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## First-principles calculations for phonons in $\text{AgGaX}_2$ ( $X = \text{Se}, \text{Te}$ ) chalcopyrite crystals

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**Abstract.** Density functional theory with the local density approximation has been used to calculate Hellmann–Feynman forces for two chalcopyrite crystals:  $\text{AgGaSe}_2$  and  $\text{AgGaTe}_2$ . Applying the direct method, phonons at all high-symmetry points of the chalcopyrite structure have been obtained. The results are in very good agreement with experimental data from Raman, infrared, and inelastic neutron scattering.

### 1. Introduction

In last decade, first-principles calculations have been successfully used to obtain different properties of materials. The structural parameters and dynamical properties of crystals determine a wide range of microscopic and macroscopic behaviour: diffraction, sound velocity, elastic constants, Raman and infrared absorption, inelastic neutron scattering, specific heat, etc. Additionally, low-frequency modes could be associated with the phase transitions. From this point of view, calculation for phonons from first principles has recently become a very important topic.

Density functional theory (DFT) in the local density approximation (LDA), using the pseudopotential plane-wave method, has already been adopted for calculating phonon dispersion curves for monatomic (K, Li, Na, Si) [1, 2], binary (GeS, TiC,  $\text{ZrO}_2$ , SiO, GaAs, MgO) [2–8], and ternary ( $\text{AgGaSe}_2$ ,  $\text{SrTiO}_3$ ) [2, 9, 10] compounds. In  $\text{ZrO}_2$  and  $\text{SrTiO}_3$ , soft modes have been found.

The present work deals with the  $\text{AgGaX}_2$  ( $X = \text{Se}, \text{Te}$ ) set of compounds, which belong to the group of semiconducting materials crystallizing in the chalcopyrite structure with the tetragonal space group  $I\bar{4}2d$  ( $D_{2d}^{12}$ ). These ternary compounds have a small energy gap between the valence and conducting bands and proved to be of great interest as non-linear optical materials [11, 12].

The structural and dynamical properties of chalcopyrites are well known and have been described in a number of papers [14–22]. For  $\text{AgGaS}_2$  and  $\text{CdGeAs}_2$  the lattice dynamics has been studied by Tyuterev and Skachkov [23, 24] using Keating's model. Five model parameters: one angle-bending and two bond-stretching constants as well as two effective point charges, have been determined by a least-squares fit to the Raman scattering data. Only the optical parts of the phonon dispersion curves with LO/TO splitting that are obtained match experimental data. *Ab initio* studies of the lattice dynamics for  $\text{AgGaSe}_2$  have already been carried out by Karki *et al* [9] and Ackland *et al* [2]. Both of these calculations were based on minimizing the

total energy of the crystal structure by the pseudopotential method within the LDA, evaluating the force constants between atoms, and constructing the dynamical matrix at a given point of the Brillouin zone and diagonalizing it. However, reference [9] provides only the zone-centre phonons, and the calculations made by Ackland *et al* in reference [2] were carried out on a supercell restricted to a primitive unit cell with eight atoms; this gives exact phonon values only at the  $\Gamma$  point.

The aim of this work is to determine phonon dispersion relations at all high-symmetry points of the chalcopyrite structure for AgGaSe<sub>2</sub> and AgGaTe<sub>2</sub> from *ab initio* calculations using the direct method [1, 8, 25, 26] and a crystallographic unit cell with 16 atoms. Additionally, the phonon density of states (DOS) has been derived.

## 2. Method

The calculations for phonons were carried out in two steps using the *ab initio* package CASTEP [27] for the total-energy minimization and the program PHONON [28]. At the outset, using CASTEP, the crystal structure was optimized and Hellmann–Feynman (HF) forces were evaluated; then, using the direct method, the phonon dispersion curves and phonon DOS were obtained.

The total-energy minimization, the theory of which is described in detail by Payne *et al* [29], uses norm-conserving pseudopotentials. The 17 500-plane-wave basis set with an 890 eV energy cut-off was applied. The local density approximation was used for the exchange energy term of the valence states of the Hamiltonian [30]. The integration over the Brillouin zone was performed with two wave vectors generated by the Monkhorst–Pack scheme [31]. The correction for the finite plane-wave basis set was included in the total energy.

In the direct method [26], the phonon frequencies  $\omega(\mathbf{k}, j)$  are calculated as square roots of eigenvalues of the supercell dynamical matrix:

$$\mathcal{D}^{SC}(\mathbf{k})e(\mathbf{k}, j) = \omega^2(\mathbf{k}, j)e(\mathbf{k}, j) \quad (1)$$

where the  $e(\mathbf{k}, j)$  are the polarization vectors. The supercell dynamical matrix is defined as

$$D^{SC}(\mathbf{k}; \mu\nu) = \frac{1}{\sqrt{M_\mu M_\nu}} \sum_{\mathbf{m} \in SC} \Phi^{SC}(0, \mu; \mathbf{m}, \nu) \exp(-2\pi i \mathbf{k} \cdot [\mathbf{R}(0, \mu) - \mathbf{R}(\mathbf{m}, \nu)]) \quad (2)$$

where: the summation over  $\mathbf{m}$  runs over all atoms of the supercell;  $M_\mu$ ,  $M_\nu$  and  $\mathbf{R}(0, \mu)$ ,  $\mathbf{R}(\mathbf{m}, \nu)$  are atomic masses and equilibrium positions, respectively; and  $\mathbf{k}$  is the wave vector. The cumulant force constants  $\Phi_{ij}^{SC}$  are the sums of terms containing the second derivatives of the ground-state energy with respect to the position vectors of interacting atoms  $i$  and  $j$  [28]. In the direct method they are derived from HF forces, using

$$F_i(\mathbf{n}, \nu) = - \sum_{\mathbf{m}, \mu, j} \Phi_{ij}^{SC}(\mathbf{n}, \nu; \mathbf{m}, \mu) u_j(\mathbf{m}, \mu) \quad (3)$$

where  $u_j(\mathbf{m}, \mu)$  is an amplitude of displacement of an atom in the supercell specially shifted from the equilibrium position.

The symmetry of the supercell and the site symmetry of the non-equivalent atoms usually considerably reduce the number of displacements needed for reconstruction of  $\Phi_{ij}^{SC}$ . In the case of chalcopyrite structure, there are seven independent displacements: in the  $x$ - and  $z$ -directions for both cations Ag, Ga, and in the  $x$ -,  $y$ -, and  $z$ -directions for the anion X. To minimize the anharmonic effects and systematic errors, the  $\Phi_{ij}^{SC}$  are calculated with equation (3) using forces arising from positive and negative displacements  $u_j$ .

For ionic crystals the macroscopic electric field must be taken into account by adding into equation (1) the non-analytical term of the dynamical matrix at the wave vector  $\mathbf{k} = 0$  [32].

However, since one knows the phonon frequencies only at discrete wave vectors, it is justified to extend the non-analytical term to the  $\mathbf{k} \neq 0$  region, through multiplying it by the Gaussian damping factor. Therefore we add to equation (1) the following expression:

$$\mathcal{D}_{\alpha,\beta}^M(\mathbf{k}; \mu\nu) = \mathcal{D}_{\alpha,\beta}^{SC}(\mathbf{k}; \mu\nu) + \frac{4\pi e^2}{V\epsilon_\infty\sqrt{M_\mu M_\nu}} \frac{[\mathbf{k} \cdot \mathbf{Z}^*(\mu)]_\alpha [\mathbf{k} \cdot \mathbf{Z}^*(\nu)]_\beta}{|\mathbf{k}|^2} \times \exp(-2\pi i \mathbf{g} \cdot (\mathbf{r}_\mu - \mathbf{r}_\nu)) \exp\left(-\pi^2 \left[ \left(\frac{k_x}{\rho}\right)^2 + \left(\frac{k_y}{\rho}\right)^2 + \left(\frac{k_z}{\rho}\right)^2 \right]\right) \quad (4)$$

where  $\mathbf{k}$  is the wave vector within a Brillouin zone with its centre at the reciprocal-lattice vector  $\mathbf{g}$ ,  $V$  stands for the volume of the primitive unit cell, and  $M_\mu$ ,  $\mathbf{r}_\mu$  are atomic masses and internal positions. The  $\mathbf{Z}^*(\mu)$  are the tensors of the Born effective charges.  $\epsilon_\infty$  is the electronic part of the dielectric constant and  $\rho$  is a damping factor, which we choose equal to 2.0; then the non-analytical term vanishes close to the zone boundary. Consideration of the effective charges leads to the LO/TO splitting at the  $\Gamma$  point observed for chalcopyrites in experiment.

By sampling the dynamical matrix at 10 000 randomly selected wave vectors, one obtains the partial and the total phonon DOS.

### 3. Results

The geometry-optimization process for both crystals was continued until the average root mean square force and root mean square stress decreased to below 0.001 eV  $\text{\AA}^{-1}$  and 0.01 GPa, respectively. The resulting structural parameters are listed together with experimental data in table 1. One can see good agreement among them.

**Table 1.** Structural parameters of AgGaX<sub>2</sub>.

	AgGaSe <sub>2</sub>		AgGaTe <sub>2</sub>	
	Present	[13, 14]	Present	[13, 15]
$a_0$ ( $\text{\AA}$ )	6.047	5.993	6.305	6.296
$c_0$ ( $\text{\AA}$ )	10.714	10.884	11.985	11.990
$u$	0.284	0.276	0.272	0.260

The primitive unit cell of the chalcopyrite structure contains eight atoms with 24 degrees of freedom. According to the group theoretical analysis, at the centre of the Brillouin zone there are 21 optical modes, which can be decoupled to irreducible representations of the point group  $D_{2d}$  as follows:

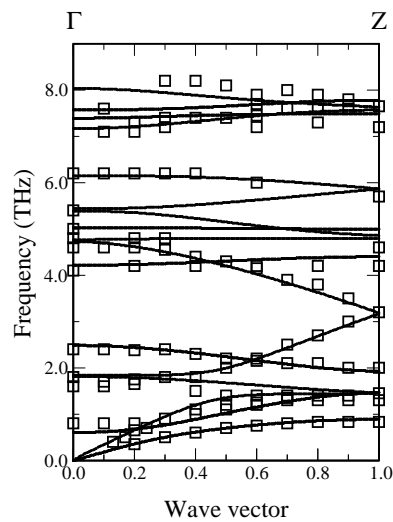
$$\Gamma = 1A_1 + 3B_1 + 3B_2 + 6E + 2A_2. \quad (5)$$

Here, three modes of symmetry  $B_2$  and six doubly degenerate modes of symmetry  $E$  are infrared active. These vibrations are also Raman active, together with the  $A_1$  and three  $B_1$  modes. The  $A_2$  modes are silent.

In table 2 we compare calculated phonon frequencies at the  $\Gamma$  point with Raman and infrared data. For AgGaSe<sub>2</sub>, inelastic neutron scattering data for the  $\Gamma$ -Z direction are also available [21]. We compare them with our results in figure 1. To obtain the LO/TO splitting we use the effective charges  $Z_{\text{Ag}}^* = 0.67$  and  $Z_{\text{Ga}}^* = 1.03$  published by Tanino *et al* [33]. The calculated phonon dispersion relations agree perfectly with the experimental ones.

**Table 2.** Frequencies of phonons at the  $\Gamma$  point (in THz). The two frequencies given for some Raman data correspond to LO and TO modes. Single values are quoted when the LO/TO splitting was not reported.

Irreducible representation	AgGaSe <sub>2</sub>			AgGaTe <sub>2</sub>		
	Present	Neutron [21]	Raman [20]	Present	Raman [22]	Infrared [22]
A <sub>1</sub>	5.39		5.43	4.02	3.87	
A <sub>2</sub>	6.15 4.73	6.25 4.68		4.32 3.87		
E	7.57 7.39 5.03 4.22 2.49 0.60	7.60 7.10 4.80 4.10 2.40 0.81	8.30/7.52 7.64 4.86/4.95 4.11/4.14 2.52 0.81	6.28 6.20 4.44 3.77 2.01 0.83	6.03 1.92	6.15 6.03 3.45 1.86 1.29
B <sub>1</sub>	7.17 4.76 1.81	7.10 4.68 1.62	7.58 4.80 1.74	6.24 4.14 1.83	6.60 2.79 1.93	
B <sub>2</sub>	7.39 4.75 1.85	8.20 4.95 1.76	7.55/8.24 4.65/4.83 1.74	6.15 4.31 1.77	6.03 4.26 1.53	6.03 3.96



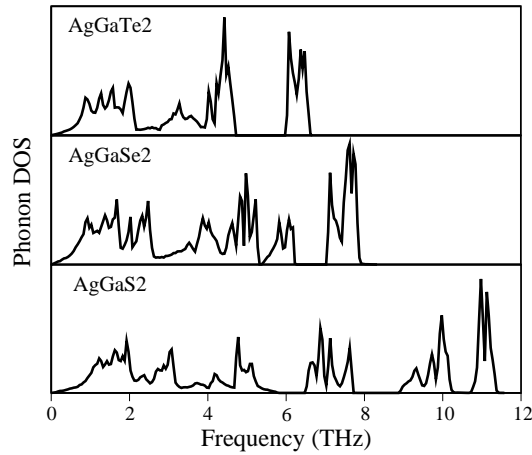
**Figure 1.** Comparison of the calculated phonon dispersion curves of AgGaSe<sub>2</sub> (lines) with experimental data (squares) [21].

The calculated frequencies at the remaining high-symmetry points: X, Z, P, and N, are presented in table 3. At the points X, Z, and P, all phonon branches are doubly degenerate, while at point N all modes are singly degenerate.

In figure 2 we show the phonon density of states for AgGaSe<sub>2</sub> and AgGaTe<sub>2</sub> compared with the previously calculated DOS for AgGaS<sub>2</sub> [34]. The highest energy bands are formed mainly from Ga and X vibrations, and their frequency decreases with increasing mass of anion X.

**Table 3.** Calculated phonon frequencies at high-symmetry points (in THz). All modes at X, Z, and P points are doubly degenerate.

AgGaSe <sub>2</sub>					AgGaTe <sub>2</sub>				
X	Z	P	N		X	Z	P	N	
0.95	0.89	1.05	0.63	4.53	0.88	0.98	0.97	0.75	4.02
1.60	1.46	1.60	1.01	4.89	1.50	1.21	1.45	0.90	4.28
1.64	1.46	1.70	1.30	4.96	1.53	1.43	1.61	1.26	4.36
2.49	1.93	2.24	1.43	5.26	1.98	1.53	1.83	1.29	4.37
3.32	3.18	3.47	1.72	5.84	2.88	2.59	3.06	1.61	4.55
3.87	4.40	3.86	2.03	6.04	3.26	3.89	3.15	1.63	4.67
4.76	4.79	4.76	2.33	7.11	4.20	4.21	4.20	2.03	6.06
5.10	5.00	5.09	2.48	7.33	4.39	4.41	4.38	2.08	6.15
5.89	5.87	5.88	3.08	7.49	4.50	4.42	4.51	2.43	6.19
7.08	7.49	7.09	3.20	7.61	6.05	6.15	6.05	2.79	6.42
7.62	7.57	7.61	3.95	7.70	6.34	6.34	6.34	3.27	6.44
7.76	7.78	7.76	3.95	7.75	6.47	6.60	6.47	3.54	6.47

**Figure 2.** The calculated total phonon density of states for AgGaX<sub>2</sub> (X = S, Se, Te). The data for AgGaS<sub>2</sub> are taken from reference [34].

#### 4. Conclusions

We conclude that first-principles calculations based on total-energy minimization give stable structures of the correct symmetry and correct values of the structural parameters for both above-mentioned chalcopyrite crystals. The vibrational properties obtained using the direct method fit very well to experimental data. The non-analytical term used in the dynamical matrix properly reconstructs the LO/TO splitting.

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