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First-principles calculations of the lattice dynamics of $CuInSe_2$

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Abstract. The structure and lattice dynamics of $CuInSe_2$ were studied using *ab initio* calculations. The phonon dispersion relations and phonon density of states were calculated using the direct method. The results are in good agreement with recently obtained inelastic neutron scattering data.

1. Introduction

First-principles calculation of crystal structure and crystal properties is becoming a standard technique, and progress in the methods, algorithms, and computer capabilities allows us to study larger and larger systems. This is true also for studies of lattice dynamics of crystals where two approaches are currently in use: the linear response method and the direct method.

In the linear response method the dynamical matrix is obtained from the modification of the electric density, via the inverse dielectric matrix. The dielectric matrix is calculated from the eigenfunctions and energy levels of the unperturbed system. The dynamical matrix can be determined at any wave vector in the Brillouin zone with the computational effort required comparable to that of a ground-state optimization. Only linear effects, such as harmonic phonons, are accessible to this technique.

The direct-method approach is based on the solution of the Kohn–Sham equation and it allows one to study both linear and non-linear effects. The calculations deal with a supercell, which allows explicit account to be taken of any perturbation. This method is rather straightforward computationally and there are a few standard software packages. The main limitation is the small number of unit cells which form the supercell. Within the direct method the phonon frequencies are calculated from Hellmann–Feynman forces generated by the small atomic displacements, one at the time. Hence, using the information of the crystal symmetry space group the force constants are derived, and the dynamical matrix is built and diagonalized, and its eigenvalues arranged into phonon dispersion relations. In this way, phonon frequencies at selected high-symmetry points of the Brillouin zone can be calculated. However, when the interaction range ceases to be within the supercell, phonons at all wave vectors are determined exactly. This statement has to be modified for polar crystals for which the macroscopic electric field splits off the infrared-active optic modes. This is the origin of LO/TO splitting, which, for very simple crystals, has been found by calculating the effective Born charge tensor and electronic dielectric constant introduced into the dynamical matrix in the form of a non-analytical term [1] or by calculating LO modes from elongated supercells [2].

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To study the crystal lattice dynamics, the direct method has been used for monatomic (K, Na, Li, Si) [3,4], binary (MgO, GeS, TiC, ZrO_2, SiO, GaAs) [2,4–8], and ternary ($SrTiO_3$) [9] compounds. These are really simple-cubic systems, where the atom positions are fixed by site symmetry and the only optimized parameter is the lattice constant. The more complicated tetragonal crystal $AgGaSe_2$ had already been studied by Karki *et al* and Ackland *et al*. The first work (reference [10]) provides only the zone-centre phonons, and the calculations made by Ackland *et al* in reference [4] were carried out for a supercell restricted to a primitive unit cell with eight atoms, which gives exact phonons only at the Γ point.

Ab initio calculations are generally expected to have predictive power [11,12]. One expects this method to be able to predict structural and dynamical properties of the crystals, including phonon frequencies, soft modes, and phase transitions at ambient and high pressures. The first step in this strategy is to calculate the harmonic phonon modes. In this case it is better to use the direct method, because it will allow the subsequent taking into account of both the harmonic and the anharmonic contributions. The price to be paid for taking this approach is the additional calculation of the LO modes for polar crystal, which, however usually do not cause phase transitions.

In this paper we consider the $CuInSe_2$ chalcopyrite (CIS) having the body-centred-tetragonal structure. We were encouraged to undertake the present work by the recent appearance of new experimental neutron scattering data for CIS [13], which allow us to test the applicability of the *ab initio* approach to the vibrational properties of the crystal. Furthermore, the family of I–III–VI_2 semiconductors, crystallizing in the chalcopyrite structure ($I\bar{4}2d$) [10, 14], is used in a number of applications [14]. Copper indium diselenide, $CuInSe_2$ (CIS), which is a typical representative of this family, has been used in high-efficiency thin-film solar cells, because of its high absorption coefficient and good chemical stability [15]. The structural, electrical, and optical properties, as well as the lattice vibrations of CIS, have been described in a number of papers [16–18]. The aim of this work is to determine the phonon dispersion relations along high-symmetry directions and the phonon density of states from first-principles calculations using the direct method.

2. Calculations

The crystal structure of CIS has an $I\bar{4}2d$ (D_{2d}^{12}) symmetry as was confirmed by the *ab initio* pseudopotential method [19] within the local density approximation (LDA) using the CASTEP package [20]. The structural optimization process was performed by solving the Kohn–Sham equation, and minimizing the total energy with respect to relaxation of electrons, ions, and unit-cell parameters. The Hellmann–Feynman (HF) forces and stresses were also derived. The norm-conserving, non-local pseudopotentials for Cu, In, and Se were used. A plane-wave basis set with a 720 eV cut-off was applied, which gives about 17 500 plane waves per band. The integration over the Brillouin zone was performed with weighted summation over two wave vectors generated by the Monkhorst–Pack scheme [21], which corresponds to a $2 \times 2 \times 1$ k-point mesh. The correction for the finite plane-wave basis set was included in the total energy. The Pulay stress [22], calculated using three different cut-off energies, was equal to -0.85 GPa. All calculations were done for a $1 \times 1 \times 1$ supercell (crystallographic unit cell) with 16 atoms. The geometry optimization was carried out with the constraints of the $I\bar{4}2d$ space group, with respect to the lattice constants a and c and the u-parameter of the Se position. In principle, such a structure can still be unstable if the symmetry constraints are removed. We have performed this check by optimizing the structure in the $1 \times 1 \times 1$ supercell without any point symmetry elements, i.e. in the space group $P1$. The structure optimized in $P1$ symmetry is stable and shows negligible changes in the lattice constants, u, and the unit-cell angles.

The phonon dispersion curves were calculated by the direct method [3, 6, 23, 24] using the program PHONON [25]. The eight coordination shells were considered with 19 independent force-constant matrices and 136 independent potential parameters. Knowledge of these force constants allows one to test the range of the interaction potential. To do that, similarly to the procedure used in reference [26], we have calculated the absolute values of the eigenvalues of the 3×3 force-constant matrices and plotted them against the distance between acting atoms. The result for the $1 \times 1 \times 1$ supercell shows that the interaction drops down within the size of the supercell by one order of magnitude in the a-direction and by at least three orders of magnitude in the c-direction. The Brillouin zone of the chalcopyrite structure has five high-symmetry points: Γ, N, P, X, and Z. According to the direct method, the $1 \times 1 \times 1$ supercell gives exact phonon frequencies at Γ and Z points only. To calculate a complete set of HF forces, seven independent displacements were required by the direct method. We used displacement amplitudes equal to 0.03 Å, and displacement directions along $\boldsymbol{x}$ and $\boldsymbol{z}$ for Cu and In, and along $\boldsymbol{x}$, $\boldsymbol{y}$, and $\boldsymbol{z}$ for the Se atom. To minimize systematic errors and anharmonic effects, the average displacements in both positive and negative directions were used.

3. Results

In table 1 the calculated structural parameters of CIS are compared with experimental data [16]. The differences are rather small and do not exceed 1%.

Table 1. Structural parameters of CIS.

	Experiment, reference [16]	*Ab initio*, this work
a_0 (Å)	5.782	5.832
c_0 (Å)	11.620	11.622
u	0.235	0.222

In table 2 the calculated frequencies at the Γ point have been compared with experimental results of infrared (IR) [27–32], Raman (R) [27, 33], and neutron (N) [13] measurements. The quite large scatter of the observed experimental frequency data is attributable to the different penetration depths in IR, Raman, and neutron scattering as well as to the different sensitivities to surface effects [13]. One can see that *ab initio* calculations reproduce the mode frequencies very well. In addition, our data relate better to neutron scattering results, which are of bulk type, than to the Raman or infrared data.

In figure 1 we present phonon dispersion curves for CIS with all high-symmetry points. Our result includes longitudinal optic–transverse optic (LO/TO) splitting [34], which is determined by the effective charge tensors and electronic dielectric constant. The splittings show up as discontinuities of phonon branches at the Γ point, characteristic for polar crystals with tetragonal structures. The current *ab initio* methods referred to in the literature [2, 35] provide the LO/TO splitting, but in each case considered the size of the simulated unit cell is small. The 16-atom body-centred-tetragonal unit cell of CIS is too large for this treatment. Additionally, it has been shown experimentally that in the CIS case the LO/TO splitting is very small and is in the range 1–2%, except for an E mode at 6.452 THz, where the difference is 9%. Therefore, we have limited our consideration to a semi-empirical method—that is, to deriving LO modes at the Γ point from experimental frequencies. We would like to stress, however, that this procedure modifies only the LO phonon branches, and does not influence the remaining phonon branches at all. In figure 1 the LO/TO splitting was found by adding to the dynamical

Table 2. Frequencies of phonons at the Γ point (in THz).

Symmetry	*Ab initio* (this work)	Activity	IR R [27]	IR [28–31]	R, 300 K R, 100 K [33]	IR [32]	N [13]
A_1	5.314	R			5.28		5.34
			5.58		5.34		
A_2	5.586	Silent					5.90
A_2	5.262	Silent					4.83
E^{LO}/E^{TO}	7.315/6.452	R, IR	8.21/7.44	6.87/6.39	6.90/6.51	6.82/6.12	6.44
			8.24/7.55		6.99/6.51		
E^{LO}/E^{TO}	6.426/6.283	R, IR				5.22/4.86	5.95
					6.90/6.81		
E^{LO}/E^{TO}	6.106/5.913	R, IR	5.73/5.64	6.36/6.21	6.33/6.33	3.85/3.66	5.42
			5.73/5.73		6.48/6.33		
E^{LO}/E^{TO}	4.487/4.487	R, IR	4.59/4.59	5.49/5.37		3.48/3.24	4.07
					5.64/5.64		
E^{LO}/E^{TO}	2.135/2.106	R, IR	2.34/2.34			2.32/2.13	2.09
			2.34/2.34		2.34/2.34		
E^{LO}/E^{TO}	1.568/1.560	R, IR		2.01/1.92	1.80/1.74	1.71/1.66	1.59
			1.83/1.83		1.80/1.83		
B_1	6.601	R					6.20
					6.87		
B_1	4.873	R					4.76
			4.74		5.37		
B_1	2.312	R					1.85
			3.51		2.01		
B_2^{LO}/B_2^{TO}	7.137/6.482	R, IR	8.21/7.44	6.96/6.42	6.99/6.45	6.85/6.25	7.15
					6.99/6.51		
B_2^{LO}/B_2^{TO}	6.452/5.925	R, IR	5.88/5.64	5.79/5.43	5.94/5.94	5.07/4.89	5.82
			5.82/5.82		6.00/5.31		
B_2^{LO}/B_2^{TO}	2.175/1.992	R, IR		1.95/1.92	2.13/2.10	2.36/2.11	1.65
			2.88/2.88		2.16/2.10		

matrix the non-analytical term proposed by Pick *et al* [34], with Born effective charges taken from reference [33] (0.475, 1.255, and −0.865 for Cu, In, and Se, respectively). As a result, modes of B_2 and E symmetries split to LO and TO components. The B_2^{TO} and B_2^{LO} modes point to Γ from the x- and z-directions, respectively. The E mode remains doubly degenerate along Γ–Z directions, but splits into E^{TO} and E^{LO} components in the plane perpendicular to the fourfold-symmetry axis. The frequency of the E^{TO} components is equal to that of the E mode, while E^{LO} occurs at higher frequencies due to a contribution from effective charges. Some E modes split very little, so the splittings are not visible in figures 1 and 2.

The primitive unit cell of chalcopyrite contains eight atoms; hence one expects 24 dispersion curves. As seen in figure 1, along the P–X direction all dispersion curves are rather flat. Indeed, because the high-symmetry points P and X are close to each other, they do not provide the possibility for a large dispersion. In addition, by symmetry, all modes along P–X are doubly degenerate, which cancels the tendency for opposite dispersions of associated modes. The phonon branches along the Γ–Z line are singly (10) and doubly (7) degenerate. In all other directions, the phonon branches are singly degenerate. One may notice a small negative region of a transverse acoustic mode near the Γ point. We believe that this is not a real

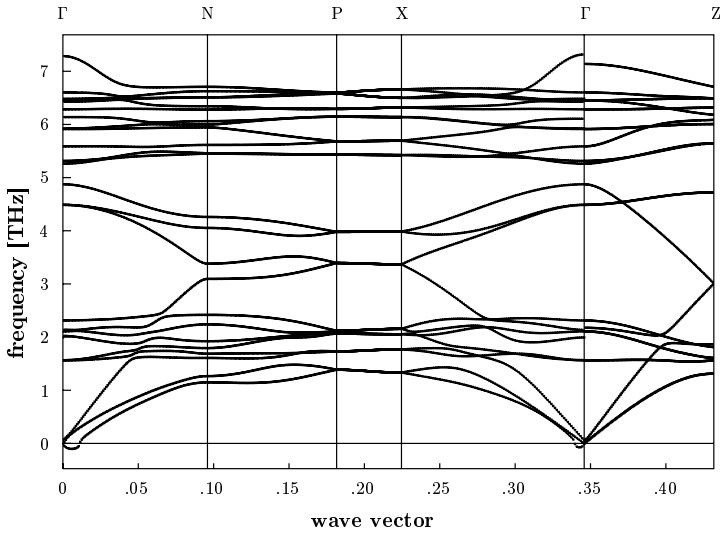

Figure 1. Calculated phonon dispersion curves for $CuInSe_2$.

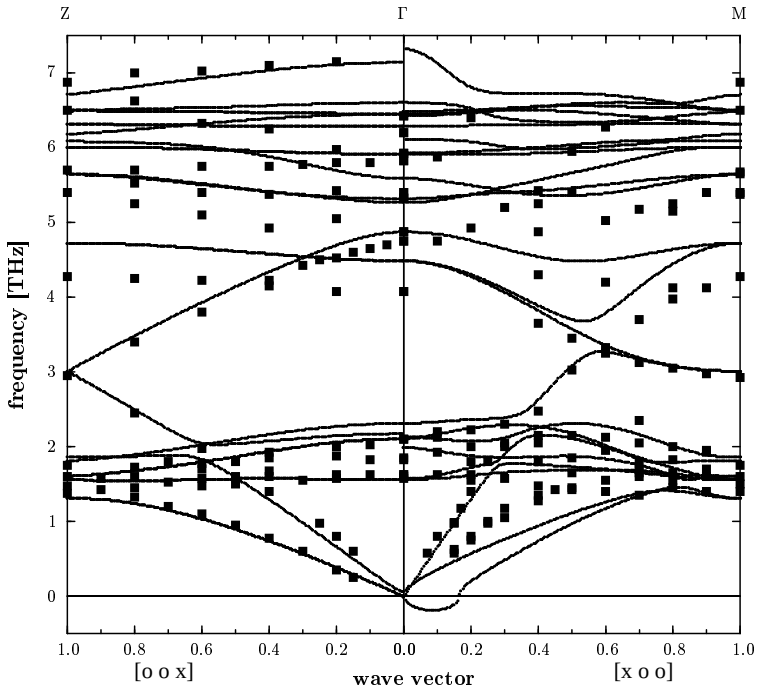

Figure 2. Comparison of the calculated phonon dispersion curves of $CuInSe_2$ (——) with experimental results (■) from reference [13].

effect but arises from the finite size of the supercell. Indeed, long-range Coulomb interaction, which dominates in this region, requires infinite summation unattainable in the direct method.

This is also probably why the transverse acoustic modes on the line Γ–M deviate so much from the experimental data (figure 2). This is just the direction with the least number of coordination shells. We assume that this problem could be minimized by enlarging the supercell size. A similar effect has been observed [36] for urea ($P\bar{4}2_1m$) where the acoustic phonon transverse mode exhibits a similar negative region. There, it was shown that it arises from the finite size of the supercell.

In figure 2 we compare our results with those measured recently by means of inelastic neutron scattering along [100] and [001] directions. One can see that in the Γ–Z ([001]) direction the agreement with experiment, except for two optic branches, is very good.

The partial and the total phonon density of states, $g_{i,\alpha}(\omega)$ (where $i = x$ or z and $\alpha =$ Cu, In, or Se) and $g(\omega)$, respectively, presented in figure 3 were obtained by sampling the dynamical matrix at 10 000 randomly selected wave vectors. The histograms are normalized to

$$\int g_{i,\alpha}(\omega)\,\mathrm{d}\omega = \frac{1}{9} \qquad \int g(\omega)\,\mathrm{d}\omega = 1$$

respectively. The total phonon density of states exhibits three well separated bands: the acoustic region (0.0–2.5THz), the low optic region (3.0–4.5 THz), and the high optic region (5.5–6.8 THz). Comparing, however, the partial phonon spectra for different atoms, one can conclude that all sublattices in CIS crystal contribute equally to these three bands. Generally, this is not always the case.

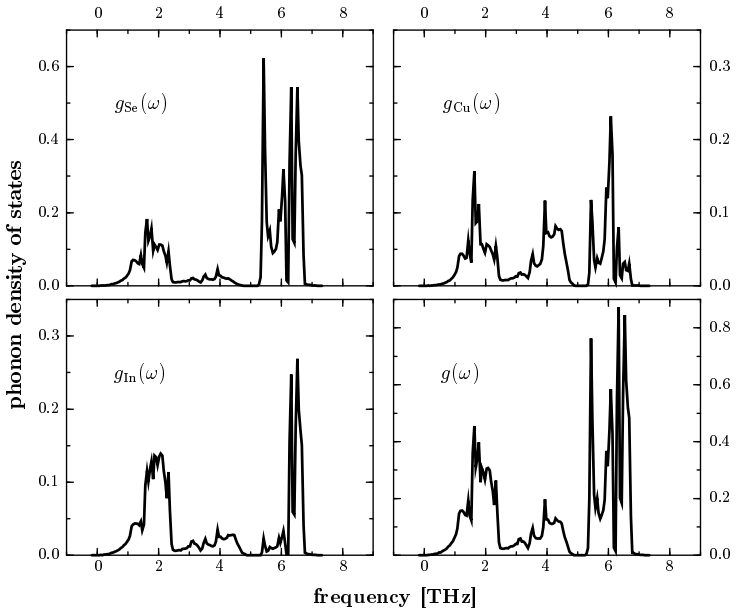

Figure 3. The calculated total phonon density of states and atomic partial densities of states for $CuInSe_2$.

4. Conclusions

We conclude that the simulated structure of $CuInSe_2$ is stable and has the same symmetry and structure as found experimentally. The calculated lattice parameters are in good agreement

with the experimental data. The calculated phonon dispersion curves fit well to the inelastic neutron scattering data in spite of the small size of the supercell.

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