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LATTICE DYNAMICS OF A'BIVCX AND A'B'B'V' SEMICONDUCTORS WITH
CHALCOPYRITE LATTICE IN A RIGID-ION MODEL

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Abstract. — A model of unpolarizable point ions linked by short-range forces with their nearest
neighbours is applied to the investigation of lattice dynamics and related optical properties in the
infrared of chalcopyrite. Compounds ZnSiP₂, CdGeP₂ and CuAlS₂.
The distribution of effective charges between the ions is in good agreement with the experiment.
The most interesting feature of the calculated spectra is the presence of forbidden bands.

At the present time there is a considerable amount of data on the phonon spectra of A'BIV'C₂ and
A'B'B'V'V' semiconductors which crystallize in the chalcopyrite lattice. The reflectivity and absorption
in the infrared (IR) [1, 2], Raman scattering (RS) of polarized light [3, 4] were measured with ZnSiP₂
crystals. IR-reflectivity measurements were performed with CdGeP₂ in references [5, 6]. For CuAlS₂, IR and
RS measurements were reported in reference [7]. There are many experimental data on IR and RS
spectra of other ternary semiconductors with chalcopyrite lattice. A group-theoretical analysis and some
qualitative conclusions on the phonon spectra of crystals with chalcopyrite lattice were made in [8].

A unit cell of chalcopyrite lattice contains 8 particles (Fig. 1) yielding 24 branches of phonon spectra.
Because of the complexity of spectrum it is necessary to begin the investigation of lattice dynamics with
the simplest models of bonding forces between the ions. The model of unpolarizable point-charge ions,
linked by a short-range forces seems to be perspective in this respect. This model turned out to be successful
in the application to the ion-covalent A'BIV'C₂ and A'B'B'V'V' semiconductors [9-12], which possess a type
of chemical bond related to A'BIV'C₂ and A'B'B'V'V' compounds. We can expect such a model to be sui-
table for a description of lattice dynamics of ternary compounds under consideration.

The radius of short-range forces was restricted by second neighbours in references [9-12]. It turned out
that first-neighbours force constants are of one order higher in magnitude than second-neighbours
parameters. In the present paper the rigid-ion model
is used for calculating phonon spectra of ternary inequivalent compounds in the first-neighbours approximation.

In our model the dynamical matrix can be written as a sum of Coulomb and non-Coulomb terms [13]. The non-Coulomb interaction in the first-neighbours approximation in the chalcopyrite is determined by two force-constant matrices which correspond to

\[
\varphi^N(0)_{17} = \begin{pmatrix}
\Delta - y + 2z & -x + y & \gamma(-x + y - z) \\
-x + y & \Delta - y & \gamma(x - y + z) \\
\gamma(-x + y - z + u) & \gamma(x - y + z) & \gamma^2(\Delta - y + z)
\end{pmatrix} + \varphi_{17}.\delta
\]

\[
\varphi^N(0)_{35} = \begin{pmatrix}
\Delta + y & -x - y & \gamma(-x - y - z) \\
x + y & A + y - 2z & \gamma(x - y + z) \\
\gamma(-x - y - z) & \gamma(x - y + z) & \gamma^2(A + y - z)
\end{pmatrix} + \varphi_{35}.\delta.
\]

Here \( \gamma = e/c \); \( c, a \) are lattice constants, and \( A, x, y, z, u \) are force constants. To obtain eq. (1) we have neglected terms above the first order in powers of \( \delta \equiv (xf - 0.25) \).

The latter describes the shift of the anions from their ideal tetrahedral positions and it is generally small [14]. Matrices \( \varphi_{17} \) and \( \varphi_{35} \) are given in appendix A. The labelling of particles corresponds to figure 1. Substituting \( \gamma = 1, \delta = y = z = u = 0 \) in eq. (1) we get equivalent bonds and corresponding force-constant matrices are similar to that describing the first-neighbours interaction in sphalerite and \( A^{IV} \) [9-12]. Three constants \( A, x, y (\delta = y = z = u = 0, \gamma = 1) \) give us two different matrices \( \varphi^N(0)_{17} \) and \( \varphi^N(0)_{35} \) although each of them preserve the form of sphalerite bond matrix. Hence parameters \( z \) and \( u \) describe asymmetry of sphalerite bonds caused by the transition to the chalcopyrite lattice.

The Coulomb part of dynamical matrix was calculated according to the Evalc17s method with the help of a computer [13]. Following the rigid-ions model we suppose

\[
e_1 = e_2 = e^{*}_{\mu(II)}, \quad e_3 = e_4 = e^{*}_{\mu(III)},
\]

\[
e_5 = e_6 = e_7 = e_8 = e^{*}_{\mu(VI)},
\]

where \( e_\mu \) is the charge of \( \mu \)th ion. The use of electrical neutrality condition for the unit cell

\[
e^{*}_{\mu(II)} + e^{*}_{\mu(III)} + 2e^{*}_{\mu(VI)} = 0
\]

gives two charge parameters of the model in addition to five force constants. In the calculation of the Coulomb part of dynamical matrix the real structure of a crystal was exactly taken into account contrary to the short-range part where the expansion in powers of \( \delta \) was used.

To check a computer programme it is convenient to use the chalcopyrite lattice with \( \delta = 0, \gamma = 1, \\) inequivalent bonds \( A^{IV}-C^{IV}(A^{I}-C^{VI}) \) \( B^{IV}-C^{IV}(B^{III}-C^{IV}) \). The remaining bonds have turned out to be equivalent to above two and the corresponding force-constant matrices can be derived with the help of symmetry relations. After imposing the necessary restrictions which follow from the space homogeneity and isotropy and also by using the Huang relation [13] the matrices of inequivalent bonds take the form

\[
Q(\mu

\begin{pmatrix}
0 \\
0
\end{pmatrix}
\]

\[
= \frac{1}{4} \sum_{\mu

\begin{pmatrix}
0 \\
0
\end{pmatrix}
\]

where the corresponding unit cell is an undistorted sphalerite cell taken four times. In that case Coulomb sums \( Q_{ij}(k) \) determined in reference [13] satisfy the relationship

\[
Q_{ij}^{\mu\nu}(k) = \left[\sum_{\mu

\begin{pmatrix}
0 \\
0
\end{pmatrix}
\right]
\]

which makes possible an additional check of computation accuracy. Here \( s \) and \( s' \) denote particles in the equivalent bonds and corresponding force-constants sphalerite unit cell \( (s = 1, 2) \). \( \mu, \nu \) are the numbers of particles in chalcopyrite which satisfy the condition

\[
R(\mu) - R(\nu) = I + R(s) - R(s'),
\]

\( I \) being the sphalerite lattice vector which connects inequivalent particles in the chalcopyrite unit cell. In the long wave limit \( k \to 0 \) \( (k \) is the wave vector) the calculated Coulomb sums take the form

\[
Q(0

\begin{pmatrix}
0 \\
0
\end{pmatrix}
\]

\[
= \begin{pmatrix}
a & 0 & 0 \\
0 & a & 0 \\
0 & 0 & b
\end{pmatrix}
\]

\[
= \begin{pmatrix}
d & 0 & 0 \\
0 & d & 0 \\
0 & 0 & f
\end{pmatrix}
\]

\[
= \begin{pmatrix}
g & 0 & 0 \\
0 & g & 0 \\
0 & 0 & h
\end{pmatrix}
\]

\[
= \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

\[
= \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

\[
= \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

\[
= \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

\[
= \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

\[
= \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

\[
= \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

\[
= \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

\[
= \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

\[
= \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

\[
= \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

\[
= \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

\[
= \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]
LATTICE DYNAMICS OF $A_{11}B_{11}V_{11}C_{11}^{Y}$ AND $A_{11}B_{11}V_{11}C_{11}^{Y}$ SEMICONDUCTORS WITH CHALCOPYRITE LATTICE C3-171

establish their correspondence with the experimental frequencies. Such a qualitative analysis can serve as a basis for deriving of force constants $\Gamma$, $x$, $y$, $z$, $u$ and ion charges from the least-squares fitting to the experimental spectrum. Parameters of the model were found with the help of a computer as the values of the variables which correspond to the minimum of a function

$$f = \sum \left( \omega_j^{\text{exp}} - \omega_j^{\text{theor}}(A, x, y, z, u, e_{\text{II}}^*, e_{\text{VI}}^*) \right)^2$$

(5)

where $\omega_j^{\text{exp}}$ are the frequencies $E$, $B_2$ found in IR experiments [1, 2], [5, 7], $\omega_j^{\text{theor}}$ are the longitudinal (L) and transversal (T) frequencies of symmetry $\Gamma_4$ and $\Gamma_5$ obtained by the diagonalization of the dynamical matrix in our model taking into consideration the real structure of crystals. A condition of the degeneracy of (L) and (T) modes was introduced into $\Gamma_4$ and $\Gamma_5$ frequencies which were not observed in the experiments.

The above method was applied to the investigation of ZnSiP$_2$, CdGeP$_2$ and CuAlS$_2$ crystals. The values of the parameters in the nearest binary analogues [9-12] (neglecting the interaction of second neighbours) were adopted as initial parameters of chalcopyrite for the minimization procedure. IR-active frequencies for ZnSiP$_2$ and CdGeP$_2$ from the latest works [1] and [6] were taken as $\omega_j^{\text{exp}}$. The minimization of $f$ for CuAlS$_2$ was performed on the basis of reference [7] in two versions. The version a) used only IR-active frequencies as $\omega_j^{\text{exp}}$. In the addition to a) we took into account two low-frequency modes $\Gamma_4$ and $\Gamma_5$ observed in RS as $\omega_j^{\text{exp}}$ in the version b). The results of minimization are presented in tables II, III. In the square brackets in table II we quote works which report on lattice parameters $a$, $c$, $x_f$. The value $f_{\text{min}}$ and the root-mean-square deviations of calculated frequencies from the experimental

$$\Delta \omega = \sqrt{\frac{f_{\text{min}}}{n}}$$

The remaining matrices can be derived using the symmetry relations. The numerical values of quantities expressed in letters are listed in table I. Coulomb matrices which correspond to the values $\gamma$ and $\delta$ for the real crystals differ from (4) by the small quantities of order 6 and 7th order respectively which cannot be solved in an analytical way. Thus the frequencies were calculated by diagonalization of the whole dynamical matrix. Polarization vectors were calculated in the long-wave limit and were used for the symmetry analysis of the calculated frequencies.

Some qualitative information can be obtained by putting $x_f = 0.25$, $y = z = u = 0$. Parameters $A$, $x$, $e_i^*$ can be taken from the calculations in references [9-11] for $A_{11}B_{11}V_{11}C_{11}^{Y}$, $A_{11}B_{11}V_{11}C_{11}^{Y}$ — nearest analogues of $A_{11}B_{11}V_{11}C_{11}^{Y}$ and $A_{11}B_{11}V_{11}C_{11}^{Y}$ compounds. Specific features of chalcopyrite are taken into account in such assumptions only through the difference of cation masses and lattice compression in the direction of tetrahedral axis. Even such a crude approximation leads to a qualitative accordance of calculated phonon spectrum with frequencies observed in optical experiments. Analysis of polarization vectors allows us to determine the longitudinal and transversal modes which can be IR-active for the light polarized parallel and perpendicular to the tetrahedral $e$-axis and to

$$Q(0)_{72} = Q(0)_{84} = Q(0)_{63} = Q(0)_{51} = \begin{pmatrix} m & n & l \\ n & m & l \\ l & m & n \end{pmatrix}.$$

TABLE I

Values of Coulomb sums for the chalcopyrite lattice ($\gamma = 1$, $\delta = 0$)

<table>
<thead>
<tr>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>$d$</th>
<th>$f$</th>
<th>$g$</th>
<th>$h$</th>
<th>$m$</th>
<th>$n$</th>
<th>$l$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.380 36</td>
<td>0.239 29</td>
<td>0.631 19</td>
<td>0.262 36</td>
<td>0.160 89</td>
<td>0.678 21</td>
<td>0.333 33</td>
<td>0.845 15</td>
<td>0.952 47</td>
<td></td>
</tr>
</tbody>
</table>

TABLE II

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a$ $\lambda$</th>
<th>$c$ $\lambda$</th>
<th>$x_f$</th>
<th>$f_{\text{min}}$ cm$^{-1}$</th>
<th>$n$</th>
<th>$\Delta \omega$ cm$^{-1}$</th>
<th>$\Delta \times 10^{-3}$ dyn/cm</th>
<th>$x \times 10^{-3}$ dyn/cm</th>
<th>$y \times 10^{-3}$ dyn/cm</th>
<th>$z \times 10^{-3}$ dyn/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSiP$_2$</td>
<td>5.399 0 [18]</td>
<td>5.217 5 [18]</td>
<td>0.269 1 [18]</td>
<td>599 12</td>
<td>5.8</td>
<td>51.44</td>
<td>41.46</td>
<td>8.78</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>CdGeP$_2$</td>
<td>5.740 19</td>
<td>5.388 5 [19]</td>
<td>0.283 19</td>
<td>94 14</td>
<td>2.6</td>
<td>45.75</td>
<td>39.90</td>
<td>7.42</td>
<td>1.61</td>
<td></td>
</tr>
<tr>
<td>CuAlS$_2$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>183 12</td>
<td>3.9</td>
<td>38.98</td>
<td>32.17</td>
<td>15.80</td>
<td>— 1.12</td>
<td></td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Compound</th>
<th>Ion</th>
<th>Our model</th>
<th>Dielectric theory</th>
<th>Binary analogues</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSiP₂</td>
<td>Zn</td>
<td>± 0.86</td>
<td>+ 0.496</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>± 0.48</td>
<td>+ 0.267</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>□ ± 0.67</td>
<td>- 0.380</td>
<td>—</td>
</tr>
<tr>
<td>CdGeP₂</td>
<td>Cd</td>
<td>± 0.95</td>
<td>+ 0.752</td>
<td>0.559 GaP [9]</td>
</tr>
<tr>
<td></td>
<td>Ge</td>
<td>± 0.45</td>
<td>+ 0.520</td>
<td>0.559 GaP [9]</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>□ ± 0.70</td>
<td>- 0.636</td>
<td>0.66 InP [22]</td>
</tr>
<tr>
<td>CuAlS₂</td>
<td>Cu</td>
<td>± 0.42</td>
<td>± 0.32</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>± 1.08</td>
<td>± 1.18</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>□ ± 0.75</td>
<td>± 0.75</td>
<td>0.934 ZnS [10]</td>
</tr>
</tbody>
</table>

are listed too, n being the number of experimental frequencies used for fitting (degenerate modes considered as distinct ones). Calculated force constants turned out to be close to the parameters of the nearest-neighbours interaction in binary analogues. We illustrate this closeness giving the example of ZnSiP₂. The parameter $u$ influences only the position of frequency which is IR-inactive and was not used for the parameter fitting. Therefore hereafter $u = 0$ for all compounds. As it is seen from table II the second asymmetry parameter $z$ is small in comparison with $\lambda$, $x$, $y$. If we neglected this asymmetry of bonds together with the corrections on the tetrahedral compression and the shift of anions from the ideal positions (that is put $\gamma = 1$, $\delta = u = z = 0$) we would get sphalerite type matrices for the bonds. The quantities $(A - y)$ and $(x - y)$ for Zn-P bond, $(A + y)$ and $(x + y)$ for the Si-P bond would play the role of sphalerite parameters $x$ and $\beta$ (sf [9-12]). The Zn-P bond $(A - y = 42.66, x - y = 32.68)$, all quantities here and below are given in units $10^3$ dyn/cm is to be compared with the bond in GaP ($x = 44.48, \beta = 33.00$ [9]). The Si-P bond $(A + y = 60.22, x + y = 50.24)$ is close to that in Si ($x = 55.5, \beta = 37.34$ [12]). Such a closeness of force constants takes place also for other compounds under consideration, supporting the idea about the similarity of type of chemical bond in binary and ternary semiconductors. The distribution of charges between the ions as a whole agrees with that calculated according to the dielectric theory of ionicity [15, 16]. It is noteworthy that simultaneous reversal of charge signs on the cation and anion sublattices does not affect the spectrum and therefore the correct sign of charge associated with any sublattice cannot be determined by optical experiments only.

The model parameters resulted from the minimization were used for the calculation of phonon spectra of crystals under consideration. Results are shown in figures 2-4. In the central part of figures is represented the dependence of frequencies in the longwave limit ($k \rightarrow 0$) against the angles between the phonon wave vector and the tetrahedral c-axis. The symmetry of frequencies and the type of vibrations (L, T) were established by analysis of polarisation vectors. It is seen from figures that frequencies with symmetry $I_4$ and $I_5$ show nonanalytic behaviour. The upper mode $\omega_{21}$ has the symmetry $I_4$ when $k \parallel c$ and it appears to be of symmetry $I_5$ when $k \perp c$. For the other orientations this mode has a symmetry $I_4 \oplus I_5$. Vibrations with frequency $\omega_{21}$ are longitudinal for any orientations of $k$. The next two modes $\omega_{19,20}$ are transversal ones for each directions of $k$, $\omega_{19}$ being of $I_3$ symmetry for $k \parallel c$, of $I_4$ for $k \perp c$ and of $I_4 \oplus I_5$ symmetry for any other directions of $k$. The mode $\omega_{20}$ doesn't change its symmetry $I_5$. The remaining modes with symmetry $I_5$ are degenerate and transversal when $k \parallel c$. For $k \perp c$ they split into the longitudinal and transversal components without changing their $I_5$ symmetry. The highest modes $\omega_{19,20,21}$ are IR-active mainly because of displacement of lighter cation with respect to the anions. Midfrequency group $\omega_{11,12,13}$ ($\omega_{11,12,14}$ in ZnSiP₂) has a dipole character mainly owing to the displacement of a heavier cation with respect to anions. The essential contribution in the above vibrations (up to 50 %) belongs to the symmetry coordinates with zero dipole moment (sf [8]). IR-activity of the remaining frequencies is mainly caused by the mutual displacement of cations. Experimental data are shown in the same (central) part of the figures. Heavy dots and squares in figure 2 show experimental values of IR-active frequencies taken from [3, 4], crosses represent IR-frequencies from [2] and triangles are the frequencies from [1], the latter being used as $\omega_{\text{exp}}$ in the minimizing of $f$. In figure 3 squares and triangles denote IR-frequencies from references [5, 6], the latter being used to fit parameters. In figure 4 triangles exhibit values of IR and RS frequencies from [7]. The symmetry interpretation according to references [1-7] is shown near the experimental points in figures 2-4. The calculated phonon spectra in points of high symmetry N, T and in high-symmetry directions A and R of the Brillouin zone are shown in the same figures. The symmetry of frequencies was established from the compatibility...
Fig. 2. — The phonon spectrum of ZnSiP₂. \( \theta \) is the angle between the wave vector and c-axis in the long-wave limit. Frequencies taken from infrared reflectivity [1] and [2]. (solid circles) show Raman scattering frequencies from [3, 4]. Light dots represent calculated frequencies.

Relations here. In the direction A a unique classification can be given, at the point T one can identify the representation and it splits in A-direction. Representations \((\tau_1 \otimes \tau_2)\) and \((\tau_3 \otimes \tau_4)\) turn into \((A_3 + A_4)\) and cannot be distinguished by compatibility relations. At the point N a double degenerate representation \(N_1\) exists. In R-direction a possible symmetry notation of branches is presented. An interesting feature of the calculated spectra is the presence of forbidden bands. The calculated values of parameters enable us to calculate oscillator strengths for the dipole frequencies and components of static dielectric tensor. In the reference [17] an expression for the low-frequency dielectric tensor of insulators was derived

\[
e_{\lambda \mu}(\omega) = e_{\lambda \mu}(\infty) + \sum_{j} \frac{S_{\lambda \mu}(j)}{\Omega^2_j - \omega^2} \tag{6}
\]

where \(e_{\lambda \mu}(\infty)\) is the high-frequency dielectric tensor

\[
S_{\lambda \mu}(j) = \frac{4\pi}{V_0} \sum_{\sigma \psi \nu m} \frac{\Delta Z^{[\sigma]}_{\mu \nu} \Delta Z^{[\psi]}_{\nu \sigma} e_{\lambda}(s \mid jn) e_{\mu}(s' \mid jn)}{\sqrt{m_\lambda m_\mu}} \tag{7}
\]

Here \(\Delta Z^{[\sigma]}_{\mu \nu}\) is the effective charge matrix of \(s\)th ion as introduced in [17], \(m_\lambda\) being its mass. \(V_0\) is the unit cell volume, \(\Omega^2_j\), \(e_{\lambda}(s \mid jn)\) are the eigenvalues and eigenvectors of analytical part of dynamical matrix; \(n\) denotes eigenvectors which correspond to the same frequency; \(\lambda, \mu\) are the Cartesian components.
Fig. 3. — The phonon spectrum of CdGeP$_2$. (■) and (▲) are the frequencies measured in infrared reflectivity experiments [5, 6].

**TABLE IV**

**IR-active frequencies and oscillator strengths**

<table>
<thead>
<tr>
<th>Symmetry of modes</th>
<th>ZnSiP$_2$</th>
<th></th>
<th></th>
<th>CdGeP$_2$</th>
<th></th>
<th></th>
<th>CuAlS$_2$</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Omega_i$ cm$^{-1}$</td>
<td>$S_{\lambda \lambda} \times 10^{-5}$ cm$^{-2}$</td>
<td>$\Omega_i$ cm$^{-1}$</td>
<td>$S_{\lambda \lambda} \times 10^{-3}$ cm$^{-2}$</td>
<td>$\Omega_i$ cm$^{-1}$</td>
<td>$S_{\lambda \lambda} \times 10^{-3}$ cm$^{-2}$</td>
<td>$\Omega_i$ cm$^{-1}$</td>
<td>$S_{\lambda \lambda}/\Omega_i^2$</td>
<td></td>
</tr>
<tr>
<td>$\Gamma_3(T)$</td>
<td>495</td>
<td>500</td>
<td>1.347</td>
<td>1.57</td>
<td>386</td>
<td>385</td>
<td>0.833</td>
<td>0.705</td>
<td>451</td>
</tr>
<tr>
<td>$E(T)$</td>
<td>459</td>
<td>—</td>
<td>0.648</td>
<td>—</td>
<td>354</td>
<td>356</td>
<td>0.891</td>
<td>0.895</td>
<td>424</td>
</tr>
<tr>
<td>$\lambda = x$</td>
<td>327</td>
<td>320</td>
<td>0.564</td>
<td>0.54</td>
<td>289</td>
<td>289</td>
<td>0.415</td>
<td>0.263</td>
<td>261</td>
</tr>
<tr>
<td>$258$</td>
<td>260</td>
<td>0.313</td>
<td>0.34</td>
<td>179</td>
<td>179</td>
<td>0.127</td>
<td>0.064</td>
<td>5</td>
<td>213</td>
</tr>
<tr>
<td>$186$</td>
<td>185</td>
<td>0.063</td>
<td>0.23</td>
<td>121</td>
<td>122</td>
<td>0.034</td>
<td>0.003</td>
<td>81</td>
<td>169</td>
</tr>
<tr>
<td>$153$</td>
<td>—</td>
<td>0.006</td>
<td>—</td>
<td>103</td>
<td>—</td>
<td>0.004</td>
<td>—</td>
<td>—</td>
<td>124</td>
</tr>
<tr>
<td>$\Gamma_4(T)$</td>
<td>492</td>
<td>491</td>
<td>1.556</td>
<td>2.47</td>
<td>383</td>
<td>387</td>
<td>0.905</td>
<td>0.787</td>
<td>449</td>
</tr>
<tr>
<td>$B_3(T)$</td>
<td>355</td>
<td>347</td>
<td>1.253</td>
<td>1.25</td>
<td>293</td>
<td>295</td>
<td>1.340</td>
<td>1.54</td>
<td>273</td>
</tr>
<tr>
<td>$\lambda = z$</td>
<td>175</td>
<td>—</td>
<td>0.146</td>
<td>—</td>
<td>112</td>
<td>—</td>
<td>0.082</td>
<td>—</td>
<td>151</td>
</tr>
</tbody>
</table>

(*) These frequencies are taken from RS-experiment.
(***) Components $S_{\lambda \lambda}$ which are not listed in the table vanish.
A comparison of expressions for the macroscopic electric field in our model with that in reference [17] gives us
\[ \Delta Z^{(\omega)}_{\mu \lambda} = E^{(\omega)}_{\mu} \cdot \delta_{\mu \lambda} \cdot \sqrt{e_\infty} ; \quad e_\infty = \sum_{\lambda} \frac{k_\lambda}{k^2} \varepsilon_{2\lambda}(\infty) \] (8)

\( k \) being the phonon wave vector. Hence \( E^{(\omega)}_{\mu} \) can be considered as a screened ion charge. According to the symmetry one gets
\[ S_{\lambda \lambda}(j) = S_{\lambda \lambda} \cdot \delta_{\lambda \lambda} ; \quad \varepsilon_{\mu \lambda}(\omega) = \varepsilon_{\lambda \lambda} \cdot \delta_{\mu \lambda} \]
\[ S_{\alpha \alpha} = S_{\beta \beta} \neq S_{\gamma \gamma} ; \quad e_{\alpha \alpha} = e_{\beta \beta} \neq e_{\gamma \gamma} ; \]
(9)

\( S_{\lambda \lambda}(j) \) can be considered as an oscillator strength associated with \( j \)th mode for the light polarized along the \( \lambda \)-axis. Results of calculations for ZnSiP\(_2\), CdGeP\(_2\) and CuAlS\(_2\) are listed in table IV. Good agreement between theoretical and experimental values of oscillator strengths is worth noting. Frequencies which were not observed in experimental works used as references in table IV should be discussed separately. In the reference [2] the peculiarity in the absorption on ZnSiP\(_2\) was discovered as a sharp peak at a frequency \( \omega = 460 \text{ cm}^{-1} \). In the reflection the peculiarity was found at the frequency \( \omega = 464 \text{ cm}^{-1} \). These frequencies are quite close to the calculated \( \omega = 459 \text{ cm}^{-1} \). Oscillator strengths are comparatively small for the remaining \( \Gamma_4 \) and \( \Gamma_5 \) frequencies not observed in IR experiments. Discrepancies between the calculated and measured values of oscillator strengths are probably due to absence of phonon damping in our
A. S. POPLAVNOI AND V. G. TJUTEREV

The static dielectric tensor

<table>
<thead>
<tr>
<th>Compound</th>
<th>theor.</th>
<th>expt.</th>
<th>theor.</th>
<th>expt.</th>
<th>e(0) (unpolarized light)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSiP₂</td>
<td>11.47</td>
<td>11.1</td>
<td>11.64</td>
<td>11.2</td>
<td>11.5 ± 0.3 [2]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.3</td>
<td></td>
<td>11.1</td>
<td></td>
</tr>
<tr>
<td>CdGeP₂</td>
<td>12.13</td>
<td>11.76</td>
<td>12.72</td>
<td>12.27</td>
<td>16.1 ± 0.3 [5]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.72</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuAlS₂</td>
<td>6.60</td>
<td>6.45</td>
<td>6.70</td>
<td>6.73</td>
<td></td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

model. Besides it should be noted that polarization vectors used in this calculation are reproduced with a greater errors than the frequencies themselves. Frequencies observed in RS but IR-inactive were not used as \( \Omega_{\text{IR}} \) in the minimization procedure. Quantitative discrepancies between theoretical and experimental values attain 50 cm⁻¹ for such modes and are to be associated with the imperfection of the model. One should note that discrepancies between values of IR [1, 2] and RS [3, 4] modes for ZnSiP₂ are of the same order of magnitude. Calculated values of static dielectric tensor are in the good agreement with the experiment (Table V). However since the experimental values of \( \varepsilon_{\text{ir}} \) were used in the calculations one should note the agreement between the theoretical and experimental differences of static and high-frequency dielectric tensors.

In conclusion it is to be noted that calculated phonon spectra of ZnSiP₂, CdGeP₂ and CuAlS₂ are expected to be useful together with reference [21] in the analysis of inelastic neutron scattering in these crystals.

Appendix A: Matrices \( \hat{\varphi}_{17} \) and \( \hat{\varphi}_{35} \)

\[
\hat{\varphi}_{17} = \begin{pmatrix}
-x + 3y + z \\
-x + 2y + z \\
0
\end{pmatrix}
\hat{\varphi}_{35} = \begin{pmatrix}
-x + 2y + z \\
-x + 3y + z \\
0
\end{pmatrix}
\]

References