Trends in the band-gap pressure coefficients and bulk moduli in different structures of $ZnGa_2S_4$, $ZnGa_2Se_4$ and $ZnGa_2Te_4$*

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We have performed a first-principles investigation for the family of compounds $ZnGa_2X_4$ (X = S, Se, Te). The properties of two possible structures, defect chalcopyrite and defect famatinite are both calculated. We reveal that $ZnGa_2S_4$ and $ZnGa_2Se_4$ have direct band gaps, while $ZnGa_2Te_4$ has an indirect band gap. The local density approximation band gaps are found to be very different in two structures, while the lattice parameters and bulk moduli are similar. We extend Cohen's empirical formula for zinc-blende compounds to this family of compounds. The pressure coefficients are calculated and metallization pressures are discussed. We find that a_g^i remains fairly constant when the group-VI element X is varied in $ZnGa_2X_4$(II–III_2–VI_4).

Keywords: electronic structure, bulk modulus, pressure coefficient

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1. Introduction

Most of the semiconductors II–III_2–VI_4 have been found to crystallize in the thiogallate structure, called defect chalcopyrite (DC), with space group $I\bar{4}$; while some of them crystallize in the defect famatinite (DF), also known as defect stannite, with higher symmetry space group $I\bar{4}2m$. The two different crystal structures are shown in Fig. 1. They usually have wide regions of transparency, high optical strength, high photosensitivity and intense luminescence, thus are promising semiconductor materials for optoelectronic applications. The tunable filters based on $CdGa_2S_4$ and UV photodetector based on $CdAl_2S_4$ have been used as devices.[1,2] These ordered vacancy compounds form a bridge between the impurity physics and crystal physics. The tetrahedral coordination of atoms in conjunction with the stoichiometric vacancies greatly simplify the doping problem and the formation of solid solutions.[3] The reduction from cubic T_d symmetry of the zinc-blende to tetragonal symmetry D_{2d} makes the chalcopyrite crystals birefringent, and thus useful for nonlinear optical frequency conversion applications, because the birefringence allows people to use angular tuning phase matching. However, many properties of them have not been studied yet because of the difficulty in the growing of single crystal.

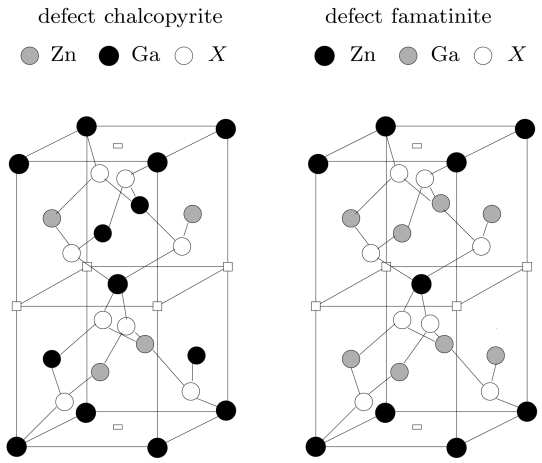


Fig. 1. DC and DF structure of $ZnGa_2S_4$, $ZnGa_2Se_4$ and $ZnGa_2Te_4$.

The structures are of interest to the pressure-induced phase transitions, yet there are only a limited number of high-pressure studies that have been carried out on II–III_2–VI_4 compounds. The structures of $ZnGa_2S_4$, $ZnGa_2Se_4$ and $ZnGa_2Te_4$ are still under

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debate in the literature. Some authors[4,5] suggested that $ZnGa_2S_4$ and $ZnGa_2Se_4$ crystallize in space group $I\bar{4}2m$. By Raman study of the optical phonon modes of $ZnGa_2Se_4$ and $ZnGa_2S_4$, Eifler *et al.*[6] concluded that $ZnGa_2S_4$ most likely crystallizes in space group $I\bar{4}2m$, while the number of modes and their symmetry assignment indicate space group $I\bar{4}$ for the $ZnGa_2Se_4$. Hanada *et al.*[7] used neutron and electron diffraction to study $ZnGa_2Se_4$ and suggested that it belongs to space group $I\bar{4}2m$. Ursaki *et al.*[8] studied the Raman spectroscopy under hydrostatic pressure. The compound $A^{II}Ga_2X_4^{VI}$ with A = Cd belongs to the DC structure characterized by totally ordered cations and stoichiometric vacancies. The compounds with A = Zn belong to the DF structure with partial disorder in the cation sublattice. However, the *ab initio* study of vibrational and electronic properties of $CdGa_2S_4$ and $CdGa_2Se_4$ under pressure casts doubt on whether $CdGa_2S_4$ and $CdGa_2Se_4$ disorder under pressure. Both DF and DC disordering into zinc-blende structure also indicates that it is difficult to determine unequivocally whether they are ordered in DC or DF phase. Allakhverdiev *et al.*[9] studied the Raman scattering spectra of $ZnGa_2Se_4$ under pressure at 300 K up to 18.9 GPa. D. Errandonea *et al.*[10] performed the high-pressure x-ray diffraction study on the structure and phase transitions of $ZnGa_2Se_4$ up to 23 GPa. They found that it exhibits a defect-stannite (DF, $I\bar{4}2m$) structure up to 15.5 GPa, under the pressure ranging from 15.5 to 18.5 GPa the low-pressure phase coexists with a high-pressure phase, which remains stable up to 23 GPa. We recently[11] calculated the bulk moduli of two compounds in DC structure. Here we extend the range of investigation to both DC and DF structures for $ZnGa_2X_4$ (X = S, Se, Te). We hope that the results of pressure coefficients trend and empirical formula of bulk moduli will contribute to the understanding of this important family of ordered-vacancy compounds.

2. Electronic structures

First-principles density functional theory (DFT) calculations are carried out in the local density approximation (LDA).[12] We performed the self-consistent total energy calculation by ABINIT software package.[13] Brillouin zone is sampled with Monkhorst–Pack scheme[14] ($8 \times 8 \times 4$ mesh). We choose the cutoff energy 60 Hartree which gives energy convergence less than 10^{-6} eV.

2.1. DC structure ($I\bar{4}$ phase)

The defect chalcopyrite can be derived from chalcopyrite by removing alternately one centred and four corner cations of chalcopyrite (see Fig. 1). For DC structure with space group $I\bar{4}$, the atomic positions are Zn $(0,0,0)$, Ga $(0.5,0.5,0)a$, Ga $(0,0.5,0.5\eta)a$, $X(x,y,z\eta)a$, $(1-x,1-y,z\eta)a$, $(0.5-y,0.5+x,(0.5-z)\eta)a$, $(0.5+y,0.5-x,(0.5-z)\eta)a$, $\square$ $(0.5,0,0.5\eta)a$; where a is the lattice constant, η is c/a ratio, X = S, Se, Te and $\square$ represents the vacancy site. The relaxed parameters are listed in Table 1. The deviation of the calculated lattice constants a and c from those of experiments[15] are within $\pm 2\%$ and $\pm 0.5\%$ respectively. The relaxed atom X moves towards the vacancy site instead of staying at the ideal positions (0.25,0.25,0.125). $ZnGa_2S_4$ and $ZnGa_2Se_4$ both have direct band gap, agreed with the results via linearized muffin-tin (LMTO) calculation.[16] However, $ZnGa_2Te_4$ has a different electronic structure, an indirect band gap, so we focus on this compound in the following discussion.

Table 1. Calculated and experimental lattice constants, internal parameters for defect chalcopyrite (DC, $I\bar{4}$), 1 Å = 0.1 nm.

	$ZnGa_2S_4$		$ZnGa_2Se_4$		$ZnGa_2Te_4$	
	Calc.	Expt.[15]	Calc.	Expt.	Calc.	Expt.
a/Å	5.17	5.26	5.39	5.48	5.83	5.92
c/Å	10.39	10.4	10.87	10.9	11.77	11.8
x	0.262	0.25	0.269	0.25	0.269	0.25
y	0.256	0.25	0.247	0.25	0.242	0.25
z	0.129	0.125	0.131	0.125	0.131	0.125

The electronic band structure and total density of states of $ZnGa_2Te_4$ are shown in Fig. 2. The band structures and total density of states are calculated using optimized atomic positions at the equilibrium volumes. The top 4∼5 eV area (upper valence band) includes mostly Te p states, also some Ga p character. The cation valence electrons (Zn s, Ga s, p) tend to concentrate in the lower part of the upper valence band. The lower portion of conduction band is dominated mainly by cation (Zn,Ga) s states.

From the band structure, $ZnGa_2Te_4$ has an indirect band gap. The highest energy in the valence band comes at symmetry point $\boldsymbol{\Gamma}$, while the lowest-lying conduction band lies at $\boldsymbol{T}$. There is no experimental band structure available for $ZnGa_2Te_4$. For similar compound like $ZnIn_2Te_4$, there have been some reports of indirect gap.[17,18] We also calculated the electronic band structure using the experimental

parameters, and a different picture appears. From Fig. 3, symmetry point $\boldsymbol{N}$ at conduction band now has the lowest value, meanwhile symmetry point at conduction bands $\boldsymbol{\Gamma}$ and $\boldsymbol{N}$ have very similar energies. $ZnGa_2Te_4$ still has an indirect gap of 0.53 eV, but the minimal gap occurs now at $\boldsymbol{N}$ instead of point $\boldsymbol{T}$ in BZ. Whether or not using the optimized parameters plays a key role in band structure calculation for $ZnGa_2Te_4$ of DC structure.

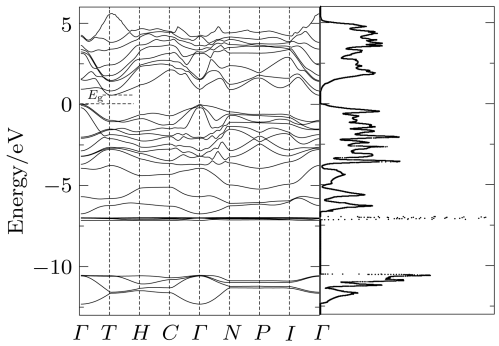


Fig. 2. Band structure and total DOS of $ZnGa_2Te_4$ in DC.

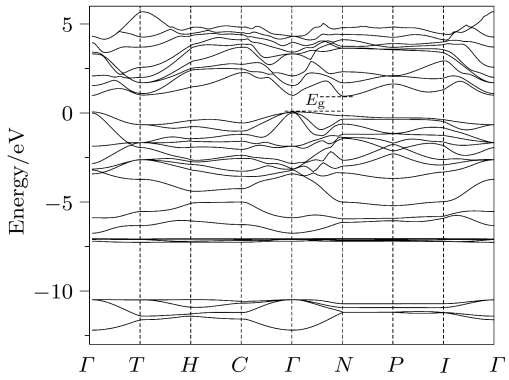


Fig. 3. Electronic band structure $ZnGa_2Te_4$ for unrelaxed DC structure.

2.2. DF structure ($I\bar{4}2m$ phase)

The defect famatinite can be derived from famatinite by removing alternately one centered and four corner cations of famatinite (see Fig. 1). For DF structure with space group $I4\bar{2}m$, the atomic positions are Zn $(0,0,0)$, Ga $(0.5,0,0.5\eta)a$, Ga $(0,0.5,0.5\eta)a$, $X(x,x,z\eta)a$, $(1-x,1-x,z\eta)a$, $(0.5-x,0.5+x,(0.5-z)\eta)a$, $(0.5+x,0.5-x,(0.5-z)\eta)a$, □ $(0.5,0,5,0)a$; where a is the lattice constant, η is c/a ratio, X = S, Se, Te and □ represents the vacancy site. The relaxed parameters are listed in Table 2. The deviation of the calculated lattice constants a and c from those of experiments[15] are also within ±2% and ±0.5% respectively. The relaxed atom X moves towards the vacancy site instead of staying at the ideal positions (0.25,0.25,0.125).

Table 2. Calculated and experimental lattice constants, internal parameters for defect famatinite (DF, $I\bar{4}2m$).

	$ZnGa_2S_4$		$ZnGa_2Se_4$		$ZnGa_2Te_4$	
	Calc.	Expt.[15]	Calc.	Expt.	Calc.	Expt.
a/Å	5.16	5.26	5.38	5.48	5.83	5.92
c/Å	10.38	10.4	10.87	10.9	11.76	11.8
x	0.264	0.25	0.270	0.25	0.270	0.25
z	0.122	0.125	0.118	0.125	0.115	0.125

Similar to the DC phase, $ZnGa_2S_4$ and $ZnGa_2Se_4$ give direct band gap at $\boldsymbol{\Gamma} \to \boldsymbol{\Gamma}$, while $ZnGa_2Te_4$ has an indirect band gap at $\boldsymbol{\Gamma} \to \boldsymbol{T}$, but with smaller value of 0.21 eV. The band structure calculated from optimized parameters is shown in Fig. 4.

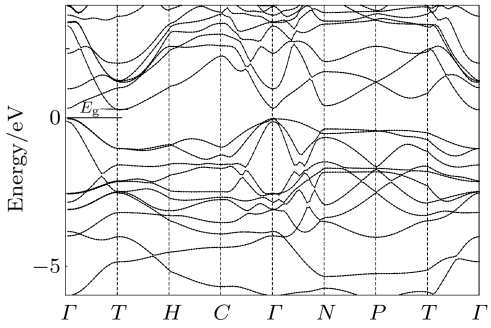


Fig. 4. Electronic band structure of $ZnGa_2Te_4$ for relaxed DF structure.

Using the experimental parameters, we obtain a different band structure (see Fig. 5). The symmetry point at conduction band $\boldsymbol{\Gamma}$ and $\boldsymbol{N}$ still have subtle energy difference as in DC phase. However, this time the minimal gap occurs at $\boldsymbol{\Gamma} \to \boldsymbol{\Gamma}$, forming a direct band gap. Again we see the importance of structural optimization in the electronic structure calculations of $ZnGa_2Te_4$ in DF structure.

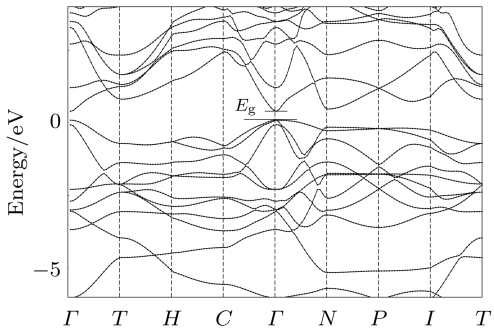


Fig. 5. Electronic band structure of $ZnGa_2Te_4$ for unrelaxed DF structure.

2.3. Comparison of band structures in DF and DC, band gap trend

The overall similarity is obvious, $ZnGa_2S_4$ and $ZnGa_2Se_4$ both have direct band gaps in DC and DF phases, while $ZnGa_2Te_4$ has an indirect band gap, which is localized at $\boldsymbol{\Gamma} \rightarrow \boldsymbol{T}$ in both structures. Previous result of $ZnGa_2Te_4$ gives direct band gap, and we have shown that it is due to the lack of structural optimization. The band structure of $ZnGa_2Te_4$ is sensitive to lattice constant and atomic positions at equilibrium configuration.

Local density approximation (LDA) is known for its underestimation of band gaps, however, the trend is very clear (Fig. 6). From S $\rightarrow$ Se $\rightarrow$ Te, the band gap decreases from 2.86 eV $\rightarrow$ 1.94 eV $\rightarrow$ 0.53 eV in DC structure; while the band gap decreases from 2.15 eV $\rightarrow$ 1.31 eV $\rightarrow$ 0.21 eV in DF structure. The reduction of gap energies are related to the strength of bonding. Overall, the DC compound has larger band gap than DF compound, the difference varies from 0.7 eV to 0.3 eV.

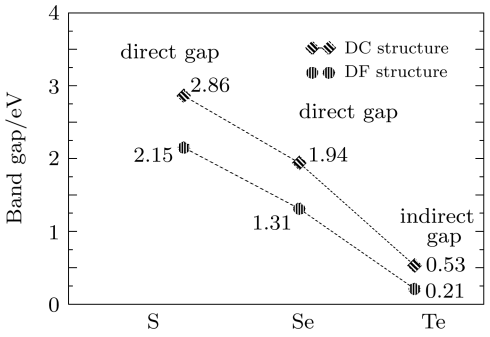


Fig. 6. LDA band gaps for DC and DF structures of $ZnGa_2S_4$, $ZnGa_2Se_4$ and $ZnGa_2Te_4$.

3. Bulk moduli and extended empirical formula

The relation between the energy and volume is fitted to the integrated form of third-order Birch–Murnaghan's equation of state.[19] The bulk modulus (B), pressure derivative (B') and equilibrium volume (V_0) can be extracted[20,21] from the following equation

$$\begin{aligned} & E(V) \\ &= E_0 + \frac{9}{8} B V_0 \left(\left(\frac{V_0}{V} \right)^{2/3} - 1 \right)^2 \\ &\times \left(1 + \left(\frac{4 - B'}{2} \right) \left(1 - \left(\frac{V_0}{V} \right)^{2/3} \right) \right). \end{aligned} \quad (1)$$

The results are listed in Table 3. The two different structures DC and DF have similar bulk moduli. The bulk modulus of DC is found to increase by 33% and 51% as Te is substituted with Se and S, respectively; while the bulk modulus of DF is found to increase by 34% and 54% as Te is substituted with Se and S, respectively. This trend is due to the change of bond length (Table 4) and bond energy.

Table 3. Calculated bulk moduli for DC ($I\bar{4}$) and DF ($I\bar{4}2m$).

	$ZnGa_2S_4$		$ZnGa_2Se_4$		$ZnGa_2Te_4$	
	DC	DF	DC	DF	DC	DF
bulk modulus/GPa	59	63	52	55	39	41
B'	3.83	4.52	4.41	4.81	4.47	4.36

Table 4. Calculated bond-length in Å (used by extended Cohen's empirical formula).

bond	$ZnGa_2S_4$		$ZnGa_2Se_4$		$ZnGa_2Te_4$	
	DC	DF	DC	DF	DC	DF
Zn–X	2.32	2.30	2.43	2.41	2.61	2.60
Ga–X	2.21	2.21	2.34	2.34	2.55	2.57
Ga–X	2.20	2.21	2.33	2.34	2.54	2.57

There are few experimental results available for the bulk moduli. D. Errandonea *et al.*[10] recently made high-pressure x-ray diffraction study on the structure and phase transitions of $ZnGa_2Se_4$ up to 23 GPa. They found that it exhibits a defect-stannite (DF, $I\bar{4}2m$) structure up to 15.5 GPa and in the range of 15.5 to 18.5 GPa the low-pressure phase coexists with a high-pressure phase, which remains stable up to 23 GPa. The high-pressure phase is assigned to a defect NaCl-type structure. For DF structure, they obtained $B_0 = 47(2)$ GPa and $B_0' = 3.9(3)$. For NaCl-type structure, they obtained $B_0 = 50(2)$ GPa and $B_0' = 4$.

The bulk modulus of a binary zinc-blende compound can be estimated by Cohen's empirical formula.[22] The original empirical formula B is appropriate for zinc-blende solids:

$$B = (1971 - 220\lambda)/d^{3.5}, \quad (2)$$

where due to different ionicity and covalency, the λ is chosen to be 0, 1 and 2 for group-IV, II–V and II–VI semiconductors, respectively, due to the increase of ionicity and loss of covalency in going from the group-IV to II–VI and II–Vi semiconductors.

Alloys and more complex structures with tetrahedral bonding may also be estimated in an approximate

way by taking average nearest-neighbour distances. We extend the formula to II–III_2–VI_4 compounds:

$$B = \frac{1971 - 220\lambda}{4} \sum_{i=1,2,3} \frac{1}{d_i^{3.5}} \tag{3}$$

for bulk modulus B in GPa and the nearest-neighbour distance d_i in Å. The distance d in equation (3) is the bond length of Zn–X, Ga–X, Ga–X. We only include three bonds because one tetrahedrally bonded atom is replaced by a vacancy. We sum them up with a factor 1/4 for each tetrahedral bond. The coefficient ($\lambda = 2$) is chosen analogous to II–VI ($\lambda = 2$) semiconductors. Using the calculated bond length (listed in Table 3), this formula gives 68 GPa, 56 GPa and 41 GPa for $ZnGa_2S_4$, $ZnGa_2Se_4$ and $ZnGa_2Te_4$, respectively. The trend is understandable if we consider the covalency increases going to the upper rows of the Periodic Table. Because of the larger contribution of covalency to B, the loss of covalent bond charge can reduce B. The different structures of DF and DC have almost the same bulk modulus from the extended Cohen's empirical formula, mainly because they have similar electronic structures and bond lengths.

Our *ab initio* results agree reasonably well with the empirical model. One might apply the extended empirical formula to estimate the bulk moduli of II–III_2–VI_4 semiconductors. We still need to investigate more compounds in this family to determine the validity of this extended empirical formula, i.e., by comparing the first-principles bulk moduli with the empirical estimation. The experimental results are needed to verify all the theoretical conclusions.

4. Predicated band-gap pressure coefficients and the empirical rule

4.1. Pressure coefficients of $ZnGa_2S_4$, $ZnGa_2Se_4$ and $ZnGa_2Te_4$ (in DF and DC)

At low pressure, we can fit energy gap $E_{\rm gap}(p)$ to the quadratic function:

$$E_{\rm g}(p) = E_{\rm g}(0) + ap + bp^2, \tag{4}$$

where $E_{\rm g}(p)$ is the band-gap energy; p is the pressure; a, b are the first-order and second-order pressure derivatives, respectively. We calculate the pressure coefficient and list results in Tables 5 and 6.

Table 5. Calculated pressure coefficients of $ZnGa_2S_4$ and $ZnGa_2Se_4$ (in DC, DF structures), $E = E_0 + ap + bp^2$, a in unit meV/kbar and b in meV/GPa; $\mathrm{d}E_{\rm g}/\mathrm{d}\ln V$ in eV; Region I corresponds to lower and negative pressure area; Region II corresponds to higher pressure area.

	DC						DF					
	region I			region II			region I			region II		
	a	b	$-\mathrm{d}E_{\rm g}/\mathrm{d}\ln V$	a	b	$-\mathrm{d}E_{\rm g}/\mathrm{d}\ln V$	a	b	$-\mathrm{d}E_{\rm g}/\mathrm{d}\ln V$	a	b	$-\mathrm{d}E_{\rm g}/\mathrm{d}\ln V$
S	9.26	-4.47	5.50	–2.51	0.117	–2.031	7.19	–4.07	4.58	–1.21	0.061	–2.12
Se	9.39	-4.10	4.89	–2.59	0.143	–2.487	7.07	–3.28	3.83	–2.08	0.127	–3.36

Table 6. Calculated pressure coefficients of $ZnGa_2Te_4$; $E = E_0 + ap + bp^2$, a in meV/kbar and b in meV/GPa.

	DC		DF	
	a	b	a	b
$\Gamma \to \Gamma$	–4.37	0.287	–3.02	0.438
$\Gamma \to T$	–5.25	0.417	–4.56	0.338
$\Gamma \to N$	1.37	–0.133	1.44	–0.105

The pressure coefficient of an interband transition i is defined as:

$$a_{\rm g}^i = \frac{\mathrm{d}E_{\rm gap}}{\mathrm{d}p}. \tag{5}$$

First we investigate the band gap variation with pressure. The $ZnGa_2S_4$ (see Fig. 7) has a direct gap and the band gap minimum lies at $\boldsymbol{\Gamma} \to \boldsymbol{\Gamma}$. The curve can be divided into two parts. In the first part (region I in Table 5), where the pressure is less than 5 GPa (including negative pressure), the band gap increases almost linearly as the pressure increases (a monotonic increasing function of pressure). In the second part (labeled as region II in Table 5), where the pressure is equal or greater than 5 GPa, the band gap decreases with higher pressure (a monotonic decreasing function of pressure). The different slopes of DC and DF cause a crossing of curves around the pressure of 57 GPa. After the crossover, DF has a higher direct energy

gap than DC.

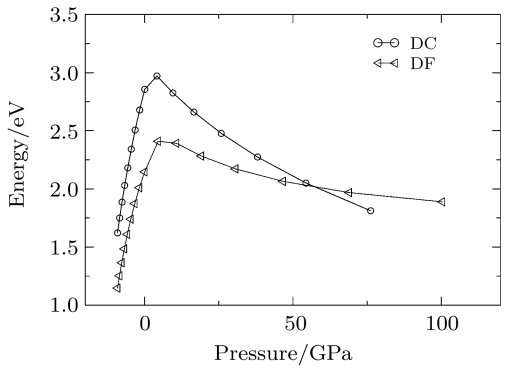


Fig. 7. Calculated direct band gap at Γ for $ZnGa_2S_4$ as a function of pressure p (GPa) for DC and DF structures.

From Fig. 8, the $ZnGa_2Se_4$ has a direct band gap at $\boldsymbol{\Gamma} \to \boldsymbol{\Gamma}$ and a similar behaviour as $ZnGa_2S_4$. Under the pressure less than 7 GPa, the energy gap is a monotonic increasing function, while it becomes a a monotonic decreasing function after the pressure is higher that 7 GPa. The slopes in region II (> 7 GPa) differ not as much as in $ZnGa_2S_4$, and there is no crossover occurred with the varying pressure, which means the DC structure always has a higher band gap energy than the DF structure.

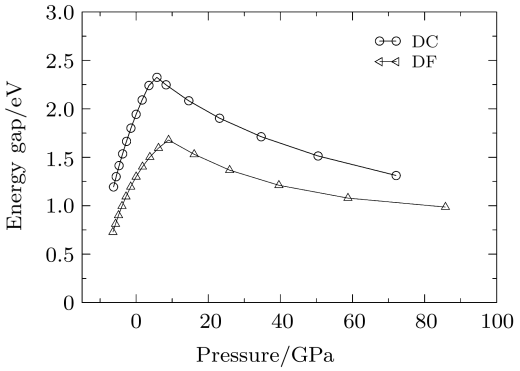


Fig. 8. Calculated direct band gap at Γ for $ZnGa_2Se_4$ as a function of pressure p (GPa) for DC and DF structures.

Neither $ZnGa_2S_4$ (in DC and DF) nor $ZnGa_2Se_4$ (in DC and DF) metallizes throughout the pressure range of our calculation. They remain direct gap semiconductors until about 100 GPa, which is the maximum pressure in this simulation. If we assume that there exist linear pressure shifts at higher pressure range, by simple linear extrapolation we obtain the metallization pressures of DC-structured $ZnGa_2S_4$ and $ZnGa_2Se_4$ to be about 200 GPa and 250 GPa, respectively. The thiogallated phase probably becomes structurally unstable prior to the metallization, because experiments show that phase transitions (e.g. order–disorder) of these compounds occur usually less than 20 GPa.[8,10] So neither $ZnGa_2S_4$ nor $ZnGa_2Se_4$ will metallize under high pressure. As for the DF-structured compounds, since the slopes are far less steep than those of DC-structured, the metallization pressures would be too high to be considered here.

For $ZnGa_2Te_4$ in DC structure, there are three curves plotted in Fig. 9, corresponding to transition $\boldsymbol{\Gamma} \to \boldsymbol{\Gamma}$, $\boldsymbol{\Gamma} \to \boldsymbol{T}$ and $\boldsymbol{\Gamma} \to \boldsymbol{N}$. The transition energy of $\boldsymbol{\Gamma} \to \boldsymbol{N}$ is a monotonic increasing function with pressure, while the other two are monotonic decreasing function. The band gap minimum always lies at $\boldsymbol{\Gamma} \to \boldsymbol{T}$. $ZnGa_2Te_4$ is predicted to metallize near 9 GPa.

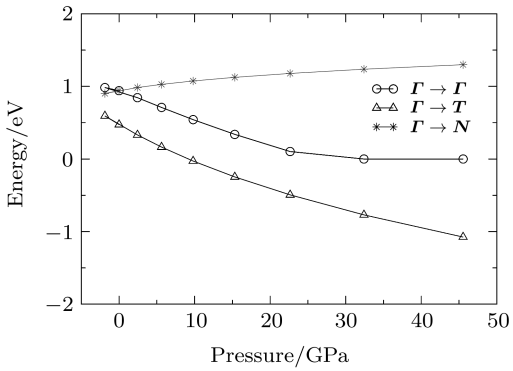


Fig. 9. Calculated direct band gap at Γ, N and T for $ZnGa_2Te_4$ as a function of pressure p (GPa) for DC structures.

For $ZnGa_2Te_4$ in DF structure, three curves cross near the equilibrium configuration (Fig. 10). The compound has a direct band gap at some negative pressure. When the pressure reaches about zero the transition energy of $\boldsymbol{\Gamma} \to \boldsymbol{T}$ becomes the lowest one. At the equilibrium configuration the $\boldsymbol{\Gamma} \to \boldsymbol{\Gamma}$ transition and $\boldsymbol{T} \to \boldsymbol{\Gamma}$ transition are very close in the values of band gap shift. Using the unrelaxed lattice constants and atomic positions, which is equivalent to put some negative pressure on the crystal, one might have concluded that $ZnGa_2Te_4$ had a direct band gap at $\boldsymbol{\Gamma} \to \boldsymbol{\Gamma}$. $ZnGa_2Te_4$ in DF structure is predicted to metallize near 6 GPa.

We also calculate the volume deformation potential

$$a_{\mathrm{V}}^{i} = \frac{\mathrm{d}E_{\mathrm{g}}}{\mathrm{d}\ln V}. \tag{6}$$

In Fig. 11, the energy gap of $ZnGa_2S_4$ is plotted as a function of $\ln V$. Compared with Fig. 7, the linearity of E_{g} as a function of $\ln V$ is higher than that of a linear function of p. Similar conclusion can be drawn for $ZnGa_2Se_4$ (Fig. 12). As for the absolute value, from S $\to$ Se, $\mathrm{d}E_{\mathrm{g}}/\mathrm{d}\ln V$ decreases from 16.98

→ 14.67. However, thanks to the decrease of bulk modulus B (from 59→52), the above two effects offset each other, so $a_{\rm g}^{\Gamma\to\Gamma}$ is nearly independent of group VI element.

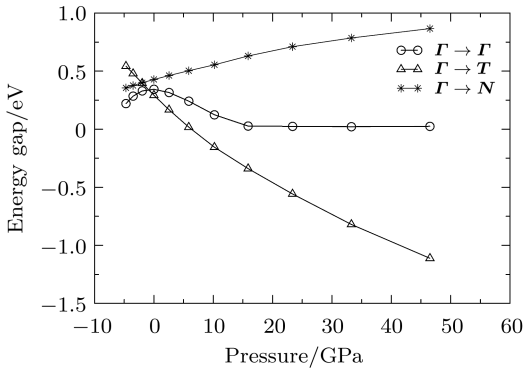


Fig. 10. Calculated direct band gap at Γ, N and T for $ZnGa_2Te_4$ as a function of pressure p (GPa) for DF structures.

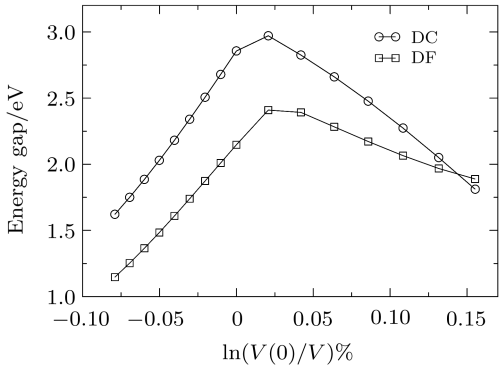


Fig. 11. Calculated direct band gap at Γ for $ZnGa_2S_4$ as a function of pressure $\ln(V_0/V)$ for DC and DF structures.

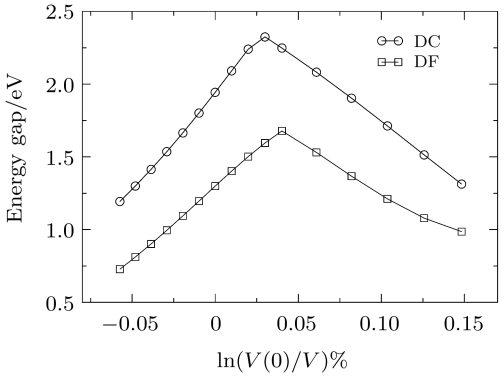


Fig. 12. Calculated direct band gap at Γ for $ZnGa_2Se_4$ as a function of pressure $\ln(V_0/V)$ for DC and DF structures.

4.2. The empirical rule

According to William Paul, the pressure coefficients of zinc-blende structures have an "empirical rule":[23] for a given interband transition type i, the pressure coefficient $a_{\rm g}^{(i)}$ depends mainly on the symmetry of the transition i. In tetrahedrally coordinated compounds, the $a_{\rm g}^{(i)}$ are similar for transitions involving the same symmetry of transition i. Wei *et al.*[24] tested the applicability of such a rule to chalcopyrites ABC_2. They calculated the direct band gap pressure coefficient $a_{\rm g}$ for a series of Ga and In semiconductor compounds (e.g., $CuGaSe_2$ and $CuInSe_2$), and found $a_{\rm g}$ in chalcopyrite is fairly constant when the group-I transition metal A is varied, but when the group-III cation B is changed from Ga to In, $a_{\rm g}$ can decrease by as much as 40%. Since defect chalcopyrites and defect famatinites can also be considered as tetrahedrally coordinated, we investigate if the "empirical rule" applies here. We simulated the pressure coefficients of $ZnGa_2X_4$ with anions X varying from S → Se → Te. Since Te compound has different properties and an indirect gap at transition $\Gamma \to T$, we only consider S → Se here.

Near the zero pressure, the pressure coefficients of $ZnGa_2S_4$ and $ZnGa_2Se_4$ are 9.26 meV/kbar and 9.39 meV/kbar in DC structure, while they are 7.19 meV/kbar and 7.07 meV/kbar in DF structure. We conclude that in AB_2C_4(II–III_2–VI_4), $a_{\rm g}^{\Gamma\to\Gamma}$ remains fairly constant when group VI element changes, and the "empirical rule" is valid here. There are more than 20 compounds in this family, so in order to conclude that the "empirical rule " holds for the whole family, we need to do a systematic calculations, which is our plan in near future.

5. Conclusion

In summary we have investigated the properties of the compound family $ZnGa_2X_4$ (X = S, Se, Te). The two possible structures, defect chalcopyrite (DC) and defect famatinite (DF) are studied via *ab initio* calculations. The results are summarized in the following.

(i) The band gap of $ZnGa_2Te_4$ is indirect in both DC and DF structures. Meanwhile $ZnGa_2S_4$ and $ZnGa_2Se_4$ both have direct band gaps. The LDA band gaps are found to be very different in DC and DF structures, while the lattice parameters, bond lengths and bulk moduli are similar.

(ii) We extend Cohen's empirical formula for zinc-blende materials to these compounds. The results are verified by first-principles calculations. The bulk moduli of DC are found to increase by 33% and 51% (34% and 54% for DF) as Te is substituted with Se and S, respectively. These can be explained by the change of bond length and covalency.

(iii) We have simulated the pressure coefficients for these compounds. The linearity of pressure coefficient E_g as a function of $\ln V$ is higher than that as a linear function of p. In $ZnGa_2X_4$ (II–III_2–VI_4), $a_g^{\Gamma\to\Gamma}$ remains fairly constant when group VI element X is varied, and the "empirical rule" is valid.

(iv) By linear extrapolation, the metallization pressures are discussed. For the DC-structured $ZnGa_2S_4$ and $ZnGa_2Se_4$, we predict that the metallization pressures are about 200 GPa and 250 GPa, respectively. As for the DF-structured compounds, the metallization pressures would be too high to be considered. However, they will not metallize with high pressure, because some phase transition will occur before they reach the metallization pressure. The DC-structured $ZnGa_2Te_4$ will metallize near 9 GPa, while DF-structured $ZnGa_2Te_4$ will metallize near 6 GPa.

References

[1] Georgobiani A N, Radautsan S I and Tiginyanu I M 1985 *Sov. Phys. Semicond.* **10** 121

[2] Radautsan S I and Tiginyanu I M 1993 *Jpn. J. Appl. Phys.* **32** (*Suppl.* 3) 5

[3] Bernard J E and Zunger A 1988 *Phys. Rev.* B **37** 6835

[4] Antonioli G, Lottici P P and Razzetti C 1989 *Phys. Status Solidi* B **152** 39

[5] Lottici P P and Mazzetti C 1983 *Solid State Commun.* **46** 681

[6] Eifler A, Krauss G, Riede V, Kramer V and Grill W 2005 *J. Phys. Chem. Solids* **66** 2052

[7] Hanada T, Izumi F, Nakamura Y, Nittono O, Huang Q and Santoro A 1998 *Physica* B **241-243** 373

[8] Ursaki V V, Burlakov I I, Iignyanu I M, Raptis Y S, Anastassakis E and Anedda A 1999 *Phys. Rev.* B **59** 257

[9] Allakhverdiev K, Gashimzade F, Kerimova T, Mitani T, Naitou T, Matsuishi K and Onari S 2003 *J. Phys. Chem. Solids* **64** 1597

[10] Errandonea D, Kumar R, Manjon F J, Ursaki V V and Tiginyanu I M 2008 *J. Appl. Phys.* **104** 063524

[11] Jiang X S, Mi S, Sun P J and Liang J Q 2009 *Chin. Phys. Lett.* **26** 077102

[12] Kohn W and Sham L J 1965 *Phys. Rev.* A **140** 1133

[13] Gonze X, Beuken J M, Caracas R, Detraux F, Fuchs M, Rignanese G M, Sindic L, Verstraete M, Zerah G, Jollet F, Torrent M, Roy A, Mikami M, Ghosez P, Raty J Y and Allan D C 2002 *Computat. Mater. Sci.* **25** 478

[14] Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188

[15] Hahn H, Frank G, Klinger W, Störger A D and Störger G 1955 *Z. Anorg. Allg. Chem.* **279** 241

[16] Jiang X S and Lambrecht W R L 2004 *Phys. Rev.* B **69** 035201

[17] Manca P, Raga F and Spiga A 1973 *Phys. Status Solidi* (a) **16** K105

[18] Manca P, Raga F and Spiga A 1974 *Nuovo Cimento* B **19** 15

[19] Francis Birch 1947 *Phys. Rev.* **71** 809

[20] Wang Y J and Wang C 2009 *Chin. Phys.* B **18** 4339

[21] Li D H 2010 *Acta Phys. Sin.* **59** 2004 (in Chinese)

[22] Cohen M L 1985 *Phys. Rev.* B **32** 7988

[23] Paul W 1998 *High Pressure in Semiconductor Physics* ed. Suski T and Paul W (San Diego: Academic)

[24] Wei S H and Zunger A 1998 *Phys. Rev.* B **58** 1710