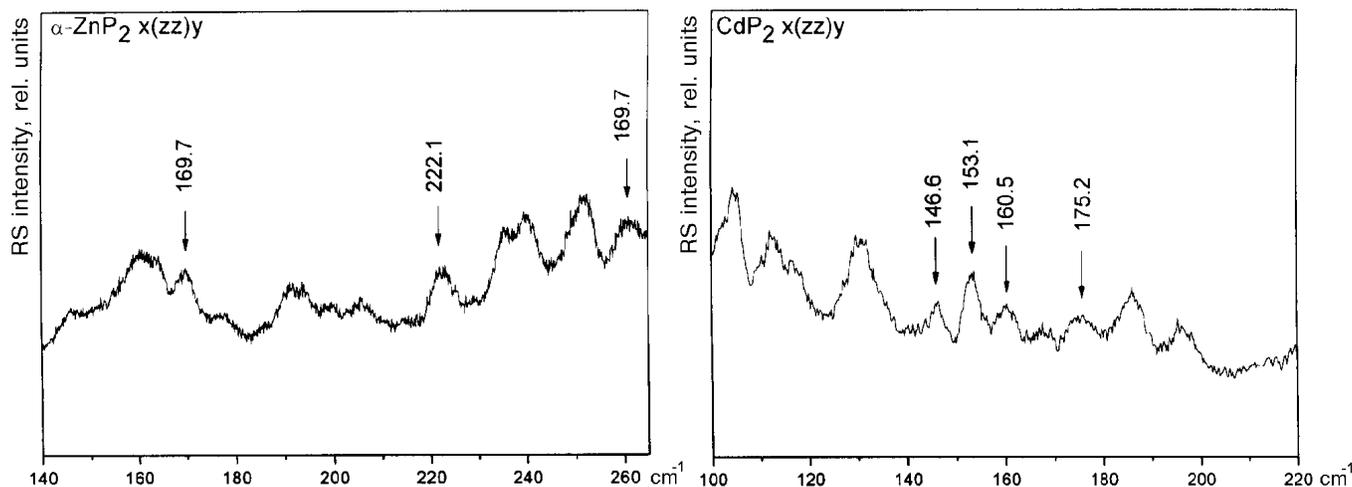


Fig. 3. Two-phonon RS spectra (the low-frequency region) in the crystals of  $\alpha$ -ZnP<sub>2</sub> and CdP<sub>2</sub>,  $T = 293$  K

#### 4. Conclusions

The derived selection rules together with the data on the zero-slope points of the dispersion curves of phonons for certain directions allow us to assume that the bands in second-order RS spectra can be associated with overtones in view of their relatively small half-widths. Indeed, it is improbable that two-phonon spectra contain the lines corresponding to the overtones of vibrations at point X, because the dispersion curves of phonon states have nonzero slope at this point along the direction  $\Gamma - X$ . On the other hand, we may assume

the possibility of the existence of a contribution of the vibrational transitions occurring with the participation of phonons at points A and M to second-order spectra. We emphasize once more that this conclusion concerns only overtones. The conclusion is based on the fact that, at the polarization  $x(xx+xy)z$ , the transitions occurring with the participation of the phonons of symmetries  $\Gamma_1$ ,  $\Gamma_3$ , and  $\Gamma_4$  are allowed. That is, the spectrum will have, with high probability, the intensity not less than that in other polarization-involved geometries. Indeed, the high-frequency section of the two-phonon spectrum at the mentioned polarization is most intense in the case of

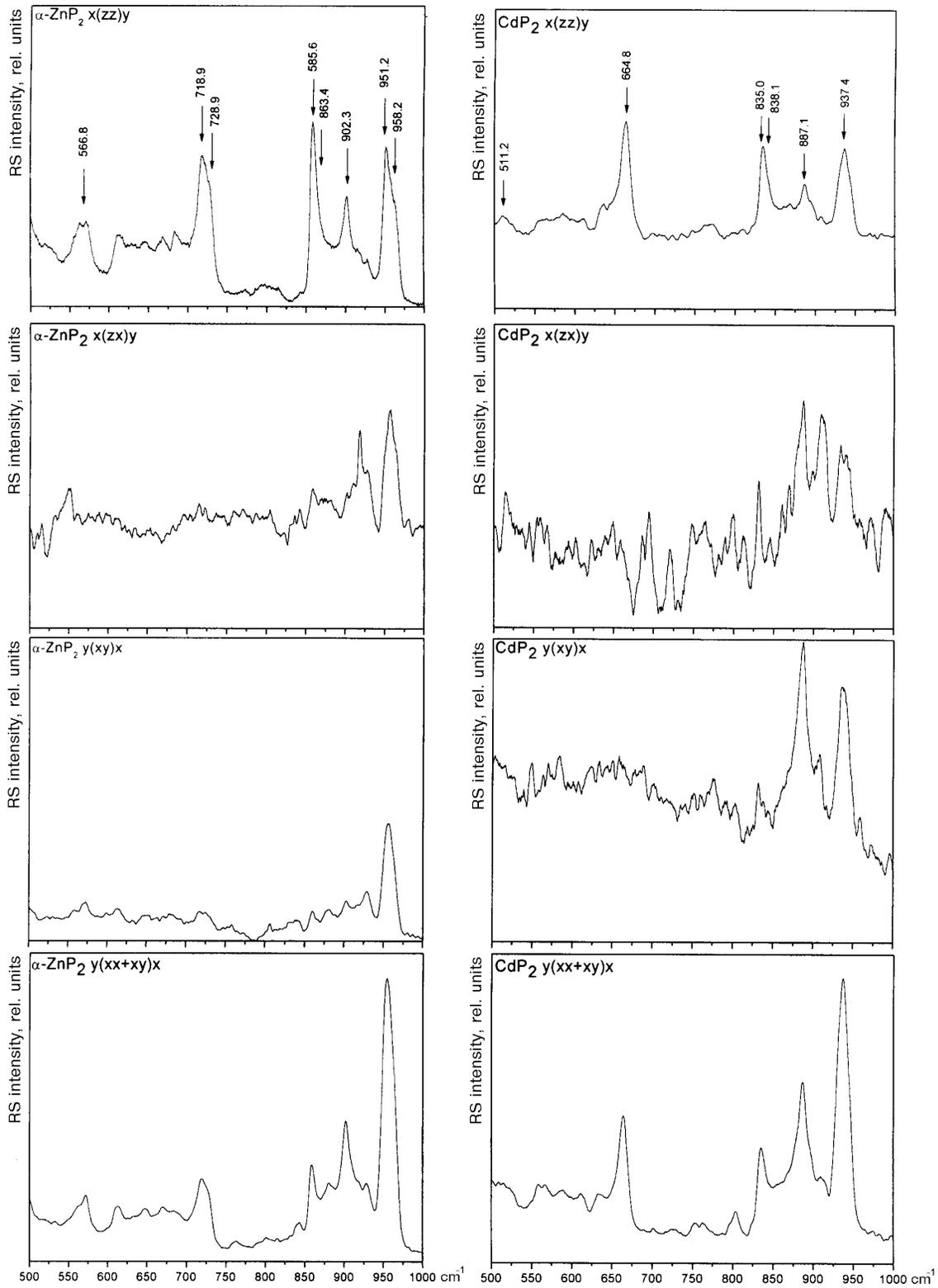


Fig. 4. Two-phonon RS spectra (the high-frequency region) in the crystals of  $\alpha$ -ZnP<sub>2</sub> and CdP<sub>2</sub>,  $T = 293$  K

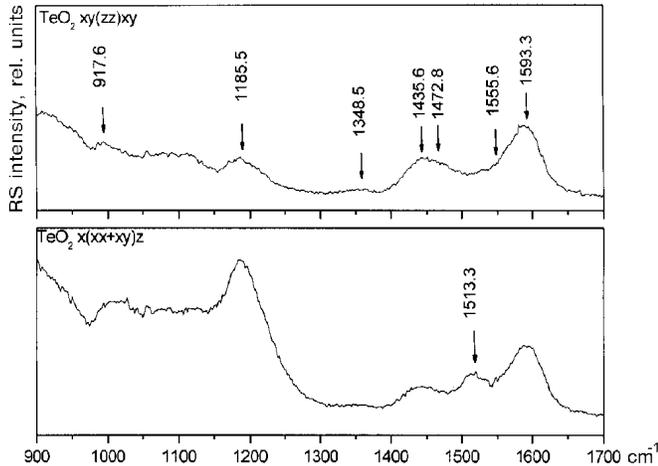


Fig. 5. Two-phonon RS spectra of the crystals of paratellurite,  $T = 293$  K

the crystals of  $\text{ZnP}_2$  and  $\text{CdP}_2$ . In addition, we observe the change of the ratio of the intensities of RS lines upon the passage to the other polarization-involved geometries (Fig. 3)

The lines of  $169.7$ ;  $222.1$ ;  $260.5$ ;  $728.9$ ;  $858.6$ ; and  $951.7$   $\text{cm}^{-1}$  in  $\text{ZnP}_2$ ;  $146.6$ ;  $153.1$ ;  $160.5$ ;  $175.2$ ;  $664.6$ ;  $835.3$ ; and  $937.1$   $\text{cm}^{-1}$  in  $\text{CdP}_2$ , and  $1185.5$ ;  $1435.6$ ; and  $1513.3$   $\text{cm}^{-1}$  in  $\text{TeO}_2$  can be considered to be the overtones of vibrations at the Brillouin zone center. They correspond to the scattering frequencies which are twice higher, in the limits of measurement errors, than the frequencies of vibrations observed in the first-order RS spectra of the crystals of  $\text{ZnP}_2$  and  $\text{CdP}_2$  and have comparatively small half-width. For the crystal of paratellurite, we make conclusion about the overtones of point  $\Gamma$  by basing on the fact that the high-frequency section of the spectra of this crystal is similar by structure to the spectra of diphosphides. As indicated above, we may assume basing on the selection rules for two-phonon transitions occurring in the crystals under study and on the ratios of the intensities of various lines at different polarizations ( $566.7$ ;  $718.9$ ;  $863.4$ ;  $902.3$ ; and  $958.2$   $\text{cm}^{-1}$  in the spectrum of the crystal of  $\text{ZnP}_2$ ;  $511.3$ ;  $887.3$ ;  $\text{cm}^{-1}$  in the spectrum of the crystal of  $\text{CdP}_2$ , and  $991.6$ ;  $1348.5$ ;  $1472.8$ ;  $1555.6$ ; and  $1593.3$   $\text{cm}^{-1}$  in the spectrum of the crystal of  $\text{TeO}_2$ ) that these lines correspond to points A and M of the Brillouin zone. For the crystal of  $\text{CdP}_2$ , we consider only two lines corresponding to the mentioned points, whereas we observe 5 such lines for the crystal of  $\text{ZnP}_2$ . This is related to the fact that the fine structure of similar lines in crystals of  $\text{CdP}_2$  is not seen, as it occurs in crystals of  $\text{ZnP}_2$ . The assertion that the spectra of paratellurite

and diphosphides are of the same type is supported by the facts that there exist two pairs of lines for the crystal of  $\text{TeO}_2$  and each pair forms the own common band.

## APPENDIX

**T a b l e 1A.** Characters of the irreducible projective representations of the group of a wave vector of groups  $P4_12_12$  and  $P4_32_12$  for point  $\Gamma$

| $422 (D_4)$ | Projective class | $e$ | $c_2$ | $c_4$       | $c_4^3$     | $(u_2)_1$ | $(u_2)_2$ | $(u'_2)_1$ | $(u'_2)_2$ |
|-------------|------------------|-----|-------|-------------|-------------|-----------|-----------|------------|------------|
| $\Gamma_1$  | $K_0$            | 1   | 1     | 1           | 1           | 1         | 1         | 1          | 1          |
| $\Gamma_2$  |                  | 1   | 1     | 1           | 1           | -1        | -1        | -1         | -1         |
| $\Gamma_3$  |                  | 1   | 1     | -1          | -1          | 1         | 1         | -1         | -1         |
| $\Gamma_4$  |                  | 1   | 1     | -1          | -1          | -1        | -1        | 1          | 1          |
| $\Gamma_5$  |                  | 2   | -2    | 0           | 0           | 0         | 0         | 0          | 0          |
| $\Gamma_6$  | $K_1$            | 2   | 0     | $\sqrt{2}$  | $-\sqrt{2}$ | 0         | 0         | 0          | 0          |
| $\Gamma_7$  |                  | 2   | 0     | $-\sqrt{2}$ | $\sqrt{2}$  | 0         | 0         | 0          | 0          |

**T a b l e 2A.** Characters of the irreducible projective representations of the group of a wave vector of groups  $P4_12_12$  and  $P4_32_12$  for point  $Z$

| $422 (D_4)$   | Projective class | $e$ | $c_2$ | $c_4$       | $c_4^3$     | $(u_2)_1$ | $(u_2)_2$ | $(u'_2)_1$ | $(u'_2)_2$ |
|---------------|------------------|-----|-------|-------------|-------------|-----------|-----------|------------|------------|
| $Z_1$         | $K_0$            | 1   | 1     | -1          | -1          | $i$       | $-i$      | $i$        | $-i$       |
| $Z_2$         |                  | 1   | 1     | -1          | -1          | $-i$      | $i$       | $-i$       | $i$        |
| $Z_3$         |                  | 1   | 1     | 1           | 1           | $i$       | $-i$      | $-i$       | $i$        |
| $Z_4$         |                  | 1   | 1     | 1           | 1           | $-i$      | $i$       | $i$        | $-i$       |
| $Z_5$         |                  | 2   | -2    | 0           | 0           | 0         | 0         | 0          | 0          |
| $Z_6$         | $K_1$            | 2   | 0     | $\sqrt{2}$  | $-\sqrt{2}$ | 0         | 0         | 0          | 0          |
| $Z_7$         |                  | 2   | 0     | $-\sqrt{2}$ | $\sqrt{2}$  | 0         | 0         | 0          | 0          |
| $(Z_1 + Z_2)$ | $K_0$            | 2   | 2     | -2          | -2          | 0         | 0         | 0          | 0          |
| $(Z_3 + Z_4)$ |                  | 2   | 2     | 2           | 2           | 0         | 0         | 0          | 0          |
| $Z_5$         |                  | 2   | -2    | 0           | 0           | 0         | 0         | 0          | 0          |
| $Z_6$         | $K_1$            | 2   | 0     | $\sqrt{2}$  | $-\sqrt{2}$ | 0         | 0         | 0          | 0          |
| $Z_7$         |                  | 2   | 0     | $-\sqrt{2}$ | $\sqrt{2}$  | 0         | 0         | 0          | 0          |

**T a b l e 3A.** Characters of the irreducible projective representations of the group of a wave vector of groups  $P4_12_12$  and  $P4_32_12$  for point A

| $422 (D_4)$   | Projective class | $e$ | $c_2$ | $c_4$        | $c_4^3$      | $(u_2)_1$ | $(u_2)_2$ | $(u'_2)_1$ | $(u'_2)_2$ |
|---------------|------------------|-----|-------|--------------|--------------|-----------|-----------|------------|------------|
| $A_1$         | $K_0$            | 1   | -1    | $-i$         | $i$          | 1         | 1         | $i$        | $i$        |
| $A_2$         |                  | 1   | -1    | $-i$         | $i$          | -1        | -1        | $-i$       | $i$        |
| $A_3$         |                  | 1   | -1    | $i$          | $-i$         | 1         | 1         | $-i$       | $-i$       |
| $A_4$         |                  | 1   | -1    | $i$          | $-i$         | -1        | -1        | $i$        | $i$        |
| $A_5$         |                  | 2   | 2     | 0            | 0            | 0         | 0         | 0          | 0          |
| $A_6$         | $K_1$            | 2   | 0     | $\sqrt{2}i$  | $-\sqrt{2}i$ | 0         | 0         | 0          | 0          |
| $A_7$         |                  | 2   | 0     | $-\sqrt{2}i$ | $\sqrt{2}i$  | 0         | 0         | 0          | 0          |
| $(A_1 + A_3)$ | $K_0$            | 2   | -2    | 0            | 0            | 2         | 2         | 0          | 0          |
| $(A_2 + A_4)$ |                  | 2   | -2    | 0            | 0            | -2        | -2        | 0          | 0          |
| $((A_5))$     |                  | 4   | 4     | 0            | 0            | 0         | 0         | 0          | 0          |
| $(A_6 + A_7)$ | $K_1$            | 4   | 0     | 0            | 0            | 0         | 0         | 0          | 0          |

**Table 4A.** Characters of the irreducible projective representations of the group of a wave vector of groups  $P4_12_12$  and  $P4_32_12$  for point  $M$ 

| $P4_12_12$<br>and $P4_32_12$ | Projective<br>class | $e$ | $c_2$ | $c_4$        | $c_4^3$      | $(u_2)_1$ | $(u_2)_2$ | $(u_2)_1$ | $(u_2)_2$ |
|------------------------------|---------------------|-----|-------|--------------|--------------|-----------|-----------|-----------|-----------|
| $M_1$                        | $K_0$               | 1   | -1    | $i$          | $-i$         | $i$       | $-i$      | -1        | 1         |
| $M_2$                        |                     | 1   | -1    | $i$          | $-i$         | $-i$      | $i$       | 1         | -1        |
| $M_3$                        |                     | 1   | -1    | $-i$         | $i$          | $i$       | $-i$      | 1         | -1        |
| $M_4$                        |                     | 1   | -1    | $-i$         | $i$          | $-i$      | $i$       | -1        | 1         |
| $M_5$                        |                     | 2   | 2     | 0            | 0            | 0         | 0         | 0         | 0         |
| $M_6$                        | $K_1$               | 2   | 0     | $i\sqrt{2}$  | $i\sqrt{2}$  | 0         | 0         | 0         | 0         |
| $M_7$                        |                     | 2   | 0     | $-i\sqrt{2}$ | $-i\sqrt{2}$ | 0         | 0         | 0         | 0         |
| $(M_1 + M_4)$                | $K_0$               | 2   | -2    | 0            | 0            | 0         | 0         | -2        | 2         |
| $(M_2 + M_3)$                |                     | 2   | -2    | 0            | 0            | 0         | 0         | 2         | -2        |
| $M_5$                        |                     | 2   | 2     | 0            | 0            | 0         | 0         | 0         | 0         |
| $(M_6 + M_7)$                | $K_1$               | 4   | 0     | 0            | 0            | 0         | 0         | 0         | 0         |

**Table 5A.** Characters of the irreducible projective representations of the group of a wave vector of groups  $P4_12_12$  and  $P4_32_12$  for point  $X$ 

| $P4_12_12$<br>and $P4_32_12$ | Projective<br>class | $e$ | $c_2$ | $(u_2)_1$ | $(u_2)_2$ |
|------------------------------|---------------------|-----|-------|-----------|-----------|
| $X_1$                        | $K_0$               | 1   | $-i$  | 1         | $i$       |
| $X_2$                        |                     | 1   | $-i$  | -1        | $-i$      |
| $X_3$                        |                     | 1   | $i$   | 1         | $-i$      |
| $X_4$                        |                     | 1   | $i$   | -1        | $i$       |
| $X_5$                        | $K_1$               | 2   | 0     | 0         | 0         |
| $(X_1 + X_3)$                | $K_0$               | 2   | 0     | 2         | 0         |
| $(X_2 + X_4)$                |                     | 2   | 0     | -2        | 0         |
| $X_5$                        | $K_1$               | 2   | 0     | 0         | 0         |

**Table 8A.** Distribution of normal vibrations over the symmetry types at points  $\Gamma$ ,  $Z$ , and  $A$  of the Brillouin zone of the tetragonal crystals of  $ZnP_2$ ,  $CdP_2$  and  $TeO_2$ 

| Point of the zone | $ZnP_2, CdP_2$   | $TeO_2$   |
|-------------------|--|---|
| $\Gamma$          | $9\Gamma_1 + 8\Gamma_2 + 9\Gamma_3 + 9\Gamma_4 + 17\Gamma_5$ | $4\Gamma_1 + 4\Gamma_2 + 5\Gamma_3 + 4\Gamma_4 + 8\Gamma_5$ |
| $Z$               | $18[Z_6 + Z_7]$  | $9[Z_6 + Z_7]$  |
| $A$               | $18[(A_6 + A_7)]$  | $9[(A_6 + A_7)]$  |
| $M$               | $9[M_1 + M_2 + M_3 + M_4 + 2M_5]$                            | $4M_1 + 5M_2 + 5M_3 + 4M_4 + 9M_5$                          |
| $X$               | $36X_5$  | $18X_5$   |
| $R$               | $18[(R_1 + R_4) + (R_2 + R_3)]$                              | $9[(R_1 + R_4) + (R_2 + R_3)]$                              |

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**Table 6A.** Characters of the irreducible projective representations of the group of a wave vector of group  $P4_12_12$  for point  $R$ 

| $P4_12_12$    | Projective<br>class | $e$ | $c_2$ | $(u_2)_1$ | $(u_2)_2$ |
|---------------|---------------------|-----|-------|-----------|-----------|
| $R_1$         | $K_0$               | 1   | $-i$  | $-i$      | 1         |
| $R_2$         |                     | 1   | $-i$  | $-i$      | -1        |
| $R_3$         |                     | 1   | $i$   | $-i$      | -1        |
| $R_4$         |                     | 1   | $i$   | $i$       | 1         |
| $R_5$         | $K_1$               | 2   | 0     | 0         | 0         |
| $(R_1 + R_4)$ | $K_0$               | 2   | 0     | 0         | 2         |
| $(R_2 + R_3)$ |                     | 2   | 0     | 0         | -2        |
| $((R_5))$     | $K_1$               | 2   | 0     | 0         | 0         |

**Table 7A.** Characters of the irreducible projective representations of the group of a wave vector of group  $P4_32_12$  for point  $R$ 

| $P4_12_12$    | Projective<br>class | $e$ | $c_2$ | $(u_2)_1$ | $(u_2)_2$ |
|---------------|---------------------|-----|-------|-----------|-----------|
| $R_1$         | $K_0$               | 1   | $i$   | $i$       | -1        |
| $R_2$         |                     | 1   | $i$   | $-i$      | 1         |
| $R_3$         |                     | 1   | $-i$  | $i$       | 1         |
| $R_4$         |                     | 1   | $-i$  | $-i$      | -1        |
| $R_5$         | $K_1$               | 2   | 0     | 0         | 0         |
| $(R_1 + R_4)$ | $K_0$               | 2   | 0     | 0         | -2        |
| $(R_2 + R_3)$ |                     | 2   | 0     | 0         | 2         |
| $((R_5))$     | $K_1$               | 2   | 0     | 0         | 0         |

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ЗАСТОСУВАННЯ МЕТОДУ ПРОЕКТИВНИХ ПЕРЕДСТАВЛЕНЬ ДО АНАЛІЗУ СПЕКТРІВ КОМБІНАЦІЙНОГО РОЗСІЯННЯ СВІТЛА ДРУГОГО ПОРЯДКУ В ЕНАНТИОМОРФНИХ ТЕТРАГОНАЛЬНИХ КРИСТАЛАХ

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Резюме

Запропоновано методику знаходження правил добору для двофононних переходів та визначення точок нульового нахилу в

зоні Бріллюена з використанням незвідних проєктивних представлень і виконано відповідні розрахунки для точок  $\Gamma$ ,  $Z$ ,  $A$ ,  $M$ ,  $X$  та  $R$  першої зони Бріллюена тетрагональних енантіоморфних кристалів, що описуються просторовими групами си-

метрії  $P4_12_12$  та  $P4_32_12$ . Результати цих розрахунків застосовано до аналізу спектрів двофононного комбінаційного розсіяння світла у кристалах дифосфідів цинку і кадмію ( $\alpha$ -ZnP<sub>2</sub> і CdP<sub>2</sub>) та парателуриту TeO<sub>2</sub>.