

Ab-initio study of thermodynamic properties of CdGa₂Se₄ crystal

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Abstract

Density functional theory (DFT) is used to calculate the density of phonon energy states and the phonon spectrum at symmetric points and lines of the Brillouin zone. Using the phonon spectrum and the phonon density of states, the molar entropy, the internal energy of phonons, and the temperature dependence of the heat capacity at constant volume for CdGa₂Se₄ in the range 0÷400 K were calculated from first principles. It is shown that the molar heat capacity varies according to the cubic Debye law T^3 at temperatures below 6,1 K. The calculated frequencies of optical phonons were compared with the experimentally determined frequencies from the infrared absorption (IR) and Raman spectra (R), and it was shown that they are in good agreement.

Keywords: CdGa₂Se₄ ; DFT; Fonon spectrum; thermodynamic properties

1. Introduction

$A^{II}B_2^{III}C_4^{VI}$ (A - Zn, Cd; B - In, Ga; C - S, Se, Te) compounds crystallized in the space group ($I\bar{4}$) are analogues of crystal chemical compounds of sphalerite and chalcopyrite structures. These compounds are characterized by optical anisotropy,

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birefringence, high nonlinear absorption coefficients, high photosensitivity and bright luminescence. These properties and the presence of a large energy band gap make these compounds promising materials for use in semiconductor devices [1,2].

Combined theoretical and experimental studies of phonon spectra and lattice dynamics at the center of the Brillouin zone (point Γ), allows to get information about phonon frequencies, phonon-electron, phonon-phonon interactions, etc.

Quantities characterizing the thermodynamic properties of solids - molar entropy, heat capacity, enthalpy and temperature dependence of free energy are the main functions that characterize the stability of compounds depending on temperature and pressure. These functions also determine the direction and rate of chemical reactions, and the probability of occurrence of pressure- and temperature-dependent phase transitions. By applying the thermodynamic function and thermodynamic laws, it is possible to determine the stability of various states of substances, the force constants between atoms, and the thermal oscillation frequencies and amplitudes of atoms.

Optical phonons of CdGa_2Se_4 crystal were studied by infrared spectroscopy and Raman scattering in [3–5].

This paper presents thermodynamic functions of CdGa_2Se_4 crystal calculated from fundamental principles, phonon spectrum and density of phonon states at highly symmetric points and lines of the Brillouin zone.

2. Crystal structure of CdGa_2Se_4 and method of calculation.

CdGa_2Se_4 is a crystal chemical analogue of compounds that crystallize in the sphalerite (T_d) and chalcopyrite (D_{2d}^{12}) structures. In the crystal cell, each cation atom is surrounded by four anion atoms. Crystal cell parameters and atomic coordinates determined by X-ray diffraction of CdGa_2Se_4 crystal [6] are listed in Table 1. According to these data, the $d(\text{A}-\text{C})$ interatomic bond length is greater than the $d(\text{B}-\text{C})$ bond length. This indicates that the chemical connection in the compound is ion-covalent in nature [7].

CdGa_2Se_4 crystal has 7 atoms in unit cell. Crystallographic coordinates and Wyckoff position of atoms in the unit cell are as follows [6]:

Cd (2a)	0	0	0
Ga1 (2b)	0	0	0.5
Ga2 (2c)	0	0.5	0.25
Se (8g)	0.2936	0.229	0.1448

Calculations were performed by the Density Functional Method in the linear response approximation with the pseudopotential method using the ABINIT software package [8]. In the calculations, the wave functions are ordered by plane waves. The exchange-correlation interaction is described in Local Density Approximation (LDA) according to the scheme [9] and using norm-preserving

Troullier-Martins (TM) [10] pseudopotentials. Plane waves with an energy of up to

Table 1. Calculated and experimentally determined cell and chalcogen parameters for CdGa₂Se₄ crystal.

Cell and chalcogen parameter	Theory	Exper.[6]
$a, \text{Å}$	5.573	5.317
$c, \text{Å}$	10.756	10.286
x	0.2886	0.294
y	0.2311	0.229
z	0.1493	0.145

80 Ry were used in the expansion of wave functions, which ensures a sufficient convergence of energy. Brillouin zone integration was performed with a $4 \times 4 \times 4$ division according to the Monkhorst-Pack scheme [11]. The unit cell parameters and the equilibrium position of the atoms were found from the condition of minimizing the Hellman-Feynman forces acting on the atoms. The minimization process was continued until the force moduli were smaller than 10^{-7} Hartree/Bohr. Lattice dynamics were calculated using Density Functional Perturbation Theory (DFPT) [12-14].

3. Phonon spectrum and density of states in CdGa₂Se₄.

As mentioned above, the studied compound has 7 atoms in the unit cell. Accordingly, the vibration spectrum consists of 21 phonon modes and is expressed by the following irreducible representations:

$$\Gamma = 3A(R) + 6B(IR,R) + 6E(IR,R) \quad (1)$$

3 A symmetry mode is allowed in Raman spectra. 5 B and 5 E symmetry modes are allowed in both infrared absorption spectra and Raman scattering spectra. One B and one E symmetry modes are acoustic modes. Fully symmetrical A-type oscillations are associated with displacements of anion sublattice atoms along the x, y, and z crystallographic axes. The atoms of the cation sublattice do not participate in vibrations. B-type oscillations are related to the displacement of cation sublattice atoms along the tetragonal axis c with respect to the anion sublattice.

The double degenerate Ex and Ey modes are associated with displacements of the cation sublattice atoms along the crystallographic x and y axes, respectively. Table. 2 shows experimental and theoretically calculated frequencies of A, B and E symmetry modes. It can be seen that there is good agreement between the calculated and experimentally determined frequencies. The difference between calculated and experimental frequencies is small (5-6%).

Table 1. Theoretically calculated and experimentally determined frequencies of optical phonons in CdGa₂Se₄ crystal (in cm⁻¹ unit).

Symmetry	Theory	[3]	IR[4]	R [5]
A	137.5	141		140
	183.2	188		189.9
	200	210		266
	76.8	78	122	75
B	124	127	125	127/127
	198	202	198	225
	210.5	237	225	247
	256.8	286	275	275
	65.6			
E	68.2	70		67.6
	101.3			
	103	107		104.4
	178.5	178	180	181
	185			
	233			
	240	241	242	242
	245.5			
267	262	274	278	

Fig. 1 and Fig. 2 respectively show the phonon dispersion and density of phonon states in CdGa₂Se₄ in the Brillouin zone. As can be seen from Fig. 1, the phonon spectrum consists of three regions: in the CdGa₂Se₄ crystal, a high density of energetic states is observed in the frequency interval of 51–130 cm⁻¹, 179–281 cm⁻¹, and a low density of energetic states is observed in the frequency interval of 120–180 cm⁻¹. It can also be seen from Figure 1 that in the $\Gamma - Z$ direction of the Brillouin zone (along the tetragonal c-axis) optical phonons have a weak dispersion, which indicates that the phonon-phonon interaction along the tetragonal axis is weak. However, in the direction X–P–N a different picture is observed. In this direction, acoustic branches intersect with low-frequency optical modes. The latter is indicative of significant phonon-phonon interaction in the xy plane. It should be noted that this result was confirmed experimentally in [15]. Thus, it can be concluded from the above that the phonon-phonon interaction in the xy plane is greater than the interaction along the c tetragonal axis. Frequencies observed experimentally in the infrared absorption and Raman scattering spectra of light and

the calculated frequencies of the optical phonons are in good agreement (Table 2). It is known that the long-range electric field in polar crystals causes dipole optical oscillations to split into transverse (TO) and longitudinal (LO) optical modes.

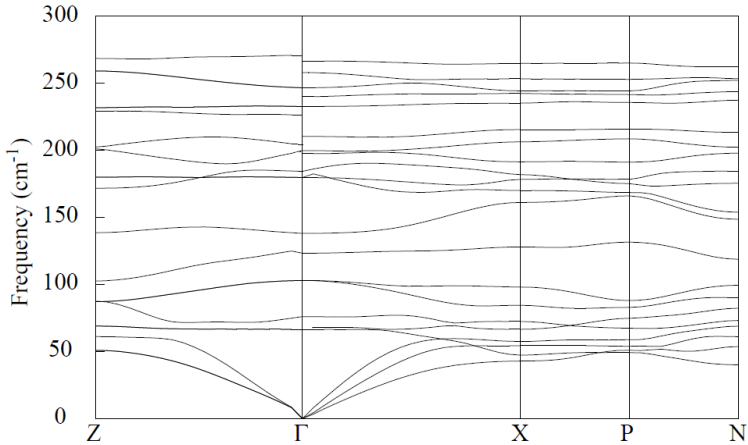


Fig. 1. Phonon dispersion of CdGa₂Se₄.

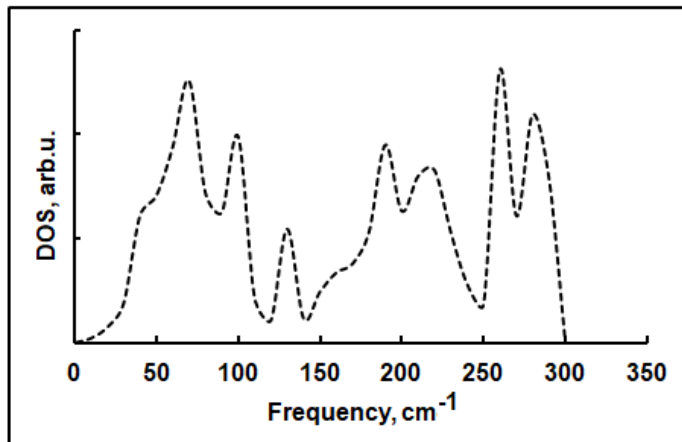


Fig. 2. Phonon density of states of CdGa₂Se₄.

These splittings at the Γ point in the CdGa₂Se₄ crystal appear as discontinuities and jumps in the phonon modes, as can be seen from Fig. 1.

4. Temperature dependence of molar heat capacity, free energy and entropy in CdGa₂Se₄ crystal.

It is known that the temperature dependence of the molar heat capacity $C_V(T)$ at constant volume is calculated using the phonon density of states $g(\omega)$ by the following formula:

$$C_V(T) = 3nNk_B \int_0^{\omega_{max}} \frac{(\hbar\omega/k_B T)^2 e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} g(\omega)$$

where n - the number of atoms in a molecule ($n=7$ in our case), k_B - Boltzmann's constant, $g(\omega)$ -normalized phonon state density, ω_{max} -the maximum possible phonon frequency in matter, N - the normalizing constant determined in the harmonic approximation.

Fig. 3 shows the graph of molar heat capacity at constant volume calculated from basic principles in the temperature range 0÷400K. Analysis of the temperature dependence of the heat capacity from the graph shows that the molar heat capacity varies according to Debye's T^3 cubic law at temperatures below 6.1 K.

The temperature dependence of the molar free energy of the CdGa₂Se₄ crystal is shown in Fig. 4, and the temperature dependence of the molar entropy is shown in Fig. 5. The stable equilibrium state of a physical system at constant temperature and volume occurs at the minimum of the Helmholtz free energy. In other words, macroscopic parameters such as pressure and temperature remain stable at their minimum point in this system.

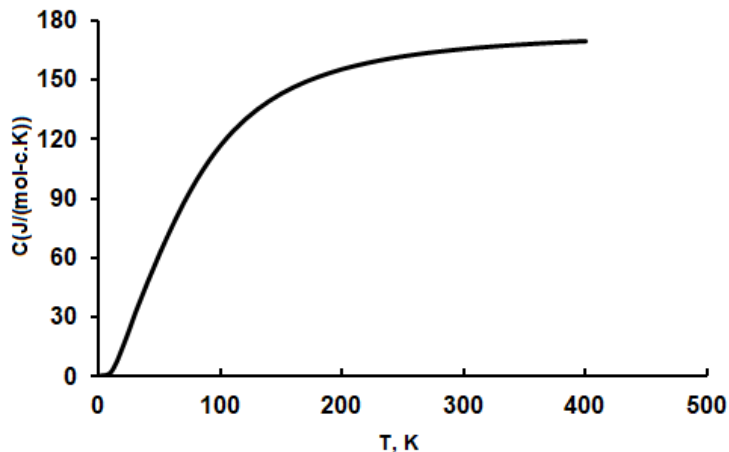


Fig. 3. *Ab-initio* calculated constant volume molar heat capacity of CdGa₂Se₄ crystal.

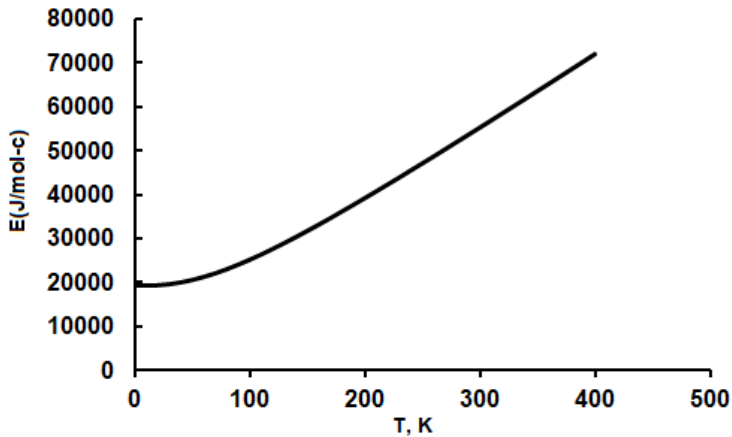


Fig. 4. Temperature dependence of the ab-initio calculated molar free energy of CdGa_2Se_4 crystal.

It is known that the degree of defectiveness of crystalline structures of solids is directly determined by entropy. By calculating the entropy from the basic principles, it is possible to investigate the formation of vacancies, dislocations, in short, defects of various nature, and the migration of atoms within the crystal. Such microscopic processes, in turn, characterize macroscopic effects such as melting and sublimation. Phase transitions and state diagrams can also be predicted using these thermodynamic quantities determined from fundamental principles.

5. Conclusion

In the CdGa_2Se_4 crystal, the phonon dispersion along the symmetrical points, symmetrical lines of the Brillouin zone, and the phonon density of states were calculated using the ABINIT software package by expansion the wave functions into plane waves by the linear response method. The values of the theoretically calculated phonon frequencies agree satisfactorily with the experimentally determined frequencies from infrared absorption and Raman spectra. From the analysis of the phonon dispersion spectra, it can be concluded that the phonon-phonon interaction along the tetragonal axis is practically absent. However, the low-frequency optical phonons in the Γ -X-P-N direction intersect with the acoustic phonon branches. As a result, significant phonon-phonon interaction occurs in the xy plane. For this reason, the probability of scattering of acoustic phonons from optical phonons increases and leads to a decrease in thermal

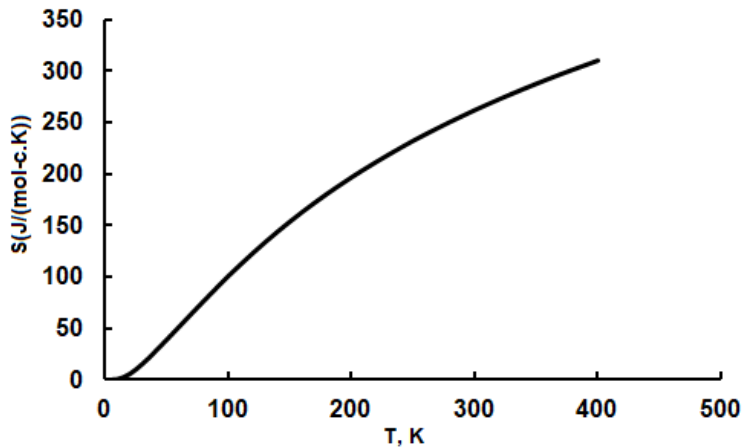


Fig. 5. Temperature dependence of the ab-initio calculated molar entropy of the CdGa₂Se₄ crystal.

conductivity. Using the phonon spectrum and the phonon density of states, the temperature dependence of the molar entropy, phonon internal energy and heat capacity at constant volume for CdGa₂Se₄ in the interval 0÷400 K was calculated from basic principles and it was shown that the molar heat capacity varies according to Debye's T³ cubic law at temperatures below 6.1 K.

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