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Ab initio elasticity and lattice dynamics of AgGaSe₂

B B Karki, S J Clark, M C Warren, H C Hsueh, G J Ackland and J Crain

Department of Physics and Astronomy, The University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, UK

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Abstract. The structural, elastic and vibrational properties of the ternary semiconductor AgGaSe₂ chalcopyrite are studied using the pseudopotential method within the local density approximation. The lattice constants and internal parameter are in good agreement with experiments. The elastic moduli derived from the stresses generated by small strains compare favourably with experiments and the material is elastically anisotropic. All zone-centre phonons are determined by diagonalization of the dynamical matrix derived from the forces generated by small ionic displacements. The calculated phonon frequencies are in excellent agreement with experiment and can be grouped into three bands. Two silent Γ_2 modes are also obtained. The eigenvectors are used to discuss the three-band phonon spectrum and the spectroscopic activity of the modes.

1. Introduction

Silver gallium diselenide (AgGaSe₂) is an important member of the ternary semiconductor family $A^I B^{II} X_2^{VI}$ (where A = Cu, Ag; B = Al, Ga, In, Tl and X = S, Se, Te) which are isoelectronic analogues of the II–VI binary semiconductors. They adopt the characteristic chalcopyrite structure (figure 1) with a tetragonal space group $I42d$ [1]. The chalcopyrite structure shows two distortions, namely tetragonal ($\eta = c/2a \neq 1$) and tetrahedral (an internal parameter u), with respect to the zincblende cubic structure [2, 3]. Because of these added structural (η, u) and chemical ($A \neq B$) degrees of freedom relative to their binary analogue, the ternary semiconductors exhibit a far wider range of physical and chemical properties. The present increasing interest in these compounds is related to their applications in solar energy conversion, light emitting diodes and various non-linear optical devices [4]. The recent x-ray diffraction and absorption studies [5] have shown that the chalcopyrite structure for AgGaSe₂ is stable up to 2.6 GPa with four successive phase transitions at higher pressures. The elastic constants and zone-centre phonon frequencies of AgGaSe₂ chalcopyrite are experimentally known at ambient conditions [2, 6]. Despite an increasing use of first-principles computer simulations in calculating different properties of semiconductors [7, 8] in recent years, the ternary semiconductors (including AgGaSe₂) are almost unapproached so far by the first-principles techniques. Here we use the *ab initio* pseudopotential method to determine the optimized structure of AgGaSe₂ at zero pressure and calculate its elastic moduli and zone-centre phonons.

2. Structural optimization

The first-principles pseudopotential method was used within the local density approximation (LDA) [9]. The method involves computation of the self-consistent total energies,

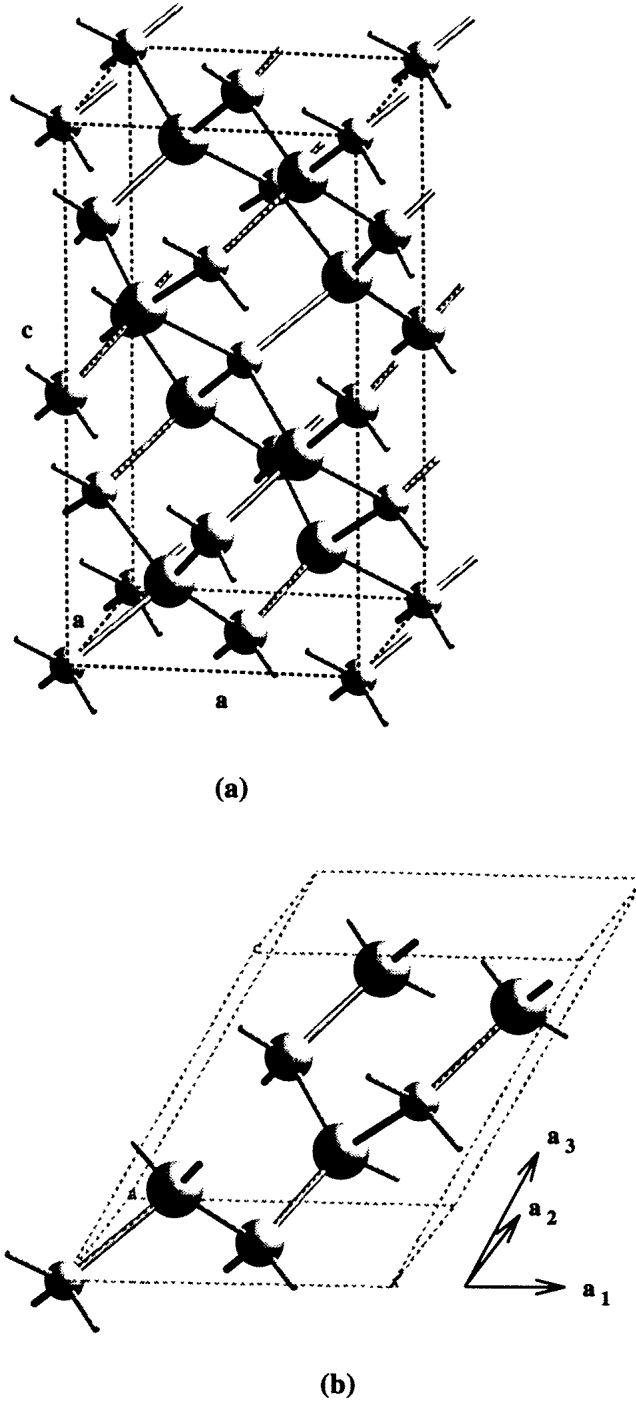


Figure 1. The body-centred tetragonal conventional unit cell (a) and the primitive cell (b) of the AgGaSe₂ chalcopyrite structure. The primitive lattice vectors are $\mathbf{a}_1 = a(1, 0, 0)$; $\mathbf{a}_2 = a(0, 1, 0)$ and $\mathbf{a}_3 = a(0.5, 0.5, \eta)$. The small, medium and large spheres represent Ag, Ga and Se ions respectively.

Hellman–Feynman forces and stresses by solution of the Kohn–Sham equations, and the subsequent relaxation of the electrons, ions and unit cell. The norm-conserving, non-local pseudopotentials generated by the Kerker method [10] were used in the Kleinman–Bylander form [11]. The parametrization of Perdew and Zunger was used for the exchange–correlation potential [12]. A plane wave basis set was used with 400 eV cutoff which gives about 3600 plane waves per band at each of six special-points in the $3 \times 3 \times 3$ Monkhorst–Pack k-mesh [13]. The finite-plane-wave-basis-set corrections were included in total energies and stresses (the Pulay stress = -0.8 GPa) [14]. A preconditioned conjugate gradient scheme was used to relax electrons, conjugate gradients to relax ions and steepest descents to optimize cell parameters. The details of the method have given elsewhere [15, 17].

Only a single primitive cell of AgGaSe₂ chalcopyrite shown in figure 1 was simulated at zero pressure. The ions were relaxed until the Hellman–Feynman forces were below $0.001 \text{ eV } \text{Å}^{-1}$ and the cell parameters were relaxed until total stresses were below $0.001 \text{ eV } \text{Å}^{-3}$. The calculated structural parameters are in good agreement with experimental values [3] as given in table 1. The slight underestimation of the lattice constants is attributed to LDA. Our calculated structure of AgGaSe₂ is more distorted than the observed structure as seen from the large bond-length mismatch (table 1).

Table 1. Calculated and experimental values [3] of the cubic lattice constant a , the tetragonal distortion parameter $\eta = c/2a$, the internal parameter u and the bond lengths d_{AgSe} and d_{GaSe} of AgGaSe₂ chalcopyrite in the units of Å. The parameter u gives a measure of degree of bond-length mismatch [2, 3] through the relation $(u - 0.25)a^2 = d_{AgSe}^2 - d_{GaSe}^2$.

	a	η	u	d_{AgSe}	d_{GaSe}
calc	5.934	0.899	0.295	2.654	2.337
expt	5.985	0.896	0.276	2.601	2.416
expt	5.973	0.911	0.270	2.585	2.443

Table 2. Calculated elastic stiffness constants of AgGaSe₂ chalcopyrite in the units of GPa compared with ultrasonic data [6].

	c_{11}	c_{33}	c_{12}	c_{13}	c_{44}	c_{66}
calc	92	70	60	56	26	17
expt	89.8	58.0	65.7	45.1	21.7	13.3

3. Elastic moduli

The chalcopyrite structure is characterized by six elastic stiffness constants, c_{11} , c_{33} , c_{12} , c_{13} , c_{44} and c_{66} [18]. We determined the complete elastic constant tensor (c_{ij}) from computation of the stresses generated by small deformations of the equilibrium primitive cell [15, 19]. We applied three types of strain: tetragonal, orthorhombic and shear. The ion positions were re-optimized in the strained lattice in order to include the coupling between the vibrational modes and elastic constants in AgGaSe₂ [19]. Our calculated elastic constants for AgGaSe₂ chalcopyrite are within a few percent of the experiment [6] as shown in table 2. The estimated aggregate (Voigt–Ruess–Hill) bulk and shear moduli are $K = 65 \pm 1.2$ and $G = 18 \pm 1.0$ GPa respectively compared to $K = 58 \pm 3.0$ and $G = 16 \pm 0.7$ GPa

from ultrasonic [6] and $K = 65 \pm 10.0$ GPa from diamond cell experiments [5]. The slight overestimation of the elastic moduli is consistent with slight underestimation of the lattice constants. The material shows strong elastic anisotropy with two very different axial compressibilities: $k_a = 0.0032$ and $k_c = 0.0092$ GPa⁻¹ [18]. The relatively higher *c*-axis compressibility suggests that the degree of the distortion in the chalcopyrite structure might increase with pressure.

4. Zone-centre phonons

For zone-centre phonons, the dynamical matrix D is related to force constants ϕ by

$$D_{\alpha\beta}^{\kappa\kappa'} = \frac{1}{\sqrt{m_\kappa m_{\kappa'}}} \sum_{l=0}^L \phi_{\alpha\beta}^{\kappa\kappa'}(l) = \frac{1}{\sqrt{m_\kappa m_{\kappa'}}} \frac{F_{\alpha\kappa}}{\epsilon_{\beta\kappa'}}.$$

Here $F_{\alpha\kappa}$ is the force experienced by the κ ion in the α direction due to the displacement ($\epsilon_{\beta\kappa'}$) of the κ' ion from equilibrium in the β direction [16, 17]. The computation of the Hellmann–Feynman forces by simulating the primitive cell with one atom displaced from the equilibrium position provides one row of elements in the dynamical matrix. Using symmetry information on the system, only seven independent displacements (two for Ag, two for Ga and three for the Se ion) in the primitive cell were performed to calculate the required dynamical matrix and then the corresponding eigenproblem was solved to obtain the zone-centre phonons of AgGaSe₂ chalcopyrite. The calculated frequencies are transverse frequencies since the long-range macroscopic polarization fields are not accessible at strictly zero wave vector.

The chalcopyrite AgGaSe₂ has eight atoms (two formula units) per primitive cell so one expects 24 zone-centre vibrational modes (21 optic and three acoustic) which are

$$1\Gamma_1 + 2\Gamma_2 + 3\Gamma_3 + 4\Gamma_4 + 7\Gamma_5$$

in Γ representations of the tetrahedral space group, where Γ_5 is doubly degenerate [1, 2]. As shown in table 3, the calculated transverse frequencies agree very closely with those from Raman experiments and can be grouped into three frequency bands in agreement with experiment and group theory [1, 2]. Our calculated vibrational modes are (1) a high frequency group of four modes ($\Gamma_3 + \Gamma_4 + 2\Gamma_5$) in the range from 255 to 245 cm⁻²; (2) an intermediate frequency group of six modes ($\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 + 2\Gamma_5$) from 182 to 145 cm⁻¹; and (3) a low frequency band of four modes ($\Gamma_1 + \Gamma_4 + 2\Gamma_5$) from 88 to 26 cm⁻¹. In addition, two Γ_2 modes which cannot be observed in first-order Raman scattering have frequencies 156 and 215 cm⁻¹. The inspection of the calculated eigenvectors (table 3) suggests that the three-band picture of the phonon spectrum of AgGaSe₂ could arise from the relative degree of motion of two types of cation since the calculated force constants associated with Ga–Se bonds are much stronger than those for Ag–Se bonds [1, 20]. The modes highly dominated by the motion of lighter Ga cations belong to the highest-frequency band and those dominated by the motion of heavier Ag cations fall into the lowest band whereas those involving similar motions of both the cations constitute the intermediate band. However, the grouping of Γ_5 modes into the lower two bands is not straightforward.

As given in table 3, the calculated atomic displacements are not purely along the Cartesian axes in all modes due to strong coupling among different directions [21]. We used the eigenvectors to determine to which Γ representation each mode belongs and found consistency with group theory analysis. Since the chalcopyrite structure is non-centrosymmetric, a mode can be both Raman and infrared active [1, 2]. However, the four modes (Γ_1 and Γ_3) are only Raman active since they involve only an out of phase motion

Table 3. Calculated transverse frequencies (ω_{cal}) in cm^{-1} and eigenvectors in reduced mass coordinates of all zone-centre optic phonons of AgGaSe₂ chalcopyrite. The experimental frequencies (ω_{exp}) are from Raman data at 77 K and longitudinal frequencies are given in parentheses [2]. In the eigenvectors, the upper signs (+ or -) correspond to the displacement patterns for one Ag, one Ga and two Se ions while the lower signs to the displacement patterns for the remaining one Ag, one Ga and two Se ions in the primitive cell.

Mode	ω_{cal}	ω_{exp}	Eigenvector			
			Ag	Ga	Se	Se
Γ_4	255	252 (275)	0 0 -0.01	0 0 0.45	0 \mp 0.33 -0.20	\mp 0.33 0 -0.20
Γ_5	254	255	0.01 \mp 0.02 0	-0.23 \pm 0.40 0	-0.17 0 0	0.38 0 \pm 0.34
Γ_5	252	251 (277)	\mp 0.04 0.03 0	\mp 0.29 0.49 0	0 -0.11 \mp 0.09	0 -0.39 0
Γ_3	245	253	0 0 \mp 0.03	0 0 \pm 0.55	\mp 0.32 0 0	0 \pm 0.32 0
Γ_2	215		0 0 0	0 0 0	0 \mp 0.37 -0.33	\pm 0.37 0 0.33
Γ_1	182	181	0 0 0	0 0 0	\pm 0.50 0 0	0 \pm 0.50 0
Γ_5	167	162 (165)	-0.21 \pm 0.37 0	-0.04 \pm 0.05 0	-0.07 0 0	0.36 0 \mp 0.42
Γ_3	164	160	0 0 \mp 0.31	0 0 \mp 0.41	\mp 0.34 0 0	0 \pm 0.34 0
Γ_4	159	155 (161)	0 0 0.34	0 0 0.19	0 \pm 0.30 -0.29	\pm 0.30 0 -0.29
Γ_2	156		0 0 0	0 0 0	0 \mp 0.33 0.37	\pm 0.33 0 -0.37
Γ_5	145	137 (138)	\mp 0.25 0.39 0	\pm 0.35 -0.10 0	0 0 \pm 0.13	0 -0.36 0
Γ_5	88	84 (84)	\mp 0.11 0.36 0	\mp 0.35 -0.28 0	0 -0.24 \mp 0.32	0 0.08 0
Γ_4	61	58 (58)	0 0 0.47	0 0 -0.23	0 \mp 0.23 -0.09	\mp 0.23 0 -0.09
Γ_3	60	58	0 0 \pm 0.63	0 0 \mp 0.18	\mp 0.18 0 0	0 \pm 0.18 0
Γ_5	26	27	0.11 \mp 0.54 0	-0.11 \mp 0.09 0	-0.24 0 0	0.21 0 \mp 0.29

of the ions and hence do not induce an oscillating dipole moment. The Γ_2 mode involves only out of phase (resultant) motions of two anion pairs along the principal axis, giving zero dipole moment. The Γ_4 mode consists of an in-phase motion of each type of cation and that of two anion pairs along the principal axis, and hence has a finite dipole moment in that direction. In the Γ_5 mode, the resultant motion of each cation pair and that of each anion pair are along either of two axes (x and y) giving twofold degeneracy and inducing finite dipole moment in a plane perpendicular to the principal axis (the x - y plane).

5. Conclusion

We have made a detailed study of the structural, elastic and vibrational properties of the prototypical ternary semiconductor AgGaSe₂ chalcopyrite using first-principles computer simulation. The calculated properties are in very good agreement with experiments. The results indicate that the material is highly elastically anisotropic. The zone-centre phonons can be grouped into three frequency bands as also explained by the examination of the eigenvectors.

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