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Ab initio vibrational and dielectric properties of chalcopyrite $CuInS_2$

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Abstract. We have performed a first-principles study of structural, dynamical, and dielectric properties of the chalcopyrite semiconductor $CuInS_2$. The calculations have been carried out within the local density functional approximation using norm-conserving pseudopotentials and a plane-wave basis. Born effective charge tensors, dielectric permitivity tensors, the phonon frequencies at the Brillouin zone center and mode oscillator strengths are calculated using density functional perturbation theory. The calculated properties agree with infrared and Raman measurements.

PACS. 63.20.Dj Phonon states and bands, normal modes, and phonon dispersion – 77.22.Ch Permittivity (dielectric function) – 78.30.Hv Other nonmetallic inorganics

1 Introduction

Cu-based ternary chalcopyrite semiconductors have been a subject of investigation for possible solar energy and nonlinear optical applications [1]. Solar conversion efficiencies of 19% and 12% have been achieved with $CuInSe_2$ and $CuInS_2$, respectively. The $CuInS_2$ system is also of technical interest owing to its perfect lattice matching with Si. Over the past three decades the lattice dynamical properties of Cu-based chalcopyrite semiconductors have been studied experimentally as well as theoretically by a number of groups (for a thorough review of experimental phonon frequencies of chalcopyrite semiconductors see Ref. [2]). Brillouin-zone-center (BZC) phonon frequencies of $CuInS_2$ have been measured by Raman [3,4] and infrared [3] spectroscopies. Theoretical studies of BZC-mode frequencies of $CuInS_2$ are reported by Koschel and Bettini [3] who used an extended Keating model and by Ohrendorff [2] using a rigid ion model. Owing to inconsistencies in the experimental data as well as inadequacies of the interactions taken into account in these phenomenological models, a first-principles investigation of lattice dynamical properties of $CuInS_2$ should provide valuable additional information.

The first-principles investigation of phonon frequencies can be performed within a density-functional perturbation theory (DFPT) [5], or with the direct method (or frozen-phonon) approach. Both techniques have their respective advantages and disadvantages. In polar crystals, the nonanalyticity of the dynamical matrices in the long wave limit produces the LO-TO splitting of the polar modes. This splitting depends on the effective charges and dielectric tensors of the system which are not directly accessible to the direct method. These can be supplied by a separate calculation using Berry's phase approach [6], borrowed from density-functional perturbation theory calculations, taken from experimental values, or obtained from the use of an elongated supercell. For a review of DFPT and this issue, one can consult reference [5]. In contrast to the direct-method calculations of phonon frequencies, the linear response approach allows to obtain the effective charges and dielectric tensors directly. First-principles calculations of phonon frequencies for several chalcopyrite semiconductors using the direct method [6–11] as well as the linear response approach [12,13] have been reported.

In this paper, we investigate the equilibrium lattice structure, Born effective charge tensors, dielectric permitivity tensors, zone-center phonon frequencies, and mode oscillator strengths of $CuInS_2$ using the density-functional and density-functional perturbation theories [5,14,15] with norm-conserving pseudopotentials and the local density approximation (LDA) exchange-correlation energy. Lazewski *et al.* recently reported a similar calculation of the dynamical properties of $CuInS_2$ using the direct method with ultrasoft pseudopotentials and the generalized-gradient-approximation (GGA) corrected exchange-correlation energy [6]. We compare and discuss the relative merits of both approaches.

2 Method of calculation

The present results have been obtained with the ABINIT code [16,17], which is based on pseudopotentials and plane

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waves. It relies on an efficient Fast-Fourier-Transform algorithm [18] for the conversion of wavefunctions between real and reciprocal space, on the adaptation to a fixed potential of the band-by-band conjugate-gradient method [19], and on a potential-based conjugate-gradient algorithm for the determination of the self-consistent potential [20]. The norm-conserving pseudopotentials of Troullier-Martins type have been generated with the FHI98PP code [21]. The need to include semicore Cu $3d$-states as valence states requires a high kinetic-energy cutoff for the plane-wave expansion. To achieve a convergence better than 0.01 eV for the total energy, the cutoff energy must be at least 45 Ha. The Brillouin zone is sampled by 12 special k-points. This is found to be sufficient for the convergence of static as well as response calculations.

The technical details about the computation of responses to atomic displacements and homogeneous electric fields can be found in reference [14], while reference [15] presents the subsequent computation of dynamical matrices, Born effective charges, dielectric permittivity tensors, and interatomic force constants.

3 Results

3.1 Atomic structure

The chalcopyrite structure (space group D_{2d}^{12}, No. 122) can be considered as derived from the cubic zinc-blende structure (space group T_d^2) by populating one of the face-centered-cubic sublattices with group VI atoms and the other one with equal amounts of group I and III atoms in a regular fashion. In general, the I-VI and III-VI bond lengths are not equal. In consequence, the chalcopyrite unit cell is distorted from the cubic zinc-blende one in two ways. First, the lattice parameters a and c are related by $\eta = c/a$ with $\eta \neq 2$. Second, the tetrahedral environment of the anions is deformed in the xy-plane. This is measured by an internal parameter u which characterizes the reduced anion positions, either (u 0.25 0.25) or (0.25 u 0.25), for distorted tetrahedra along x or y, respectively; u equals 0.25 for the cubic zinc blende. The cations are located at $4a$ and $4b$, while the anions are located at $8d$ Wyckoff positions.

The lattice parameters are determined from atomic and structural relaxation. They are compared to experimentally available data and to the previous *ab initio* results of reference [6] in Table 1. Considering that the zero-point motion and thermal effects are not taken into account, the calculated a, η, and u values agree quite well with the experimental ones. The slightly higher lattice constants calculated in reference [6] are presumably due to the use of the GGA, as the GGA tends to overestimate lattice constants [24].

3.2 Born effective charge tensors

For insulators, the Born effective charge tensor for atom κ, $Z^\star_{\kappa,\beta\alpha}$, quantifies to linear order the polarization per unit cell, created along the direction β when the atoms of sublattice κ are displaced in the direction α under the condition of zero electric field. It can be calculated either from the Berry phase or using perturbation theory.

Table 1. A comparison of optimized structural parameters of $CuInS_2$ with the experimental data and a previous calculation. a is in a.u. while η and u are dimensionless.

	Theory		Experiment	
	This work	Ref. [6]	Ref. [22]	Ref. [23]
a	10.46	10.53	10.43	10.44
η	1.998	2.018	2.006	2.014
u	0.245	0.221	0.200	0.223

We calculate effective charge tensors of $CuInS_2$ with perturbation theory [15]. Owing to finite k-point sampling, there is a deviation from charge neutrality which is smaller than 0.02 electrons per unit cell. The form of the effective charge tensors results from the site symmetry of the ions. Cations, located at $4a$ and $4b$ sites, have diagonal effective charges with $Z^\star_{\mathrm{Cu},xx} = Z^\star_{\mathrm{Cu},yy} = 0.67$, $Z^\star_{\mathrm{Cu},zz} = 0.63$ and $Z^\star_{\mathrm{In},xx} = Z^\star_{In,yy} = 2.66$, $Z^\star_{\mathrm{In},zz} = 2.56$. The anisotropy of the effective charges of the cations is small; $(Z^\star_{xx} - Z^\star_{zz})/Z^\star_{zz} \approx 0.06$ and 0.04 for Cu and In, respectively. Owing to the tetrahedral distortion, anions have a lower site symmetry. The distortion generates four different configurations. The resulting effective-charge-tensor elements can be divided into two classes, according to whether u is along the x or y-direction. The magnitude of the zz-component, $Z^\star_S = -1.60$, is the same for all anions. $Z^\star_{S,xx}$ and $Z^\star_{S,yy}$ take the values -1.59 or -1.70 for x-distortions, and *vice versa* for y-distortions. Also, the off-diagonal components are different from zero, and depending on the distortion they are $Z^\star_{S,zx} = \pm 0.64$ and $Z^\star_{S,xz} = \pm 0.67$, or $Z^\star_{S,yz} = \pm 0.64$ and $Z^\star_{S,zy} = \pm 0.67$. The averages of the diagonal elements of $Z^\star$ can be used for a qualitative comparison with experimental values. We find 0.657, 2.627, and -1.643 for Cu, In, and S, respectively. These values are similar to those calculated for $CuGaS_2$ [12]. Lazewski *et al.* report Born effective charges of $CuInS_2$ calculated with the Berry phase technique [6]. These tensors are similar in form to ours, however with averages 1.06, 2.91 and -2.0 for Cu, In, and S, respectively. The difference between our results and those of reference [6] might be due to the use of different types of pseudopotentials. Assuming a Cu(+1)-In(+3)-S(-2) static ionic configuration for this compound, we remark that the calculated Born effective charges are not very different from the static charges. The anomalous Born effective charge phenomenon, which is common in perovskites [25], is not observed in chalcopyrites.

3.3 Phonons

Since the body-centered-tetragonal primitive unit cell of the chalcopyrite structure contains eight atoms, there is a total of 24 vibrational modes. A detailed discussion of the

Table 2. Frequencies of phonons at the Γ point (in cm^{-1}).

Mode	Theory		Experimental results	
	This work	Ref. [6]	IR/R [3]	R [4]
Γ_1	313	272	294	292
Γ_2	334	296		
Γ_2	311	270		
Γ_3	345	308		
Γ_3	183	155		
Γ_3	111	93		
$\Gamma_4^{TO}/\Gamma_4^{LO}$	347/364	301/327	323/352	320/
	278/295	231/256	234/266	
	85/87	77/78	79/79	75/-
$\Gamma_5^{TO}/\Gamma_5^{LO}$	337/349	292/313	321/332	320/-
	321/332	282/290	295/314	
	290/301	238/253	244/260	245/-
	168/169	138/138	140/140	
	94/94	83/84	88/88	85/-
	84/84	69/69	67/67	65/-

group theoretical properties of chalcopyrite zone-center phonons is found in reference [26]. The irreducible representations at the center of the Brillouin zone are

$$\Gamma_{\rm opt} = 1\Gamma_1 \oplus 2\Gamma_2 \oplus 3\Gamma_3 \oplus 3\Gamma_4 \oplus 6\Gamma_5$$

for the optical modes, and

$$\Gamma_{\rm aco} = 1\Gamma_4 \oplus 1\Gamma_5$$

for the acoustic ones. Optical modes of Γ_1 or Γ_2 symmetries involve only displacements of cations. For Γ_3, Γ_4 and Γ_5 modes anions also move. Both Γ_4 and Γ_5 modes belong to vector transforming representations, and they are thus IR active. The inclusion of the long range polarization interaction results in the splitting of the Γ_4 and Γ_5 modes into TO and LO components giving nine polar vibrations, three with polarization along c (Γ_4 modes) and six along x or y (Γ_5). This produces a different number of IR modes active for $E \| c$ and for $E \perp c$. Except for the modes of Γ_2 symmetry, all optical modes are Raman active.

In Table 2 our calculated zone-center phonon frequencies and their symmetry assignments are listed and compared with the results of infrared and Raman measurements of references [3,4] and with first-principles calculations of reference [6]. The agreement of our results with the experimental data is generally satisfactory, except for some mid-frequency Γ_4 and Γ_5 modes. The experimental determination of the zone-center phonon frequencies of Cu-based chalcopyrites has been difficult, in part due to the complex mode structure and in part owing to experimental problems. For example, the spread in experimental data for the mid-frequency Γ_4 and Γ_5 modes of $CuInSe_2$ and $CuGaS_2$, which have been experimentally investigated by many more groups than $CuInS_2$, is greater than 60 % [2]. Based on our previous work on $CuInSe_2$ [13] and $CuGaS_2$ [12], we expect that new measurements of the BZC-modes of $CuInS_2$ might give phonon frequencies that will be closer to our results than those reported in references [3,4].

As can be seen from Table 2, the overall agreement between our calculated results and the experimental data [3] is rather similar to that of reference [6]. Lazewski *et al.*'s results are better for low frequency modes while ours are somewhat better for high frequency ones. A general feature of the comparison of the two calculated sets is a consistent over- and underestimation of the BZC-mode frequencies by the linear response (our calculation) and by the direct method (the calculation Ref. [6]), respectively. It is a general feature of density-functional-theory calculations that LDA overestimates and GGA underestimates the phonon frequencies [24]. We believe that a large portion of the differences between our results and these of reference [6] is due to the use of different exchange-correlation functionals.

3.4 Lattice dielectric tensors

The form of the dielectric tensors results from the body-centered-tetragonal symmetry of the crystal. The calculated electronic (ϵ_∞) and static (ϵ_0) dielectric tensors are diagonal and have two independent components $\epsilon^{||}$ and $\epsilon^{\perp}$ along and perpendicular to the c axis, respectively. We compare our calculated dielectric tensor components to the model calculations of reference [27] in Table 3. The averages of ϵ_∞ and ϵ_0, obtained from the expression ϵ_∞ (or ϵ_0)$= (2\epsilon_\infty^{\perp} + \epsilon_\infty^{\|})/3$ are also shown in this table. The anisotropy of ϵ_∞ is around -5%, while the anisotropy of the static dielectric tensor is positive and around 3%, which is consistent with the fact that for $CuInS_2$ the tetragonal distortion is very small ($\eta \approx 2$). There are no experimental data for the static and high frequency dielectric constants of $CuInS_2$. The comparison with the model calculation seems to be fair when one takes into account that DFT-LDA tends to overestimate the ϵ_∞ value.

Table 3. Static and high frequency dielectric tensor components of $CuInS_2$.

	$\epsilon_\infty^{\|}$	$\epsilon_\infty^{\perp}$	ϵ_∞	$\epsilon_0^{\|}$	$\epsilon_0^{\perp}$	ϵ_0
This work	7.51	7.86	7.74	9.68	9.71	9.70
Ref. [27]	6.0	6.2	6.1	8.4	8.6	8.5

The static dielectric tensor can be decomposed into contributions of different modes as follows [14]

$$\epsilon_{\alpha\beta}^0 = \epsilon_{\alpha\beta}^\infty + \frac{4\pi}{\Omega_0} \sum_m \frac{S_{m,\alpha\beta}}{\omega_m^2} \qquad (1)$$

where Ω_0 is the volume of the primitive unit cell, ω_m is the frequency of mode m and $S_{m,\alpha\beta}$ is the oscillator-strength tensor which is related to the eigen-displacements $U_m(\kappa\alpha)$

and Born-effective-charge tensors by

$$S_{m,\alpha\beta} = \left(\sum_{\kappa\alpha'} Z^{\star}_{\kappa,\alpha\alpha'} U^{\star}_{m}(\kappa\alpha')\right)\left(\sum_{\kappa'\beta'} Z^{\star}_{\kappa',\beta\beta'} U^{\star}_{m}(\kappa'\beta')\right). \quad (2)$$

Similarly, one can define a mode effective-charge tensor as:

$$Z^{\star}_{m,\alpha} = \frac{\sum_{\kappa\beta} Z^{\star}_{\kappa,\alpha\beta} U_m(\kappa\beta)}{\left[\sum_{\kappa\beta} U^{\star}_{m}(\kappa\beta) U_m(\kappa\beta)\right]^{1/2}}. \quad (3)$$

For IR-active modes, the relevant components of the oscillator-strength tensor ($zz-$component for Γ_4 modes and xx or $yy-$component for Γ_5 modes) and the magnitude of the mode effective-charge tensors are displayed in Table 4. For both Γ_4 and Γ_5 symmetries, higher frequency modes have higher mode effective charges and oscillator strengths. Our calculated oscillator-strength values for the Γ_4 modes show a reasonable agreement with both sets of experiments. S_m for the three lowest frequency modes of Γ_5 symmetry are very small compared to the higher frequency modes of the same symmetry.

Table 4. Oscillator-strength tensor S_m (in 10^{-4} $\mathrm{m}^3/\mathrm{s}^2$), magnitude of the mode-effective-charge vectors $Z^{\star}_m$, and LO-frequencies ω_m (in cm^{-1}) of $CuInS_2$.

	S_m	$Z^{\star}_m$	ω_m
Γ_4	3.32	1.38	87
	18.08	3.50	295
	16.11	3.14	364
Γ_5	0.63	0.33	84
	0.56	0.62	94
	0.73	0.77	169
	17.69	3.49	301
	15.75	3.18	332
	7.22	1.35	349

4 Conclusion

We have investigated both static and dynamical properties of the ternary semiconductor $CuInS_2$ using density-functional perturbation theory. Results are given for Born effective-charge tensors, Brillouin zone-center phonon frequencies, as well as static and high frequency dielectric tensors. Born effective charges are found to be rather similar to static charges. The calculated static and high frequency dielectric tensors are almost isotropic. For the zone-center phonon modes we find a reasonable agreement with the experimental data except for some modes which we believe should be further investigated experimentally.

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