Physics of the Solid State, 2022, Vol. 64, No. 6

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Elastic constants and interatomic bond force constants of $A^{II}B_2^{III}C_4^{VI}$ compounds

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Received January 27, 2022
Revised January 27, 2022
Accepted February 6, 2022

The density functional theory (DFT) was used to calculate the elastic constants c_{ij} of $CdGa_2S_4$, $CdGa_2Se_4$, $CdGa_2Te_4$, and $ZnGa_2Se_4$ thiogallates. The values of B bulk modulus of elasticity have been calculated. The regularities in the dependences of the optical phonons frequencies on the masses of atoms of compounds are established. The force constants of interatomic bonds in $CdGa_2Te_4$ and $ZnGa_2Se_4$ compounds have been determined.

Keywords: elastic constants, force constants, phonons, raman scattering, tetragonal syngony, reduced mass, chalcopyrites.

DOI: 10.21883/PSS.2022.06.53821.283

1. Introduction

Semiconductor compounds of the group $A^{II}B_2^{III}C_4^{VI}$ (A — Zn, Cd; B — Ga; C — S, Se) are thiogallates to be crystallized to a tetragonal structure with a spatial group of symmetry I_4^- (point group S_4) [1]. This group of thiogallates is characterized by an ordered cation vacancy, which distinguishing them from crystal-chemical and isoelectronic counterparts with a chalcopyrite and sphalerite structure, therefor the compounds of this group are also called defective chalcopyrite (DC). The compounds $A^{II}B_2^{III}C_4^{VI}$ (A — Zn, Cd; B — In, Ga; C — S, Se, Te) are promising in connection with their usability in the semiconductor instrumentation [2]. These compounds are characterized by birefringence, significant values of the coefficient of nonlinear susceptibility, and bright photoluminescence [3]. A large band gap (2–4.0 eV) and high photosensitivity stimulate creation of ultraviolet radiation detectors, which are already used in medicine, biology, space physics, and other fields. Crystals of the group $A^{II}B_2^{III}C_4^{VI}$, and, in particular, $CdGa_2S_4$ are promising materials for creating retunable narrow-band optical filters due to the presence of the so-called „isotropic point“, at which the dispersion curves of the ordinary and extraordinary refraction indices intersect [4]. Recently, $CdGa_2S_4$ and $CdGa_2Se_4$ crystals have been positioned as materials for solar batteries [5].

If optoelectronic properties of the compounds $A^{II}B_2^{III}C_4^{VI}$ are studied in relative detail, then it should be noted that there is a lack of information about thermodynamic and thermal properties (heat capacity, thermal expansion, thermal conductivity) closely correlated to elastic properties of these compounds. Values of the seven elastic constants c_{11}, c_{33}, c_{12}, c_{13}, c_{44}, c_{66}, c_{16}, which are inherent to the compounds $A^{II}B_2^{III}C_4^{VI}$, $CdGa_2S_4$ and $CdGa_2Se_4$ calculated *ab initio*, are given in the paper [6]. According to [6], if in $CdGa_2S_4$ the elastic constant $c_{11} = 61.77$ GPa is above $c_{33} = 50.02$ GPa, then in $CdGa_2Se_4$ the value $c_{11} = 52.46$ GPa is below $c_{33} = 60.0$ GPa. Similar *ab initio* calculations for $HgGa_2S_4$ [7] and $HgGa_2Se_4$ [8] lead to significantly lower anisotropy of elastic forces: $c_{11} = 65.6$ GPa, $c_{33} = 63.4$ GPa for $HgGa_2S_4$ [7] and $c_{11} = 54.2$ GPa, $c_{33} = 55.5$ GPa for $HgGa_2Se_4$ [8]. According to [9], in the defective chalcopyrite $ZnGa_2Te_4$ $c_{11} = 45.4$ GPa, $c_{33} = 48.47$ GPa.

Thus, despite available data on the values of the elastic constants of the compounds $A^{II}B_2^{III}C_4^{VI}$, there is evident scattering in anisotropy of the elastic constants and a lack of data on individual compounds $A^{II}B_2^{III}C_4^{VI}$, which requires additional studies. The present article provides results of the *ab initio* calculations of the values of the elastic constants c_{11}, c_{33}, c_{12}, c_{13}, c_{44}, c_{66}, c_{16} $CdGa_2S_4$, $CdGa_2Se_4$, $CdGa_2Te_4$ and $ZnGa_2Se_4$, values of bulk moduli B determined based thereon, which are compared with experimentally measured and theoretically calculated values known from the literature. There are also evaluations of force constants of interatomic bonds f_n, accounted for frequencies of optical phonons.

2. Elastic constants

It is well known that stresses and deformations are described by means of second-rank tensors (σ_{ij} and ε_{kl}) in the three-dimensional space and have 9 components each. Within the generalized Hooke's law (1) they are correlated to a fourth-rank tensor c_{ijkl}, which is called an elasticity tensor and generally contains 81 coefficients (elastic constants):

$$\sigma_{ij} = c_{ijkl}\,\varepsilon_{kl}. \tag{1}$$

A requirement of symmetry of the stress and deformation tensors (2) leads to reduction of a number of independent elastic constants to 36.

$$c_{ijkl} = c_{jikl} = c_{ijlk} = c_{jilk}. \tag{2}$$

Taking into account that the elastic deformation energy W:

$$W = \frac{1}{2}\,c_{ijkl}\varepsilon_{ij}\varepsilon_{kl}. \tag{3}$$

It follows therefrom that $c_{ijkl} = c_{klij}$ and a number of the independent elastic constants reduces to 21. Thus, in the most generalized case of low-symmetrical crystals there are 21 independent components of the elasticity tensor.

Next, taking into account a specific crystal lattice allows even more substantially reducing the number of the independent elastic constants. For example, more highly-symmetrical crystals with the tetragonal symmetry and the structure of defective chalcopyrites are described by means of seven elastic constants. According to the W. Voigt notation, the elements of the elasticity tensor c_{ijkl} can be written using the following index replacement $11 \to 1$, $22 \to 2$, $33 \to 3$, $23, 32 \to 4$, $12, 21 \to 6$, as the matrix 6×6:

$$\begin{bmatrix} c_{11} & c_{12} & c_{13}\ldots 0 \ldots 0 \ldots c_{16} \\ c_{12} & c_{11} & c_{13}\ldots 0 \ldots 0 \ldots -c_{16} \\ c_{13} & c_{13} & c_{33}\ldots 0 \ldots 0 \ldots 0 \\ 0 \ldots 0 \ldots & 0 \ldots c_{44} \ldots 0 \ldots 0 & \\ 0 \ldots 0 \ldots & 0 \ldots 0 \ldots c_{44} \ldots 0 & \\ 0 \ldots 0 \ldots & 0 \ldots 0 \ldots 0 \ldots c_{66} & \end{bmatrix}. \tag{4}$$

It should be noted that for the tetragonal symmetry crystals there are two Laue classes (Laue group) — TI and TII [8]. For the Laue class TII, to which the defective chalcopyrites belong, the seven elastic constants are intrinsic thereto, and for TI — the six elastic constants c_{11}, c_{12}, c_{13}, c_{33}, c_{44}, c_{66}. Formulas for calculation of the elastic moduli using the elastic constants of the TII Laue group can not be obtained analytically due to a non-diagonal elastic shift constant c_{16}, which is usually not zero. However, it is possible to convert the seven components c_{ij} of the elasticity tensor of the crystal TII to the six components of the elasticity tensor c_{ij} of the crystal TI [8]. For this purpose, it is necessary to convert by rotating around the tetragonal axis by the angle:

$$\varphi_{\kappa,\gamma} = \frac{1}{4}\arctan\left(\frac{4c_{16}}{c_{11} - c_{12} - 2c_{66}}\right), \tag{5}$$

here $0 < \varphi_\kappa < |\pi/2|$, $\varphi_\gamma = \varphi_\kappa + \pi/4$. The paper [8] shows that in such a conversion the values of the six elastic constants c_{11}, c_{12}, c_{13}, c_{33}, c_{44}, c_{66} of the defective chalcopyrites almost do not change.

The elastic constants in the crystals should have certain relationships satisfied therebetween, which succeed from an equilibrium condition of the crystal lattice. Its main requirement is a minimum energy density. These relationships called the Born–Huang stability criteria succeed from a necessity to fulfil a stability criterion of the crystal lattice [10]. In order to make the lattice stable, the energy density must be of a positively defined square form so that the energy increases at any small deformation. If the square form coefficients are arrayed as a matrix (4), without the elastic constant c_{16}, then, according to a well algebraic theorem, this square form is positively defined, when determinants of all matrices of successive ranks (major minors) are positive. That is, the following c_{66}, $c_{44}c_{66}$, $c_{44}^2c_{66}$, $c_{33}c_{44}^2c_{66}$, $(c_{11}c_{33} - c_{13}^2)c_{44}^2c_{66}$, $(c_{11}-c_{12})(c_{11}c_{33} + c_{12}c_{33} - 2c_{13}^2)$ must be positive. Thus, the following conditions must be met:

$$\begin{gathered} c_{11} > 0;\ c_{44} > 0;\ c_{66} > 0;\ c_{11} - c_{12} > 0, \\ c_{11}c_{33} - c_{13}^2 > 0, \\ c_{11}c_{33} + c_{12}c_{33} - 2c_{13}^2 > 0. \end{gathered} \tag{6}$$

Similar relationships for the hexagonal symmetry crystals are give in the paper [11].

3. Method of calculation of elastic constants

The *ab initio* calculations of the elastic constants of the compounds $CdGa_2S_4$, $CdGa_2Se_4$, $CdGa_2Te_4$ and $ZnGa_2Se_4$ have been carried out by Density Functional Theory (DFT) [12–14] using the pseudopotential method on the base of plane waves realized in the code ABINIT [15]. For a pseudopotential and exchange correlation potential, one used form-conserving pseudopotentials Hartwigsen–Goedecker–Hutter [16] and generalized gradient approximation (GGA) [17]. The wave functions have been expanded by taking into account the plane waves with the energy up to 80 Ry, which provides good convergence of the full energy. The Brillouin zone summations have been carried out on the Monkhorst–Pack $4 \times 4 \times 4$ grid [18]. The lattice parameters and equilibrium positions of atoms in the lattice cell have been determined by minimizing the Hellmann–Feynman forces. The equilibrium positions of atoms in the lattice cell have been found by the BFGS method (Broyden–Fletcher–Goldfarb–Shanno) using experimental data as initial values. The minimization process has continued until the force moduli were below 10^{-8} Ry/Bohr.

Table 1 contains the values of the elastic constants of the compounds as calculated *ab initio* by us: $CdGa_2S_4$, $CdGa_2Se_4$, $CdGa_2Te_4$ and $ZnGa_2Se_4$, and the data on the values of the elastic constants c_{ij} of other defective chalcopyrites as well (the data is known from the literature).

Table 1. Values of the elastic constants c_{ij} of the defective chalcopyrites in GPa (the square brackets hold a reference to a work from which the data are derived)

Compounds	Elastic constants c_{ij}, GPa						
	c_{11}	c_{12}	c_{13}	c_{33}	c_{44}	c_{16}	c_{66}
$CdGa_2S_4$ This work	66.1	31.4	37.2	68.9	35.7	−1.9	34.3
$CdGa_2Se_4$ This work	71.1	29.7	40.6	74.5	39	−0.78	31.7
$CdGa_2Te_4$ This work	57	22.9	29.4	55.9	28.8	−0.083	25.1
$ZnGa_2Se_4$ This work	87.2	41.1	42.5	90.1	49.5	−0.61	50.7
$CdGa_2S_4$ Ref. [6]	61.8	24.7	35.7	50.0	33.9	−2.7	27.0
$CdGa_2Se_4$ Ref. [6]	52.5	20.4	38.8	60.0	31.6	−1.9	16.0
$HgGa_2S_4$ Ref. [7]	65.6	32.5	38	63.4	35.6	−2.0	31.6
$HgGa_2Se_4$ Ref. [8]	54.2	24.3	31.2	55.5	29.9	−0.3	26.2
$ZnGa_2Te_4$ Ref. [9]	45.4	19.8	26.2	48.5	25.7	–	26.5

Table 2. Values of the bulk modulus B determined theoretically and from experimental studies. Each cell contains the values of B, the determination method (theoretically or experimentally) and a work reference (in square brackets)

Compounds	Bulk modulus B, GPa			
$CdGa_2S_4$	45.8 theor This work	58.4 theor Ref. [6]	46 theor Ref. [23]	64 exp Ref. [24]
$CdGa_2Se_4$	48.7 theor This work	36.1 theor Ref. [6]	41 theor Ref. [23]	41.5 exp Ref. [26]
$CdGa_2Te_4$	37 theor This work	–	–	–
$ZnGa_2Se_4$	57.4 theor This work	52 theor Ref. [25]	–	–
$ZnGa_2Te_4$	30 theor Ref. [9]	31.3 exp Ref. [9]	40 exp Ref. [27]	39 theor Ref. [25]

4. Bulk moduli

In practice, besides the elastic constants, there are bulk moduli B used. For example, for calculation of the Gruneisen parameters [19], coefficients of volumetric thermal expansion and other anharmonic effects [20]. By definition, the bulk moduli are determined from the relationship:

$$W = \frac{1}{2} B\xi^2. \tag{7}$$

Here, the volumetric deformation is correlated to diagonal components of the deformation ε_{ii} tensor by the relationship:

$$\frac{\xi}{3} = \varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33}. \tag{8}$$

Taking into account (8), it is easy to obtain from (3) and (7) a correlation of the bulk modulus to the elastic constants for the tetragonal symmetry crystals:

$$B = \frac{1}{9}(2c_{11} + c_{33} + 2c_{12} + 4c_{13}). \tag{9}$$

For the bulk modulus B of the tetragonal symmetry crystals, the expression similar to (9) was used in the papers [21,22]. For the cubic symmetry crystals $c_{11} = c_{33}$ and $c_{12} = c_{13}$, the expression (9) transforms into correlation of the bulk modulus to the elastic constants for the cubic symmetry crystals:

$$B = \frac{1}{3}(c_{11} + 2c_{12}). \tag{10}$$

The values of the bulk modulus can also be experimentally determined from the known Birch−Murnaghan equation of state [23,24]:

$$P = \frac{3}{2} B_0 (x^{7/3} - x^{5/3}) \left[1 + \frac{3}{4}(B_0^I - 4)(x^{2/3} - 1)\right]. \tag{11}$$

Here $x = V_0/V$, P — hydrostatic pressure, V_0 — initial volume, B_0 — bulk modulus, B_0^I — first order volume derivate of the bulk modulus.

Table 2 shows the values of the bulk modulus B determined theoretically and from experimental studies.

5. Optical phonons in the compounds $A^{II}B_2^{III}C_4^{VI}$

Knowingly, the lattice cell of the defective chalcopyrites of the group $A^{II}B_2^{III}C_4^{VI}$ contains 7 atoms. That is why the vibration spectrum consists in 21 modes and is described in the center of the Brillouin zone (when $q = 0$) by the following irreducible representations [28]:

$$\Gamma = 3A + 6B + 6E. \tag{12}$$

All the symmetry modes E are doubly degenerated, one mode B and one mode E are acoustic. All the optical modes ($3A$, $5B$ and $5E$) are active within the Raman scattering spectra (RS). 5 symmetry modes B allowed in polarization parallel to the tetragonal axis C and 5 doubly degenerated symmetry modes E are active in the infrared absorption spectra (IR). The modes B and E are polar, while the modes A — non-polar. The totally symmetric vibrations of the type A are correlated to shifts of anion sublattice

Table 3. Frequencies of the modes A_1, A_2 and A_3 in the compounds of the group $A^{II}B_2^{III}C_4^{VI}$

Modes	$CdGa_2S_4$ ref. [30]	$ZnGa_2S_4$ ref. [28]	$HgGa_2S_4$ ref. [31]	$CdGa_2Se_4$ ref. [32]	$ZnGa_2Se_4$ ref. [32]	$HgGa_2Se_4$ ref. [33]
A_1	219	230	220	140	143	139
A_2	310	320	300	185	180	183
A_3	359	367	358	207	209	206

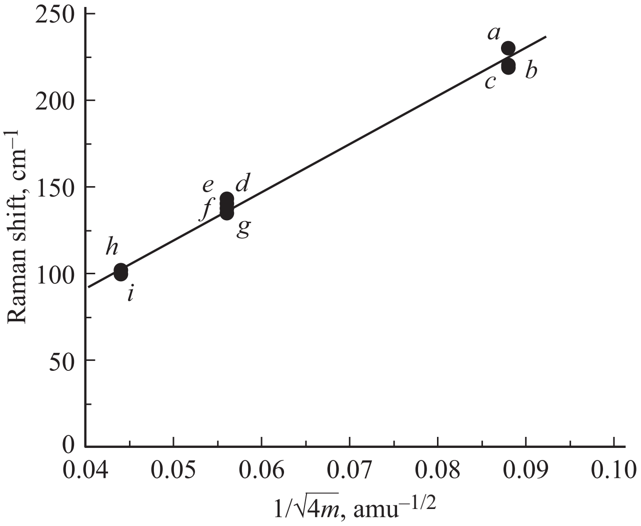

Figure 1. Dependence of the experimentally determined frequencies of the mode A_1 of the crystals $ZnGa_2S_4$ (a), $HgGa_2S_4$ (b), $CdGa_2S_4$ (c), $ZnGa_2Se_4$ (d), $CdGa_2Se_4$ (e), $HgGa_2Se_4$ (f), $ZnIn_2Se_4$ (g), $CdGa_2Te_4$ (h), $CdIn_2Te_4$ (i) on the magnitude $(4m)^{-1/2}$.

atoms along the crystallographic axes x, y, z. At this, the cation sublattice atoms do not participate in the vibrations. The vibrations of the type B are correlated to shifts of the cation sublattice atoms relative to the anion sublattice along the tetragonal axis c (along the axis z). The doubly degenerated modes E_x and E_y are correlated to shifts of the cation sublattice atoms along the crystallographic axes x and y, respectively [29].

As the vibrations of the three symmetry modes A (12) are correlated only to shifts of anion atoms S, Se and Te, then it should be expected that in compounds of the defective chalcopyrites of the group $A^{II}B_2^{III}C_4^{VI}$, containing the identical atoms of anions (for example, $CdGa_2S_4$, $ZnGa_2S_4$, $HgGa_2S_4$ or $CdGa_2Se_4$, $ZnGa_2Se_4$, $HgGa_2Se_4$), the respective frequencies of the modes A_1, A_2 and A_3 will differ slightly. Indeed, as it is clear from Table 3, the frequencies of the modes A_1, A_2 and A_3 in the compounds $CdGa_2S_4$, $ZnGa_2S_4$, $HgGa_2S_4$ and in the compounds $CdGa_2Se_4$, $ZnGa_2Se_4$, $HgGa_2Se_4$ are very close in the value.

Early studies of frequencies of RS-active modes in the defective chalcopyrites [28,34] already mention that the frequencies of the polar (E, B) and non-polar (A) modes can be approximated by the following simple relationship:

$$\omega^2 = \frac{f}{M}. \tag{13}$$

Here f — force constants of interatomic interaction, M — atomic masses. This relationship is significantly simplified, but correctly represents typical frequency regularities for isostructural crystal, for example, the compounds of the group $A_2^V B_3^{VI}$ [20]. Assuming that the most low-frequency mode A_1 in the defective chalcopyrites is due to in-phase shifts of the anion atoms, then in the relationship (13) the mass can be accepted to be $M = 4m$, where m — a mass of the anion. The Fig. 1 shows the dependence of experimentally determined frequencies of the mode A_1 of the compounds $A^{II}B_2^{III}C_4^{VI}$ on the magnitude $(4m)^{-1/2}$. As it is clear from the figure, there is an evident satisfactory dependence (13) of the frequencies of the mode A_1 on the magnitude $(M)^{-1/2}$.

Similar conclusions can be made for the polar modes E and B as well. In the compounds $A^{II}B_2^{III}C_4^{VI}$ the most low-frequency modes E seem to exist due to in-phase shifts of the atoms of the cations A (Zn, Cd, Hg) and the anions C (S, Se, Te). In this case, in (13) approximation of a linear chain it can be assumed that $M = m_A + m_C$, where m_A — a mass of the cation, m_C — a mass of the anion, as it has been done in the paper [34].

Table 4 shows values of the experimentally determined frequencies of the most low-frequency transversal modes E_{TO} of the compounds $A^{II}B_2^{III}C_4^{VI}$ together with respective references to these experimental works.

The Fig. 2 shows the dependence of the experimentally determined frequencies of the most low-frequency transversal modes E_{TO} of the compounds $A^{II}B_2^{III}C_4^{VI}$ on the magnitude $(m_A + m_C)^{-1/2}$. As it is clear from the figure, in this case there is also a well-evident linear dependence (13) of the frequencies of the most low-frequency transversal modes E_{TO} on the magnitude $(M)^{-1/2}$.

In the compounds $A^{II}B_2^{III}C_4^{VI}$ the most high-frequency longitudinal modes B_{LO} probably exist due to out-of-phase shifts of the atoms of the cations A (Zn, Cd, Hg) and the anions C (S, Se, Te). For this, the reduced mass μ is used. In [28], for calculation of the reduced mass μ of the high-frequency symmetry modes E and B of the defective chalcopyrites $A^{II}B_2^{III}C_4^{VI}$ the following relationship

Table 4. Frequencies (in cm^{-1}) of the most low-frequency transversal modes E_{TO} and magnitudes $(m_A + m_C)^{-1/2}$ (in $\mathrm{amu}^{-1/2}$) of the compounds of the group $A^{II}B_2^{III}C_4^{VI}$

	$HgGa_2Se_4$ ref. [33]	$HgGa_2S_4$ ref. [31]	$CdGa_2Se_4$ ref. [28]	$ZnGa_2Se_4$ ref. [34]	$CdGa_2S_4$ ref. [28]	$ZnGa_2S_4$ ref. [28]
Frequences	51	61	68	84	86	108
$(m_A + m_C)^{-1/2}$	0.060	0.066	0.072	0.085	0.083	0.104

Table 5. Frequencies (in cm^{-1}) of the most high-frequency longitudinal modes B_{LO} and magnitudes $\mu^{-1/2}$ (in $\mathrm{amu}^{-1/2}$) of the compounds of the group $A^{II}B_2^{III}C_4^{VI}$

	$CdGa_2Te_4$ ref. [30]	$CdGa_2Se_4$ ref. [30]	$ZnGa_2Se_4$ ref. [32]	$CdGa_2S_4$ ref. [30]	$ZnGa_2S_4$ ref. [32]
Freq.	234	275	285	389	396
$\mu^{-1/2}$	0.126	0.144	0.157	0.198	0.207

is proposed to be used:

$$\frac{4}{\mu} = \frac{2}{m_A} + \frac{1}{m_B} + \frac{4}{m_C}. \tag{14}$$

Experimentally determined frequencies of the most high-frequency longitudinal modes B_{LO} of the compounds $A^{II}B_2^{III}C_4^{VI}$ and references to the respective works are given in Table 5.

The Fig. 3 shows the dependence of the experimentally determined frequencies of the most high-frequency longitudinal modes B_{LO} of the compounds $A^{II}B_2^{III}C_4^{VI}$ on the value of the reduced mass μ, as calculated according to (14). The observed frequency dependence on the reduced mass is satisfactorily described by the linear dependence (13).

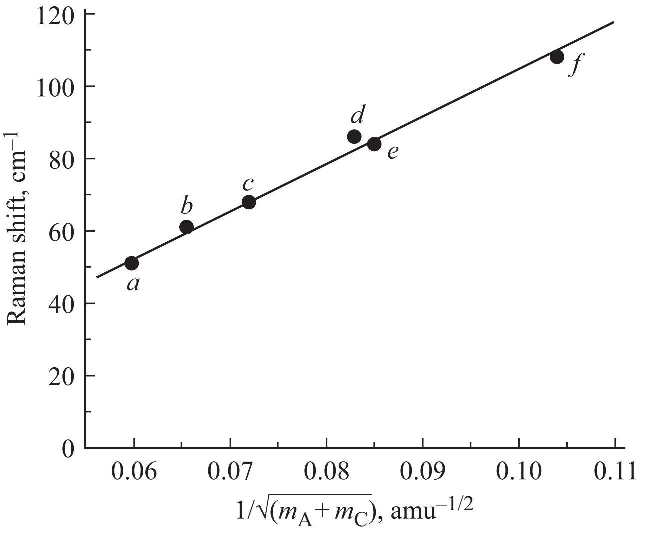

Figure 2. Dependence of the experimentally determined frequencies of the most low-frequency transversal modes E_{TO} of the crystals $HgGa_2Se_4$ (*a*), $HgGa_2S_4$ (*b*), $CdGa_2Se_4$ (*c*), $ZnGa_2Se_4$ (*d*), $CdGa_2S_4$ (*e*), $ZnGa_2S_4$ (*f*) on the magnitude $(m_A + m_C)^{-1/2}$.

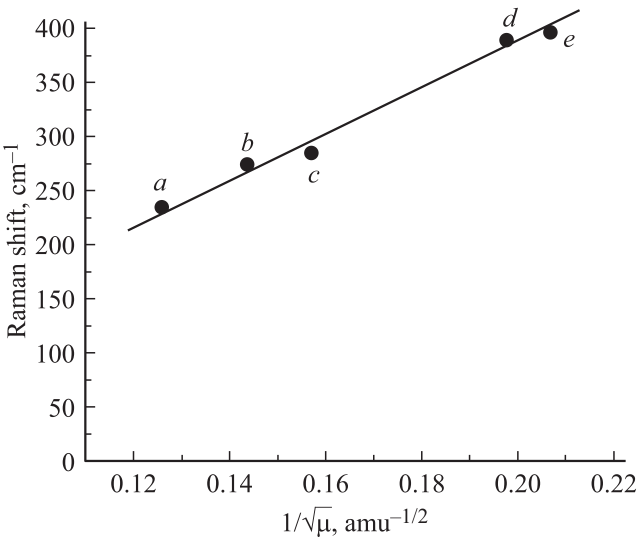

Figure 3. Dependence of the experimentally determined frequencies of the most high-frequency longitudinal modes B_{LO} of the crystals $CdGa_2Te_4$ (*a*), $CdGa_2Se_4$ (*b*), $ZnGa_2Se_4$ (*c*), $CdGa_2S_4$ (*d*), $ZnGa_2S_4$ (*e*) on the magnitude $\mu^{-1/2}$.

6. Force constants of interatomic bonds in the compounds $A^{II}B_2^{III}C_4^{VI}$

The dynamics of the lattice of the compounds $A^{II}B_2^{III}C_4^{VI}$ ($CdGa_2S_4$ and $CdGa_2Se_4$) was calculated for the first time in [35]. The calculation has been performed using the Keating model [36]. In the calculation, taking into account crystal-chemical affinity of compounds of the structure of chalcopyrite ($A^{I}B^{III}C_2^{VI}$ — $AgGaS_2$, $AgGaSe_2$) and thiogallates ($A^{II}B_2^{III}C_4^{VI}$ — $CdGa_2S_4$ and $CdGa_2Se_4$) the force constants of interatomic bonds $B^{III}{-}C^{VI}$ were taken as in $AgGaS_2$, $AgGaSe_2$, while the force constants $A^{II}{-}C^{VI}$, $V{-}C^{VI}$ (V — vacancy) were determined by fitting to the experimental frequencies using the method of least squares. It was fit by using a minor number of the frequencies (one symmetry mode *A*, two symmetry modes *B* and two symmetry modes *E*). Taking into account the above said, the dynamics of the lattice $CdGa_2Te_4$ and $ZnGa_2Se_4$ was

Table 6. Values of the force constants of interatomic bonds in $CdGa_2Te_4$, $ZnGa_2Se_4$ $CdGa_2Se_4$, $CdGa_2S_4$, in units 10^4 dyn/cm

Force constants of interatomic bonds, f_n	$CdGa_2Te_4$ (This work)	$ZnGa_2Se_4$ (This work)	$CdGa_2Se_4$ ref. [38]	$CdGa_2S_4$ ref. [38]
f_1 ($A^{II}-C^{VI}$)	13.71	9.23	13.9	14.28
f_2 ($B_1^{III}-C^{VI}$)	7.89	4.05	6.38	6.28
f_3 ($B_2^{III}-C^{VI}$)	5.61	4.01	6.87	7.89
f_4 ($A^{II}-B_1^{III}$)	−1.68	−0.08	−10.6	−0.6
f_5 ($A^{II}-B_2^{III}$)	2.99	0.38	1.68	3.0
f_6 ($B_1^{III}-B_2^{III}$)	1.87	3.92	1.03	3.0
f_7 ($C^{VI}-C^{VI}$)	1.77	1.29	1.37	0.74

calculated by applying the model of force constants [37]. Such a model was earlier used by us to calculate the dynamics of the lattice $CdGa_2S_4$ and $CdGa_2Se_4$ [38].

When making up elements of the dynamic matrix, the seven force constants were introduced (f_n, $n = 1-7$), which account for interaction both between atoms of the nearest neighbors f_1 ($A^{II}-C^{VI}$), f_2 ($B_1^{III}-C^{VI}$), f_3 ($B_2^{III}-C^{VI}$), and atoms of the cation f_4 ($A^{II}-B_1^{III}$), f_5 ($A^{II}-B_2^{III}$), f_6 ($B_1^{III}-B_2^{III}$) and anion f_7 (C−C) sublattice. In this case B_1 and B_2 — atoms of gallium Ga, which take different positions in the lattice cell. The force constants were found as values of variables corresponding to a minimum of the function $F = \Sigma\left(\omega_i^{\exp} - \omega_i(f_n)\right)^2$. The minimum has been sought by means of a standard program of minimizing the multi-variable function using the method of least squares. The atomic masses M of the relationship (13) were selected for the calculations in accordance with approaches described in the previous section 5. The force constants of interatomic bonds f_n of the compounds $CdGa_2S_4$, $CdGa_2Se_4$, $CdGa_2Te_4$, $ZnGa_2Se_4$ are given in Table 6.

It follows from the data of Table 6 that:

a) in the compounds $A^{II}B_2^{III}C_4^{VI}$, the values of the force constants f_1 ($A^{II}-C^{VI}$) significantly exceed the values of the force constants of interatomic bond f_2 ($B^{III}-C^{VI}$). This means that a nature of the chemical bond in cadmium tetrahedrons is more covalent than in gallium ones;

b) the cation-anion's bonds f_1 ($A^{II}-C^{VI}$) are significantly stronger than the cation-cations' bonds f_5 ($A^{II}-B_2^{III}$) and f_6 ($B_1^{III}-B_2^{III}$), f_3 ($B_2^{III}-C^{VI}$);

c) the sign of cation−cation's bonds f_4 ($A^{II}-B_1^{III}$) is negative, but it does not mean that the value f is negative in the relationship (13), as the value f is a complex combination of the magnitudes f_n [38], each atom in these compounds has several bonds with adjacent atoms;

d) the cation−anions' bonds f_1 ($A^{II}-C^{VI}$), f_2 ($B_1^{III}-C^{VI}$), f_3 ($B_2^{III}-C^{VI}$) are significantly stronger than the anion–anions' bonds f_7 ($C^{VI}-C^{VI}$).

7. Conclusion

The present paper provides data of *ab initio* calculations of values of the seven elastic constants c_{ij} of the compounds $CdGa_2S_4$, $CdGa_2Se_4$, $CdGa_2Te_4$ and $ZnGa_2Se_4$. It also provides the stability criteria of the crystal lattice of the defective chalcopyrites. Using the calculated magnitudes of the elastic constants, the values of the bulk moduli B have been calculated. Based on the available data of one's own studies and literature data on frequencies of optical phonons, the regularities have been established in the dependencies of the frequency values of the RS-active phonons on the atomic masses in the compounds of the group $A^{II}B_2^{III}C_4^{VI}$. The force constants of interatomic bonds of the compounds $CdGa_2Te_4$ and $ZnGa_2Se_4$ have been calculated using the method of least squares by fitting to the experimental frequencies. The obtained data on the force constants confirm that the nature of the chemical bond in cadmium tetrahedrons is more covalent than in gallium ones.

Acknowledgments

The authors dutifully express their gratitude to A.S. Bondyakov (JINR, Russia) and D.A. Kuliyev (Institute of Physics of the National Academy of Sciences of Azerbaijan), as well as to the entire staff of the data center of the Institute of Physics of the National Academy of Sciences of Azerbaijan, for provided resources and technical support for the theoretical calculations.

Funding

This study was financially supported by the Foundation for the Development of Science under the President of the Republic of Azerbaijan (grant No. EIF-BGM-3-BRFTF-2+/2017-15/02/1).

Conflict of interest

The authors declare that they have no conflict of interest.

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