

Lattice dynamics of CuAu-ordered CuInSe₂

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The lattice vibrational properties of CuInSe₂ with CuAu-type ordering of the cation sublattice are investigated theoretically by a first-principles calculations of the structure and the lattice dynamical characteristics including zone-center optical mode frequencies, phonon dispersion and density of states, and elastic constants. The results obtained for CuAu-ordered CuInSe₂ are compared with related experimental data and comparative theoretical calculations for the chalcopyrite phase of the compound. A critical analysis is given of the partly contradictory experimental lattice vibration data reported for chalcopyrite CuInSe₂.

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I. INTRODUCTION

The ternary chalcopyrite compound CuInSe₂ and its alloys with CuGaSe₂ are promising semiconductor materials with practical application as stable and radiation resistant polycrystalline thin film photovoltaic solar cells¹ with power conversion efficiencies increasing steadily over the years, now exceeding 21% in laboratory devices and being close to 15% in modules produced commercially.^{2,3} In contrast to the progress made in device development many of the fundamental properties of CuInSe₂ are still not known with sufficient reliability which is essentially a consequence of the complexity of the Cu₂Se–In₂Se₃ pseudobinary phase diagram.⁴ Bulk single crystals of CuInSe₂ with chalcopyrite structure usually grown from stoichiometric melts using the Bridgman technique reveal unavoidable compositional inhomogeneities^{5,6} independent of the specific growth conditions. The capability of the material to accommodate rather large deviations from stoichiometry observed experimentally finds its explanation in the formation of (1) high concentrations of native point defects^{7,8} (vacancies, antisite defects, interstitials) and point defect complexes,⁹ (2) structural defects^{7,10} (dislocations, stacking faults, twins), (3) orientation domains^{11,12} separated by small angle domain boundaries,¹³ and (4) inclusions of secondary phases in the chalcopyrite matrix.^{6,11,14} Considering this complex defect situation and its dependence on the specific deviation from stoichiometry,^{6,7} the possible influence of the various types of defects on the physical properties of the material must be taken into account in analyzing and interpreting related experimental data.

The lattice vibrational properties of CuInSe₂ have been

studied experimentally by a number of groups but the results reported are partly contradictory.¹⁵ First-principles calculations^{16,17} of the vibrational properties of CuInSe₂ gave agreement with several sets of experimental data, but did not give decisive hints how existing discrepancies can be explained. It has been argued that incorrect assumptions about the polarization conditions can be the reason for wrong mode assignments. The sensitivity of Raman backscattering spectra to surface preparation methods such as polishing or etching has also been demonstrated.¹⁸ However, it follows from the analysis of published results by Ohrendorf *et al.*¹⁵ that these two factors are not sufficient to explain some of the discrepancies observed in the experimental data. Indeed, there are also severe differences in some of the optical mode frequencies determined by infrared reflectivity^{19,20} and Raman scattering measurements²¹ on appropriately oriented single crystals and thus under well defined polarization conditions. Discrepancies have also been observed for the elastic properties of CuInSe₂. Linear compressibilities calculated from elastic constants determined by inelastic neutron scattering²² are in clear contradiction to the results of pressure dependent x-ray diffraction structure studies²³ and elastic constants calculated on a first-principles basis.²⁴

The possible influence of orientation domains on the lattice vibrational properties of CuInSe₂ samples has not been investigated or discussed so far. Theoretical calculations of the formation energy for different CuInSe₂ polytypes²⁵ have predicted that the type-1 CuAu structure is nearly isenthalpic with the chalcopyrite structure which suggests the coexistence of CuAu-ordered phases in nominally chalcopyrite CuInSe₂. Calculations for CuInS₂ gave similar results.²⁶ Recent experimental observations of coexisting chalcopyrite

TABLE I. Calculated lattice parameters a and c , internal parameter u , as well as bond lengths $d_{\text{Cu-Se}}$ and $d_{\text{In-Se}}$ of chalcopyrite and CuAu-ordered CuInSe₂. A comparison with room temperature experimental data.

	a (Å)	c (Å)	u	$d_{\text{Cu-Se}}$ (Å)	$d_{\text{In-Se}}$ (Å)	Method
Chalcopyrite	5.880	11.833	0.2177	2.447	2.665	<i>ab initio</i> , this work
	5.782(1)	11.620(1)	0.235(5)	2.458	2.559	x-ray powder diffr. (Ref. 43)
	5.784(1)	11.616(5)	0.224(3)	2.424	2.598	x-ray powder diffr. (Ref. 44)
	5.781(1)	11.642(3)	0.2260(2)	2.433	2.589	x-ray single cryst. diffr. (Ref. 45)
	5.760(4)	11.591(7)	0.2305(7)	2.436	2.565	x-ray single cryst. diffr. (Ref. 46)
CuAu-ordered	4.181	5.850	0.2181	2.449	2.663	<i>ab initio</i> , this work
	4.088	5.810	0.2245	2.425	2.596	electron diffr. (Ref. 28)

and CuAu-ordered phases in epitaxial layers of both CuInSe₂ (Refs. 27,28) and CuInS₂ (Refs. 29,30) confirmed these predictions. Furthermore, preliminary Raman scattering studies^{28,31,32} of these epitaxial layers revealed several additional optical modes which have been tentatively ascribed to the CuAu-ordered phase of these compounds. Taking into account that orientation domains with the type-1 CuAu structure have also been observed in CuInSe₂ single crystals¹² it cannot be excluded that the presence of these domains gives rise to modifications of the lattice vibration spectra and elastic constants measured experimentally. It was the aim of the present work to clarify this point. For this purpose, we have performed a comparative first-principles calculation of the lattice dynamical properties of CuInSe₂ in the chalcopyrite and CuAu-ordered phases. The results obtained are used to critically discuss experimental data on the lattice dynamical properties^{15,22,33} of nominally chalcopyrite CuInSe₂ published in the literature.

II. RESULTS AND DISCUSSION

A. Calculation method

The calculations were performed on a $2 \times 2 \times 1$ supercell (64 atoms) for the chalcopyrite structure (space group $I\bar{4}2d$, No. 122) and a supercell of the same size for the CuAu-ordered structure (space group $P\bar{4}m2$, No. 115) using the first-principles VASP package³⁴ in the framework of the plane augmented waves approximation^{35,36} with gradient corrections.^{37,38} In the reciprocal space summation was carried out using $2 \times 2 \times 2$ k points mesh generated according to the Monkhorst–Pack scheme.³⁹ During optimization of the structure parameters (lattice parameters a and c , internal parameter u) we used periodic boundary conditions with constraints according to the respective space groups.

The frequencies of the transverse optical phonon modes were calculated using the force constants direct method.^{40,41} The complete set of Hellmann-Feynman forces was obtained from small atomic displacements. For both the chalcopyrite and the CuAu-ordered structures a minimal set consists of seven necessary displacements: along x and z axes for Cu and In atoms and along x , y , and z for Se atoms. Using symmetry elements the force constants were derived, the dynamical matrix constructed, and finally phonon frequencies were calculated for selected k points in the Brillouin zone.

The long-range macroscopic electric field accompanying displacements of atoms in polar crystals splits longitudinal and transverse frequencies of infrared active optical modes. It can be considered in the dynamical matrix by a nonanalytical contribution, proposed by Pick *et al.*,⁴² depending on Born effective charge tensors and the high-frequency dielectric constant ϵ_∞ . In the present calculations we used Born effective charge tensors and ϵ_∞ of CuInSe₂ calculated from first principles by Parlak and Eryigit¹⁷ for chalcopyrite structure. For CuAu-ordered structure with significantly different anions neighborhood we reduced charge tensors to point effective charges.

Elastic constants were calculated from stress-strain relationships defining the elastic constants as coefficients in the generalized Hook's law.²⁴ For this purpose the crystal must be deformed from its equilibrium shape by a set of tetragonal and shear deformations of different sizes. The stress tensors calculated for each deformation are then used to build a set of linear equations for independent elastic constants. To build the equation for the elastic stiffness constants we have used five tetragonal deformations of the supercells along a and c axes and three shear deformations in α and γ angles.

B. Structure

The calculated structure parameters a , c , and u as well as bond lengths $d_{\text{Cu-Se}}$ and $d_{\text{In-Se}}$ are displayed in Table I and compared to experimental data determined by x-ray powder^{43,44} and single crystal diffraction^{45,46} for the chalcopyrite phase and by electron diffraction²⁸ for the CuAu-ordered structure. There is some scatter in the structure parameters for CuInSe₂ with chalcopyrite structure which can be ascribed to some variation of the elemental composition of the samples investigated.⁴⁷ The calculated lattice parameters a and c overestimate the experimental values for both structure types, despite the scatter in the experimental data for the chalcopyrite phase. The calculated internal structure parameters u are smaller than the experimental ones, but they are practically equal for both structures in agreement with experiment, the difference being as small as $|\Delta u| = 0.0004$. The difference in the calculated bond lengths for the chalcopyrite and CuAu-ordered structures is also small, $|\Delta d_i| = 0.002$ Å for both the Cu-Se and In-Se bonds.

In order to roughly estimate the systematic error to be expected in calculating phonon frequencies it is useful to

compare calculated and experimental bond lengths. From Table I it seems obvious that the calculated Cu-Se bond length is in the range of the experimental values. However, EXAFS determinations of the Cu-Se bond length in bulk crystals^{48,49} and thin films^{50,51} gave always values in the range $d_{\text{Cu-Se}} = 2.424$ to 2.436 Å, in agreement with the majority of x-ray diffraction measurements given in Table I. Moreover, bond lengths in the same range have been found by Merino *et al.*⁴⁷ for samples with compositions close to exact stoichiometry. Therefore, we come to the conclusion that the calculated Cu-Se bond length only slightly overestimates the true one by not more than 0.01 to 0.02 Å. On the other hand, the In-Se bond length is distinctly overestimated by more than 0.065 Å because EXAFS measurements,^{48,50} and the x-ray powder diffraction studies by Merino *et al.*⁴⁷ gave also values below or close to $d_{\text{In-Se}} = 2.60$ Å. This overestimate of the In-Se bond length is expected to give rise to an underestimate of the corresponding bond-stretching force constant,^{52,53} and consequently to a systematic underestimate of vibrational mode frequencies dominated by the In-Se nearest-neighbor interaction. Some underestimate of frequencies is also expected for modes dominated by Cu-Se nearest-neighbor interaction but this effect should be less pronounced because the difference between the calculated and experimental Cu-Se bond lengths and thus in the respective bond-stretching force constants is not as large as in case of the In-Se bond.

The coexistence of the chalcopyrite and CuAu-ordered structures in CuInSe₂ epitaxial layers²⁸ and, in particular, the presence of orientation domains with CuAu-ordered structure in bulk single crystals¹² suggest a very small total energy difference between both structure variants. The total Helmholtz free energy F of a crystal can be written as a sum of two contributions

$$F = E + F_{\text{ph}}, \quad (1)$$

where E is the ground state energy from the first-principles calculation. In harmonic approximation the phonon free energy F_{ph} of the primitive cell is given by

$$F_{\text{ph}}(T) = k_B T \int_0^\infty d\omega g(\omega) \ln\{2 \sinh[\hbar\omega/(2k_B T)]\}, \quad (2)$$

where ω denotes the phonon frequency, \hbar the Planck constant, k_B the Boltzmann constant, and T the temperature. The phonon density of states $g(\omega)$ was calculated by sampling the dynamical matrix in 50 000 randomly selected wave vectors in the whole Brillouin zone. The result of our calculations is depicted in Fig. 1. As can be seen the difference of the total Helmholtz free energies is about 1.8 meV/atom at $T=0$ K and is even slightly reduced going to higher temperatures, taking a value of about 0.8 meV at 300 K. This result agrees with the theoretical predictions by Wei *et al.*^{25,26} and explains the coexistence of both phases in epitaxial layers and bulk single crystals of the compound.

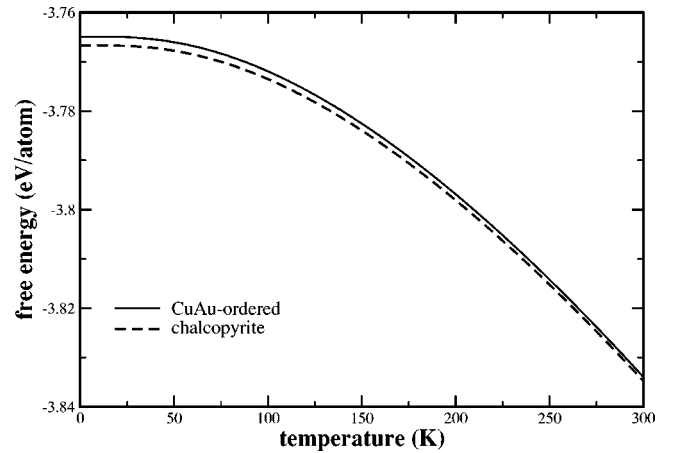


FIG. 1. A comparison of the total Helmholtz free energies of the chalcopyrite and CuAu-ordered phases of CuInSe₂.

C. Optical phonons

In order to evaluate the accuracy of our calculations we first consider the results obtained for the chalcopyrite phase of the compound. The calculated frequencies of the Raman active A_1 and B_1 modes, the optically inactive A_2 modes, and the transverse and longitudinal modes of the infrared active B_2 and E phonons are given in Table II. Because of existing discrepancies in the literature data some care is required in choosing experimental data for comparison with theory. As representative for the results of infrared and Raman scattering studies we have included in Table II the mode frequencies obtained by the only infrared reflectivity,^{19,20} and Raman backscattering measurements²¹ performed under well defined polarization conditions using single phase and appropriately oriented CuInSe₂ single crystals. Room temperature polarized and unpolarized infrared studies of (112)-oriented single crystals,^{54,55} polycrystalline bulk samples,⁵⁶ powdered material embedded in polyethylene,⁵⁵ and polycrystalline thin films,⁵⁷ polarized Raman scattering measurements on (001)- and (100)-oriented epitaxial layers,^{58,59} as well as polarized⁶⁰ and unpolarized^{18,61,62} Raman scattering studies of (112)-oriented single crystals gave always mode frequencies in good agreement with the respective room temperature data of Table II. All these modes have also been found in the Raman spectra measured at 100 K, partly with slightly enhanced frequencies as reflecting the temperature dependence of mode frequencies (Table II). In addition, Tanino *et al.*²¹ have identified three modes supposed to be of B_1 symmetry and two other modes with frequencies given in brackets in Table II and claimed to have E symmetry. The Raman scattering data²⁸ for CuAu-ordered CuInSe₂ lead us to the assumption that these two modes are caused by orientation domains with CuAu-ordered structure in the chalcopyrite matrix and are identical with the longitudinal modes at 186 and 233 cm^{-1} . Furthermore, the frequency of 179 cm^{-1} for the B_1^2 mode appears doubtful and must probably be ascribed to the A_1 mode. Indeed, mode leakage gives rise to more or less pronounced peaks of the intense A_1 mode at 178 cm^{-1} (Table II) in the spectra for all polarization configurations presented by Tanino *et al.*,²¹ and there is no reasonable argu-

TABLE II. Comparison of calculated mode frequencies (in cm^{-1}) for chalcopyrite CuInSe_2 with experimental data obtained by infrared reflectivity (IR), Raman scattering (R), and inelastic neutron scattering (N) measurements. Two numbers in a row correspond to TO/LO frequencies.

Mode	<i>ab initio</i> this work	IR(300 K) (Ref. 19)	IR(300 K) (Ref. 20)	R(300 K) (Ref. 21)	R(100 K) (Ref. 21)	N(300 K) (Ref. 33)
A_1	169			176	178	178
A_2^1	175					197
A_2^2	162					161
B_1^1	206				229	207
B_1^2	149				179	159
B_1^3	81				67	62
B_2^1	197/210	213/233	214/232	215/233	217/233	238
B_2^2	173/182	179/195	181/193	—/198	177/200	194
B_2^3	67/68	64/65	64/65	70/71	70/72	55
E^1	199/211	213/230	213/229	217/230	217/233 (227/230)	215
E^2	193/197	206/212	207/212	211/—	211/216 (188/188)	198
E^3	171/174	178/182	179/183			181
E^4	132/132					137
E^5	69/69			77/77	78/78	70
E^6	60/60			58/60	60/61	53

ment to suppose that the A_1 mode does not contribute to the spectrum selecting the very weakly scattering B_1 modes which are hardly detectable in Raman backscattering experiments of chalcopyrite compounds.¹⁵ The results of an inelastic neutron scattering study of chalcopyrite CuInSe_2 single crystals at room temperature and atmospheric pressure³³ added in the last column of Table II confirm these suppositions. In particular, all six E modes have been identified, and the two E modes missing in all room-temperature Raman spectra reported in the literature^{18,21,58,59,61,62} have been found to have frequencies of 137 and 181 cm^{-1} , the latter being identical with the mode E^3 observed in infrared reflectivity spectra (Table II). Derollez *et al.*³³ do not give error limits of their mode frequencies, but an analogous investigation⁶³ of AgGaSe_2 gave in some cases deviations up to about 7% from mode frequencies precisely determined by Raman scattering.⁶⁴ Admitting a similar maximal uncertainty in the present case the results of the neutron scattering study compare well with the infrared and Raman data. In view of this fact the infrared, Raman, and neutron scattering data given in Table II can be considered as a reliable basis for comparison between theory and experiment for chalcopyrite CuInSe_2 .

Concluding the discussion of experimental data for CuInSe_2 with chalcopyrite structure it must be noted that there is also literature data which distinctly deviates from the data of Table II. The mode frequencies determined by Gan *et al.*⁶⁵ using polarization dependent infrared reflectivity and Raman scattering measurements on nominally CuInSe_2 crystals differ completely from the results of all later investigations of the compound, but resemble the optical mode frequencies reported for CuGaSe_2 .^{15,20,66,67} Thus, it is rather likely that Gan *et al.*⁶⁵ have measured CuGaSe_2 and not

CuInSe_2 . The results of a polarization-dependent infrared reflectivity study reported by Syrbu *et al.*⁶⁸ are also inconsistent with the results of other polarized infrared investigations^{19,20,54,55} of the compound. In addition to the clearly pronounced deviations of the mode frequencies from those of Table II, the E mode spectra presented by these authors exhibit six distinct structures which has never been observed in CuInSe_2 with stoichiometric or near-stoichiometric composition, even under conditions of mode leakage effects due to incomplete polarization conditions. Syrbu *et al.*⁶⁸ do not give any information on the composition or the structure of their samples. However, if they have used only routine x-ray diffraction measurements to characterize the material, it cannot be excluded that they have measured one of the indium-rich compounds of the Cu-In-Se system such as, for instance, $\text{Cu}_2\text{In}_4\text{Se}_7$ or CuIn_3Se_5 which also crystallize in tetragonal structures⁶⁹ with lattice parameters very close to those of CuInSe_2 . From a comparative Raman scattering study of these compounds⁷⁰ it is evident that there are essential changes of the lattice vibrational properties going from chalcopyrite CuInSe_2 to the indium-rich compounds caused by changes in the space group and in the bond configurations.^{71,72}

Finally, the unpolarized Raman scattering study by Rincon *et al.*⁷³ can be considered as a typical example for the influence of inclusions of secondary phases in the CuInSe_2 bulk matrix on measured spectra. Six of the eight vibrational modes identified by these authors have frequencies identical with those of the A_1 , B_2^1 (LO and TO) or E^1 (LO and TO), E^2 (TO), E^5 , and E^6 modes of Table II and thus exactly reflect the number and frequencies of modes detectable in chalcopyrite CuInSe_2 by measurements at room temperature.

The remaining two modes have frequencies of 259 and 124 cm⁻¹ which are indicative of the presence of copper selenide inclusions known to exist as binary secondary phases in slightly copper-rich material.^{4,6} Indeed, the higher frequency is very close to that of the fully symmetric A_g mode at 260 cm⁻¹ in CuSe₂ (Ref. 74) and to that of an intense Raman active mode at 263 cm⁻¹ in CuSe,⁷⁵ and both compounds have also Raman active modes around 120 cm⁻¹.

Now, comparing our calculated optical mode frequencies with the experimental data compiled in Table II the following trends are obvious. First, except for the B_1^3 mode, the frequencies of the other low-energy modes B_2^3 , E^5 , and E^6 are reproduced with an accuracy which corresponds to the experimental error limits. Since the frequencies of these modes are essentially determined by bond-bending forces or interaction between second-nearest neighbors⁷⁶ it can be concluded that the corresponding interaction parameters are described with sufficient accuracy in the theoretical approach used in the present study. Secondly, the greatest underestimate of mode frequencies in the range of 7 to 11 % is observed for the A_2^1 , B_1^1 , B_2^1 , E^1 , and E^2 modes whereas the frequencies of the modes A_1 , A_2^2 , B_1^2 , B_2^2 , E^3 , and E^4 are underestimated by less than about 4%. This tendency reflects the differences between calculated and experimental Cu-Se and In-Se bond lengths as discussed in Sec. II B. According to theoretical calculations with different phenomenological models,^{52,76} the frequencies of the former group of modes are mainly determined by the In-Se bond stretching force constant and, therefore, are expected to show a larger deviation between theory and experiment than the frequencies of the second group of modes which essentially depend on the Cu-Se bond-stretching force constant.

Taking into account these trends in the differences between theoretically calculated and experimentally measured mode frequencies of chalcopyrite CuInSe₂ we are now able to analyze the experimental Raman scattering data for the CuAu-ordered phase of the compound.^{28,77} In this structure the lattice vibration spectrum consists of 12 vibrational modes, and the 9 zone-center optical phonon normal modes decompose according to²⁸

$$\Gamma_{\text{opt}} = 1A_1 + 2B_2 + 3E, \quad (3)$$

where all modes are Raman active, and the B_2 and E modes are infrared active. Careful analysis of the spectra recorded under conditions of resonance enhancement of Raman intensities revealed two intense peaks at 186 and 233 cm⁻¹ and four much weaker peaks at 53, 130, 195, and 216 cm⁻¹. The proposed symmetry assignment²⁸ of some of these modes on the basis of polarization dependent measurements alone remained speculative because resonance enhancement is known to break the selection rules valid for nonresonant Raman scattering.⁷⁸ However, in analogy to the results of resonance Raman scattering studies on chalcopyrite compounds^{79,80} it seems justified to suppose that the strong peaks are due to longitudinal modes caused by the strong Fröhlich electron-phonon interaction.⁷⁸ The other peaks are most likely due to transverse optical modes or the only Ra-

TABLE III. Frequencies (in cm⁻¹) of optical modes in CuInSe₂ with CuAu-ordered structure. Two numbers in a row correspond to TO/LO frequencies.

Mode	Theory	Experiment
B_2^1	203/220	216/233
A_1	190	195
E^1	188/200	—/—
E^2	169/177	—/186
B_2^2	129/131	130/—
E^3	53/57	53/—

man active A_1 mode because in this case mode intensity enhancement is due to deformation potential interaction⁷⁸ which has been found to be much weaker or even negligible if compared with the intensity enhancement of longitudinal modes.^{79,80}

Table III displays the result of the theoretical calculations with the modes ordered in a sequence with descending frequency. The symmetry assignment proposed for the optical modes found experimentally is based on the following arguments. The calculated frequency of the B_2^1 mode for the CuAu-ordered structure is only slightly higher than the calculated frequencies of the E^1 and B_2^1 modes in the chalcopyrite phase (Table II). This result suggests the conclusion that, as in the chalcopyrite structure, this mode is dominated by In-Se bond-stretching vibrations with contributions of nearly the same magnitude due to bond-bending forces in both structures. But then, considering the experimental frequencies of the chalcopyrite E^1 and B_2^1 modes (Table II), it is justified to suppose that the strong peak at 233 cm⁻¹ and the much weaker structure at 216 cm⁻¹ are the B_2^1 (LO) and B_2^1 (TO) modes, respectively, of the CuAu-ordered phase. Next we have the fully symmetric A_1 mode which involves only displacements of the anions, with the cations remaining at rest in both structure types. The calculated frequency of this mode in the CuAu-ordered structure (Table III) is 21 cm⁻¹ higher than in the chalcopyrite structure (Table II). Thus, comparing with experiment the most likely candidate for this mode is the weak peak observed at 195 cm⁻¹ which is 19 cm⁻¹ higher than the experimental value of the A_1 mode frequency in chalcopyrite CuInSe₂. Since the main contribution to the frequency of this mode stems from Cu-Se and In-Se nearest neighbor interaction,^{52,76} which should be nearly equal in both structure types, this large frequency shift can only be explained by a larger contribution of the bond bending energy in the CuAu-ordered structure. It is interesting to note that a frequency shift of the A_1 mode of nearly the same magnitude has been observed experimentally and proved theoretically going from the chalcopyrite to the CuAu-ordered phase of CuInS₂.³² The two following modes E^1 and E^2 are both possible candidates for the intense longitudinal mode at 186 cm⁻¹. Taking into account that the calculated frequencies belong to transverse modes and that they probably underestimate the true frequencies by the same amount as in case of the A_1 mode we tend to identify this mode as E^2 (LO). Eventually, the symmetry assignment of

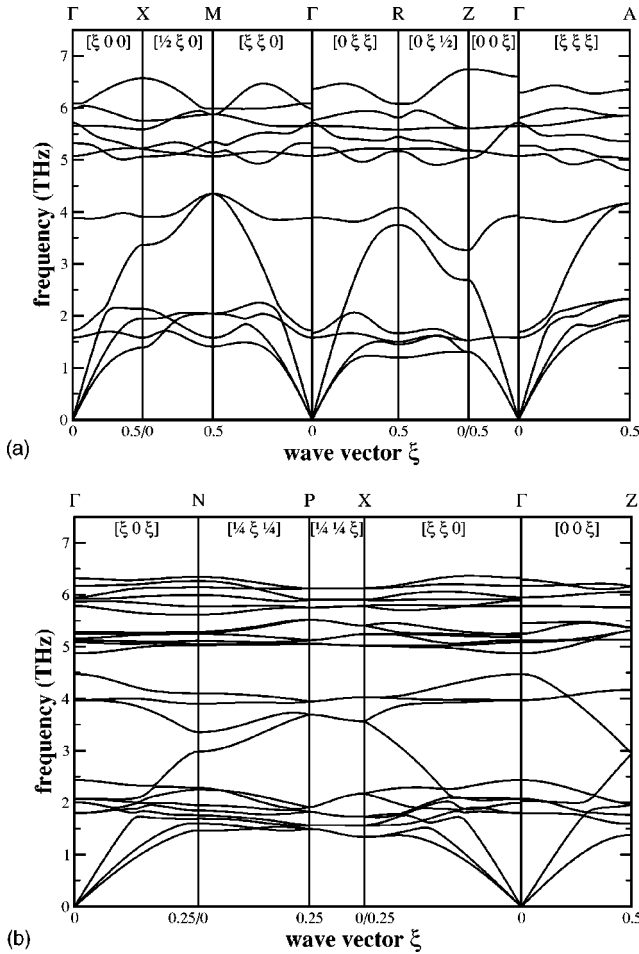


FIG. 2. Calculated phonon dispersion curves for (a) the CuAu-ordered and (b) the chalcopyrite phase of CuInSe_2 .

the two remaining structures at 53 and 130 cm^{-1} is straightforward because calculated and experimental mode frequencies are in surprisingly good agreement, similar to what is found for the low-frequency modes of chalcopyrite CuInSe_2 (Table II).

Comparing the results presented in Tables II and III it is obvious that, except minor differences in the frequencies, all the infrared active modes of the CuAu-ordered phase of CuInSe_2 have counterparts in the chalcopyrite phase. The only exception is the A_1 mode having a distinctly higher frequency in the CuAu-ordered phase. A comparison of the calculated phonon dispersion curves (Fig. 2) shows clearly that this similarity in the lattice vibrational properties of both structure types is not restricted to the zone-center phonons. In both cases there is a band of high-energy vibrational modes in the frequency range from about 5 to about 6.5 THz which is separated from the broad band of low-energy phonons by a gap having a width of about 0.5 THz . The phonon densities of states are nearly identical in both structure types (Fig. 3). Based on these results we come to the conclusion that infrared optical investigations of the lattice vibrations or measurements of material parameters depending on the phonon density of states are unsuited to distinguish between the CuAu-ordered and chalcopyrite phases of

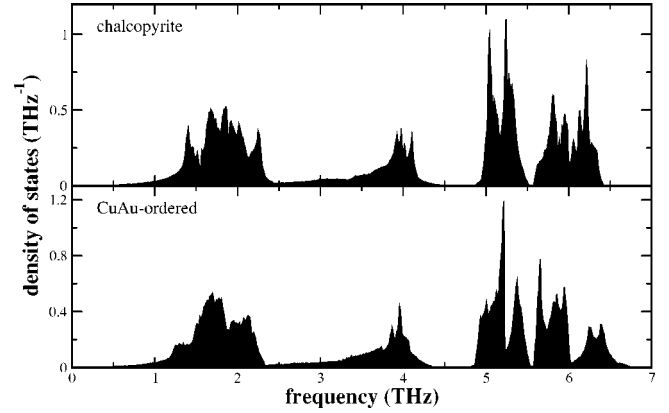


FIG. 3. A comparison of the total phonon density of states calculated for the chalcopyrite and CuAu-ordered phases of CuInSe_2 .

CuInSe_2 . Of the nondestructive optical characterization methods only Raman spectroscopy can be considered as a promising tool in order to detect traces of CuAu-ordered regions in CuInSe_2 bulk single crystals or thin films, either by employing the difference in the frequency of the fully symmetric A_1 mode or by exciting the spectra with photons close to 2.4 eV giving rise to the strong intensity enhancement of the $E(\text{LO})$ mode at 186 cm^{-1} .²⁸

D. Elastic constants

The elastic stiffness constants of chalcopyrite CuInSe_2 determined by inelastic neutron scattering²² are inconsistent with the results of pressure dependent investigations of the structure of the compound²³ and differ also considerably from stiffness constants calculated on a first-principles basis.²⁴ A number of possible reasons for these discrepancies have been discussed,²⁴ among them the existence of orientation domains with CuAu-ordered structure in the chalcopyrite matrix of the compound. To clarify the influence of such domains on the effective average elastic parameters measured experimentally we have calculated the elastic constants for CuInSe_2 with CuAu-ordered structure. The results obtained are compiled in Table IV, together with the experimental and theoretical elastic stiffness constants for the chalcopyrite phase of the compound.

From Table IV it is obvious that the elastic properties of CuAu-ordered CuInSe_2 are distinctly anisotropic, in contrast to the pseudocubic behavior observed for ternary compounds

TABLE IV. Elastic stiffness constants c_{ij} (in GPa) of chalcopyrite and CuAu-ordered CuInSe_2 .

	Chalcopyrite		CuAu-ordered
	experiment (Ref. 22)	theory (Ref. 24)	theory
c_{11}	97.0	71.0	91.8
c_{33}	108.9	63.3	69.7
c_{44}	36.2	45.5	28.2
c_{66}	31.6	47.4	12.3
c_{12}	59.7	45.3	30.5
c_{13}	86.0	45.3	46.1

with chalcopyrite or defect stannite structure having stiffness constant ratios c_{33}/c_{11} , c_{66}/c_{44} , and c_{13}/c_{12} with only small deviations from the ratios $c_{33}/c_{11}=c_{66}/c_{44}=c_{13}/c_{12}=1$ for a cubic lattice.^{24,81,82} This anisotropy is a consequence of the direction dependent cation ordering in the CuAu-ordered structure: cation planes in the [001] direction are alternating Cu and In monolayers whereas the cation planes in the [100] and [010] directions are occupied with equal numbers of Cu and In atoms.^{29,83}

Since the elastic stiffness constants of the CuAu-ordered phase differ from those of the chalcopyrite phase (Table IV) it cannot be excluded that the presence of CuAu-ordered domains leads to some differences between measured and true elastic constants of chalcopyrite CuInSe₂. To estimate the magnitude of this effect it would be necessary to analyze the elastic properties of an elastically and structurally inhomogeneous system consisting of a matrix with chalcopyrite structure and an unknown number of randomly distributed CuAu-ordered domains of varying size and different crystallographic orientation with respect to the host lattice. The presence of CuAu-ordered domains in CuInSe₂ single crystals has been proved only by highly sensitive methods, transmission electron diffraction¹² and, according to our analysis of the low-temperature Raman scattering data of Tanino *et al.*²¹ (Table II), by the occurrence of resonance enhanced but nevertheless rather weak structures in the spectra due to the two high-frequency longitudinal B_2 and E modes of CuAu-ordered CuInSe₂. On the other hand, the additional reflections characteristic of the CuAu-ordered structure²⁸ have never been observed in x-ray diffraction studies of CuInSe₂ crystals.^{45–47} Therefore, it is justified to suppose that the fraction of CuAu-ordered regions in bulk CuInSe₂ is relatively small, certainly below 2%. Consequently, only a very small or, may be, even negligible influence of the CuAu-ordered domains is expected on the measured elastic constants for a crystal with chalcopyrite structure.

III. CONCLUSIONS

We have presented the results of a comparative first-principles calculation of the structure parameters and the lattice dynamical properties for the CuAu-ordered and chalcopyrite phases of CuInSe₂. The frequencies and symmetries of five optical phonon modes are determined for CuInSe₂ with CuAu-ordered structure. Based on the experimental and theoretical results obtained it is shown that some of the inconsistencies in the experimental optical phonon data reported for chalcopyrite CuInSe₂ have their origin in the presence of CuAu-ordered domains in bulk single crystals of the compound. This result finds its explanation in the very small difference between the total energies of both structure types predicted to be below 2 meV at elevated temperatures according to our calculations. The frequency range covered by the zone-center vibrational modes, the phonon dispersion, and the phonon density of states are very similar for both structure types. Furthermore, the frequencies of the infrared modes of the CuAu-ordered phase deviate only slightly from mode frequencies observed for the chalcopyrite phase. The only exception is the fully symmetric A_1 mode having a distinctly higher frequency in CuAu-ordered CuInSe₂. The calculated elastic stiffness constants of the CuAu-ordered phase differ clearly from those calculated for the chalcopyrite phase of the compound, but the presence of CuAu-ordered domains in single crystals with predominant chalcopyrite structure cannot explain existing discrepancies in related experimental data.

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