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Pressure-induced structural and electronic transitions in kesterite-type $\text{Cu}_2\text{ZnSnS}_4$

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We have performed structural investigations of ordered kesterite-type $\text{Cu}_2\text{ZnSnS}_4$ up to 30 GPa. Our current X-ray diffraction results clearly excluded the presence of a kesterite \rightarrow disordered kesterite transition reported previously between 7 and 9 GPa. Nevertheless, specific anomalies connected with the Cu-S bond length of the starting kesterite-type phase are evidenced close to 6 GPa, indicating subtle structural effects at play in this system. Moreover, we have indexed the high-pressure modification of $\text{Cu}_2\text{ZnSnS}_4$ adopted above 16 GPa to a disordered GeSb-type structure, a tetragonally distorted rocksalt-type modification. Full decompression leads to the adoption of a disordered sphalerite/zincblende-type structure. Our complementary density functional theory calculations reproduce accurately the experimental observations and indicate the possibility of a metallic high-pressure GeSb-type phase, unlike the starting semiconducting kesterite-type $\text{Cu}_2\text{ZnSnS}_4$ structure. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5047842>

I. INTRODUCTION

The impending exhaustion of fossil fuel has prompted the exploration and exploitation of alternative energy resources, with the solar energy harvesting through photovoltaic devices spearheading these efforts. In an attempt to overcome the restraints of silicon-based materials, the direct optical bandgap (E_g) of chalcogenide-bearing solar cells offers the benefit of higher absorption in comparison to silicon. Among the various chalcogenide compounds investigated for this purpose, the quaternary semiconductor $\text{Cu}_2\text{ZnSnS}_4$ has attracted considerable attention in recent years.^{1,2} The suitability of this material for solar cell applications stems from its almost optimal bandgap ($E_g \approx 1.5$ eV), its high absorption coefficient in the visible energy range ($\sim 10^4$ cm⁻¹), and its earth-abundant, low-cost, and non-toxic elemental constituents.³⁻⁵ Given the fact that the current power conversion efficiency record for $\text{Cu}_2\text{ZnSnS}_4$ thin films is $\sim 9\%$,⁶ a value which still lies far away from the theoretical limit of $\sim 30\%$,⁷ it becomes clear that further investigations are needed for improving the photovoltaic efficiency of $\text{Cu}_2\text{ZnSnS}_4$.

At ambient conditions, $\text{Cu}_2\text{ZnSnS}_4$ crystallizes in the tetragonal kesterite (KS) structure (space group SG $I\bar{4}$, $Z=2$, Fig. 1).^{8,9} This phase, which is structurally derived from the sphalerite/zincblende (ZB) structure and is therefore closely related to the chalcopyrite- and stannite-type phases by altering the metal/cationic ordering,¹⁰ is composed of alternating Cu/Sn and Cu/Zn layers along the long c -axis interrupted by sulfur anions, with all the Cu, Zn, and Sn cations tetrahedrally coordinated with respect to the S anions

(Fig. 1). Even though the KS phase represents an ordered cationic arrangement, with each cation occupying a unique Wyckoff site, cationic disorder is quite common in this material.^{8,11-15} Such cationic disorder may have notable effects on the photovoltaic properties of $\text{Cu}_2\text{ZnSnS}_4$. For example, one of the most common types of cationic disorder in $\text{Cu}_2\text{ZnSnS}_4$ is the mixed occupancy between the Cu and Zn sites lying in the $z=1/4$ and $z=3/4$ cationic layers, which results in a disordered kesterite configuration (SG $I\bar{4}2m$, $Z=2$, DKS) and a concomitant reduction of the $\text{Cu}_2\text{ZnSnS}_4$ bandgap E_g by 0.1–0.15 eV.^{3,16,17}

Both the sensitivity towards cationic disorder and the inherent anisotropy of the tetragonal $\text{Cu}_2\text{ZnSnS}_4$ KS structure strongly imply that the physical and chemical properties of this material are susceptible to external perturbations such as temperature T and pressure P . Indeed, increasing T leads to a KS \rightarrow DKS transition at ca. 550 K, whereas a DKS \rightarrow disordered ZB-type structural transition has been observed above 1300 K.^{9,18-20} On the other hand, the effect of compression on $\text{Cu}_2\text{ZnSnS}_4$ has been only recently investigated. *Ab initio* theoretical studies showed that the application of compressive (tensile) stress increases (decreases) the bandgap E_g , whereas a transition of the KS phase towards a stannite modification (SG $I\bar{4}2m$, $Z=2$), which exhibits a different stacking of cationic layers along the c -axis compared to the KS phase with alternating layers of tetrahedrally coordinated Zn/Sn and Cu ions, was predicted to take place close to 32 GPa.²¹⁻²³ Subsequent high-pressure X-ray diffraction (XRD) experimental investigations, however, contradicted the predicted KS \rightarrow stannite structural transition. In particular, compression of $\text{Cu}_2\text{ZnSnS}_4$ at ambient temperature led to a KS \rightarrow DKS transition between 7 and 9 GPa, whereas the

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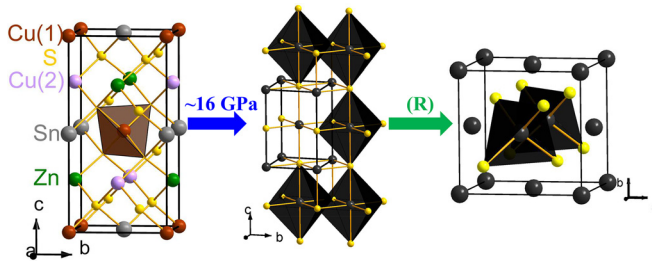


FIG. 1. Structural representations of the ordered ambient-pressure kesterite-type $\text{Cu}_2\text{ZnSnS}_4$ phase (SG $I4$, $Z=2$, left), the high-pressure disordered GeSb-type modification adopted close to 16 GPa (SG $I4/mmm$, $Z=2$, middle), and the disordered sphalerite/zincblende-type polymorph (ZB, SG $F43m$, $Z=4$, right) adopted upon full pressure release (R). The brown, purple, green, gray, and yellow spheres represent Cu(1), Cu(2), Zn, Sn, and S ions, respectively, and the dark spheres in the GeSb-type and ZB-type phases depict the mixed and random Cu/Zn/Sn cationic occupancy. The respective KS \rightarrow GeSb-type transition pressure is also provided (see also Table I).

DKS modification transformed into a disordered rocksalt-type (RS) structure close to 15 GPa; the latter was accompanied by an increase in the respective cationic coordination from fourfold to sixfold.²⁴ An overview of the reported high-pressure $\text{Cu}_2\text{ZnSnS}_4$ modifications is listed in Table I.

Here, we have expanded upon the investigation of the pressure-induced structural response of ordered $\text{Cu}_2\text{ZnSnS}_4$ up to 30 GPa by means of high-pressure XRD measurements. One of the primary motivations was the re-investigation of the aforementioned KS \rightarrow DKS transition between 7 and 9 GPa; given that the previous XRD study was performed with argon serving as a pressure transmitting medium (PTM, Table I), we considered the possibility of non-hydrostatic conditions imposing the KS \rightarrow DKS transition. Hence, we used neon PTM in an XRD run up to 11.4 GPa. In a nutshell, the neon PTM XRD experiments did not show the KS \rightarrow DKS transition; following this result, a second XRD experiment was performed with argon as PTM did not again yield the KS \rightarrow DKS transition. Closer inspection of the collected XRD images indicated an argon-related Debye diffraction ring in the first experiment as the origin behind this discrepancy (Figs. S1 and S2 in the [supplementary material](#)). Moreover, the high-pressure $\text{Cu}_2\text{ZnSnS}_4$ modification stable above 14–16 GPa was assigned to a disordered GeSb-type structure (SG $I4/mmm$, $Z=2$), a tetragonally distorted modification of the previously reported RS-type phase.²⁴ Upon

full decompression, we recovered a disordered ZB-type structure. We have additionally performed density functional theory (DFT) calculations, which reproduced the experimental observations. In addition, the high-pressure GeSb-type phase is predicted to exhibit metallic conductivity, unlike the starting semiconducting KS structure.

II. METHODS

A. Experimental details

The investigated ordered $\text{Cu}_2\text{ZnSnS}_4$ sample was available in polycrystalline powder form. Synthesis and characterization details can be found elsewhere.^{25–27}

Angle-resolved high-pressure XRD measurements were performed at the Extreme Conditions Beamline (ECB) P02.2 of PETRA III (Hamburg, Germany)²⁸ with an incident X-ray wavelength of $\lambda \simeq 0.29 \text{ \AA}$ ($E \simeq 43 \text{ keV}$) and a beam size of $2 \mu\text{m} \times 2 \mu\text{m}$. Two-dimensional XRD patterns were collected with a fast flat panel detector XRD1621 from PerkinElmer (2048 pixels \times 2048 pixels, $200 \times 200 \mu\text{m}^2$ pixel size) and processed with the FIT2D software.²⁹ Refinements were performed using the GSAS+EXPGUI software packages.³⁰

Diamond anvil cells (DACs) equipped with diamonds of $300 \mu\text{m}$ and $400 \mu\text{m}$ culet diameters were used for pressure generation. Rhenium gaskets were preindented to a thickness of $\sim 35 \mu\text{m}$, with holes of $150\text{--}200 \mu\text{m}$ diameters acting as sample chambers. Both neon and argon served as pressure transmitting media (PTM) in separate XRD runs: in the experiment with neon as PTM, XRD was measured between 4.6 and 11.4 GPa, whereas in the experiment with argon as PTM, XRD measurements were performed within the 2.5–30 GPa pressure range. Ruby luminescence (XRD with neon PTM),³¹ the equation of state (EoS) of gold (XRD with argon PTM),^{32,33} and the neon EoS^{34,35} and the argon EoS^{36,37} in the respective XRD experiments were used for pressure calibration. The Birch-Murnaghan equation of state (B-M EoS)^{38,39} was fitted to the pressure-volume P - V data of each $\text{Cu}_2\text{ZnSnS}_4$ phase.

B. Computational details

The periodic density functional theory (DFT) calculations were performed with the Vienna Ab initio Simulation Package (VASP) 5.3.5^{40–43} at the athermal limit. A plane wave basis set with an energy cutoff of 550 eV was used, in

TABLE I. Overview of the reported high-pressure phases of $\text{Cu}_2\text{ZnSnS}_4$. PTM stands for the pressure transmitting medium used in each experiment. Data presented here are shown in grey shadings.

$\text{Cu}_2\text{ZnSnS}_4$ phase	Method	PTM	Pressure stability range ΔP (GPa)
Kesterite-type (KS, SG $I4$, $Z=2$)	Raman and XRD ^a	Argon	<7–9 GPa
Disordered kesterite-type (DKS, SG $I42m$, $Z=2$)	Raman and XRD ^a	Argon	7–9 GPa < P < 15 GPa
Disordered rocksalt-type (RS, SG $Fm\bar{3}m$, $Z=4$)	Raman and XRD ^a	Argon	>15 GPa
Stannite-type (ST, SG $I42m$, $Z=2$)	DFT-PBE ^b	...	>32 GPa
Kesterite-type (KS, SG $I4$, $Z=2$)	XRD	Argon and Neon	<14–16 GPa
Disordered GeSb-type (SG $I4/mmm$, $Z=2$)	XRD	Argon	>14–16 GPa
	DFT-PBE	...	16
Disordered zincblende-type (ZB, SG $F43m$, $Z=4$)	XRD	Argon	Full pressure release

^aLiterature results are from Ref. 24.

^bLiterature results are from Ref. 22.

order for the total energy to converge to the sub-milli-Hartree regime. We used projector-augmented wave (PAW) potentials,^{44,45} whereby the 4s and 3d electrons of Cu and Zn, the 5s, 5p, and 4d electrons of Sn, and the 3s and 3p electrons of S were explicitly considered. The electronic convergence criteria were set at least to 10^{-5} eV, whereby the Blocked-Davidson algorithm was applied as implemented in VASP. The structural relaxation of internal and external lattice parameters was set to a force convergence of 4×10^{-2} eV/Å², performed with the conjugate-gradient algorithm implemented in VASP.⁴⁶ The freedom of spin polarization was enabled, and a Gaussian smearing approach with a smearing factor σ of 0.01 eV was utilized. For all structures, we simulated 16 atoms, which correspond to the number of atoms in the kesterite unit cell (Fig. S3 in the [supplementary material](#)). For the GeSb-type and RS-type structures, we created $1 \times 1 \times 12$ supercells to match the number of atoms of the other structure models. The cells were fully optimized with a $8 \times 8 \times 4$ k-grid constructed via the Monkhorst-Pack scheme⁴⁷ and centered at the Γ -point with the Perdew, Burke, and Ernzerhof (PBE) functional.⁴⁸ The DKS Cu₂ZnSnS₄ phase was treated in the same manner as stated before.¹⁷ On top of the PBE-optimized structures, single point calculations for the bandgap E_g and the electronic density of state (DOS) with the Heyd-Scuseria-Ernzerhof HSE06-functional^{49–52} were performed with a $4 \times 4 \times 2$ k-grid to account for an accurate electronic structure (Fig. S4 in the [supplementary material](#)). For systems with a finite bandgap, the tetrahedron method with Blöchl corrections⁵³ was applied for the band structure evaluation.

The pressure dependence was determined by selecting volume points in a range of about ± 100 Å³ around the minima. This corresponds to a pressure range of 0–100 GPa. We used a step size of 8 Å³ which led to 23 (KS and DKS) and 24 (GeSb-type) volume points, respectively. At each volume point, we optimized the cell shape and the atomic positions. We fitted the B-M EoS function^{38,39} to the total energy as a function of volume for each Cu₂ZnSnS₄ phase. Then, the pressure of each volume was obtained from the $P(V)$ formulation of the same B-M EoS (Fig. S5 in the [supplementary material](#)).

III. RESULTS AND DISCUSSION

A. Structural compression of Cu₂ZnSnS₄ up to 14 GPa: KS \rightarrow DKS transition?

A former investigation showed that KS-type Cu₂ZnSnS₄ undergoes a structural transition into a DKS modification between 7 and 9 GPa.²⁴ This transformation was evidenced by a kink in the pressure-induced evolution of the c -axis between 7 and 9 GPa, whereas the a -axis became almost incompressible after the transition. In order to verify the aforementioned transition, we performed two separate high-pressure XRD experiments with neon and argon serving as PTM up to ~ 11 GPa and ~ 14 GPa, respectively.

In Fig. 2, we show selected XRD patterns collected with Ne as PTM and the pressure-induced evolution of the Cu₂ZnSnS₄ tetragonal a and c lattice parameters from all the different high-pressure XRD experiments. Before proceeding

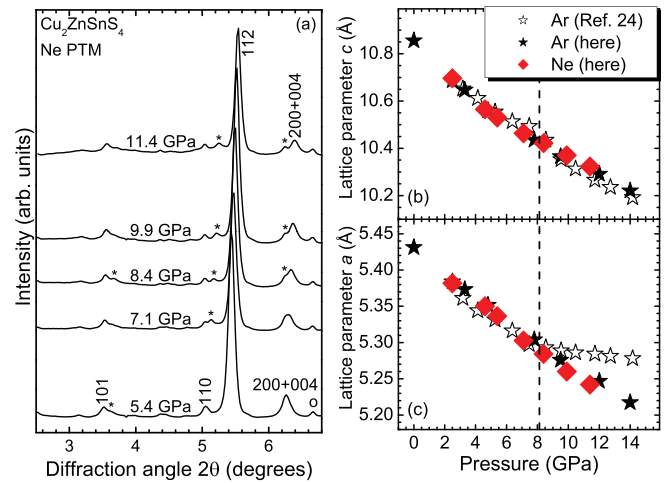


FIG. 2. (a) Enhanced view of the Cu₂ZnSnS₄ XRD patterns within the 2.5°–6.5° 2θ diffraction angle range, collected with Ne as PTM ($\lambda = 0.2910$ Å). The background has been subtracted with the help of Chebyshev polynomial functions. The hkl Miller indices for specific KS Bragg peaks are shown. Asterisks mark the strongest Cu₂S impurity Bragg peaks (see the text). (b) Plot of the Cu₂ZnSnS₄ a and c axes as a function of pressure for different high-pressure XRD runs. The vertical dashed line represents the KS \rightarrow DKS transition pressure reported before.²⁴ Error bars are smaller than the symbol size. Asterisks and the circle mark the strongest Cu₂S impurity and ruby Bragg peaks, respectively.

further, we should note the following: (a) the Cu₂ZnSnS₄ sample contains a small fraction of Cu₂S impurity (SG $P2_1/c$, $Z = 48$),^{54,55} estimated close to $\sim 3\%$ – 5% from the relative Bragg peak intensity ratio at ambient conditions;²⁴ the presence of this Cu₂S impurity phase appears to be a common byproduct of Cu₂ZnSnS₄ synthesis.¹⁵ (b) Cu₂S is known to undergo two structural transitions at 3.2 GPa and 7.4 GPa towards two different monoclinic phases (and one additional structural transition into an unidentified phase at 26 GPa);⁵⁶ the 7.4 GPa Cu₂S transition is also observed in our 7.1 GPa XRD pattern with neon PTM (denoted as asterisks in Fig. 2).

Direct comparison of the pressure-induced evolution of the Cu₂ZnSnS₄ tetragonal lattice parameters reveals that in the present experiments, with either argon or neon serving as PTM, there are no visible anomalies in the lattice parameters. This observation is in contrast to the previous argon PTM XRD data (Fig. 2). A careful comparison of the measured Debye-Scherrer rings between the former and current high-pressure XRD runs with argon PTM reveals that the inconsistency between the XRD experiments arose due to the incorrect assignment of the Bragg peaks located at 6°–6.8° in the previous argon PTM XRD experiment. In particular, the former argon PTM XRD study recorded two separate Bragg peaks within the 6°–6.8° 2θ region, where the 200 and 004 KS Bragg peaks are expected. Consequently, these two Bragg features were assigned to the 200 and 004 KS Bragg peaks. Considering the newer argon and neon PTM XRD experiments presented here, we could conclude that one of these Bragg peaks was actually originating from the 111 Bragg peak of the argon PTM.³⁷ This misinterpretation of the collected XRD data led to the observed incompressibility of the a -crystallographic axis in the first argon XRD experiment and the basic argument behind the KS \rightarrow DKS transition in Cu₂ZnSnS₄ (Fig. 2). A direct

comparison between the Debye-Scherrer rings and the respective integrated XRD diffractograms of the various XRD experiments at 12 GPa are provided in Figs. S1 and S2 in the [supplementary material](#).

Despite the apparent absence of a “clear” KS \rightarrow DKS transition in $\text{Cu}_2\text{ZnSnS}_4$, a more accurate way to identify subtle anomalies in the structural parameters under pressure is through the plotting of the normalized stress F as a function of the Eulerian strain f_E .⁵⁷ Generally, the F - f_E parameters should exhibit a linear relationship, with any divergence from a linear trend hinting potential structural changes.⁵⁸ Such a deviation was, e.g., observed in the previous report on the KS \rightarrow DKS transition in $\text{Cu}_2\text{ZnSnS}_4$ between 7 and 9 GPa.²⁴ The relevant F - f_E plots for the volume V (F_V - f_{EV}) and for the tetragonal $\text{Cu}_2\text{ZnSnS}_4$ a (F_a - f_{Ea}) and c (F_c - f_{Ec}) lattice parameters obtained from both the argon and neon PTM XRD experiments here are shown in Fig. 3. From these plots, we can immediately observe a break in both the F - f_E plots of the a - and c -axes taking place close to 6 GPa; on the

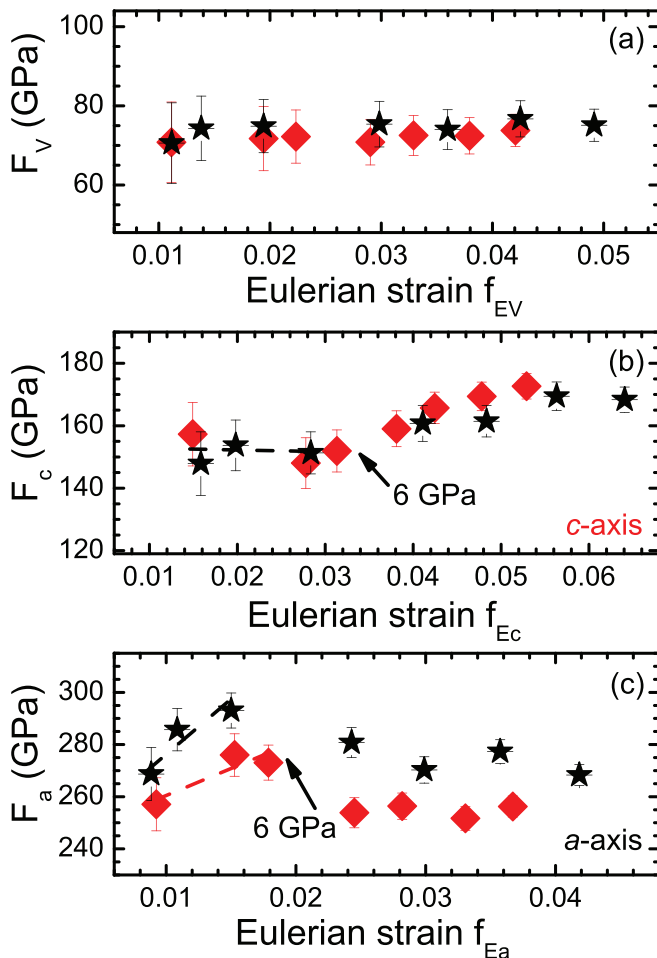


FIG. 3. Plot of the normalized stress F as a function of the Eulerian strain f_E for (a) the volume V and (b) the c - and (c) a -axes for the KS tetragonal $\text{Cu}_2\text{ZnSnS}_4$ phase. The argon and neon PTM XRD data are shown as black star and red rhombic symbols, respectively. The F - f_E quantities for the volume are calculated from the structural data (Fig. 2) as follows: $f_{EV} = [(V_0/V)^{2/3} - 1]/2$ and $F_V = P/3f_{EV} (1 + 2f_{EV})^{5/2}$, where V_0 is the ambient-pressure volume of the KS phase, V is the volume, and P is the pressure (in GPa).⁵⁷ For the lattice parameters: $f_{Ea} = [(a_0/a)^2 - 1]/2$ and $F_a = P(ac_0/a_0c)^{2/3} / f_{Ea}(1 + 2f_{EV})^{5/2}$ for the a -axis and $f_{Ec} = [(c_0/c)^2 - 1]/2$ and $F_c = P(a_0c/ac_0)^{4/3} / f_{Ec}(1 + 2f_{EV})^{5/2}$ for the c -axis.⁵⁹

other hand, no effect can be seen in the respective F - f_E volume plots for either PTM XRD run [Fig. 3(c)]. We attribute these F - f_E anomalies close to 6 GPa to a subtle pressure-induced change in the compressibility mechanism/behavior of the KS $\text{Cu}_2\text{ZnSnS}_4$ structure.

More information on this pressure-induced structural effect observed in the KS $\text{Cu}_2\text{ZnSnS}_4$ structure close to 6 GPa can be obtained from the pressure-induced evolution of the relevant interatomic parameters. In the KS structure, the metal cations are located in special Wyckoff positions, with the Cu(1), Cu(2), Zn, and Sn cations occupying the 2a (0, 0, 0), 2c (0, 0.5, 0.25), 2d (0, 0.5, 0.75), and 2b (0, 0, 0.5) sites, respectively.^{9,26,60} On the other hand, the S anion resides in the general Wyckoff position 8g (x, y, z), with the S- x , S- y , and S- z atomic coordinates free to vary upon the increase in pressure. This variation is depicted in Fig. 4. We can readily observe a change in the pressure-slopes of the S- x and S- y coordinates around 6 GPa, in excellent agreement with the F - f_E anomalies (Fig. 3). This is also reflected in the pressure dependence of the Cu(1)-S interatomic bond length (Fig. 4).

In order to check for a possible pressure-induced KS \rightarrow DKS transition in $\text{Cu}_2\text{ZnSnS}_4$ as the origin behind these anomalies, as speculated previously,²⁴ we have calculated the respective enthalpy difference between the KS and DKS

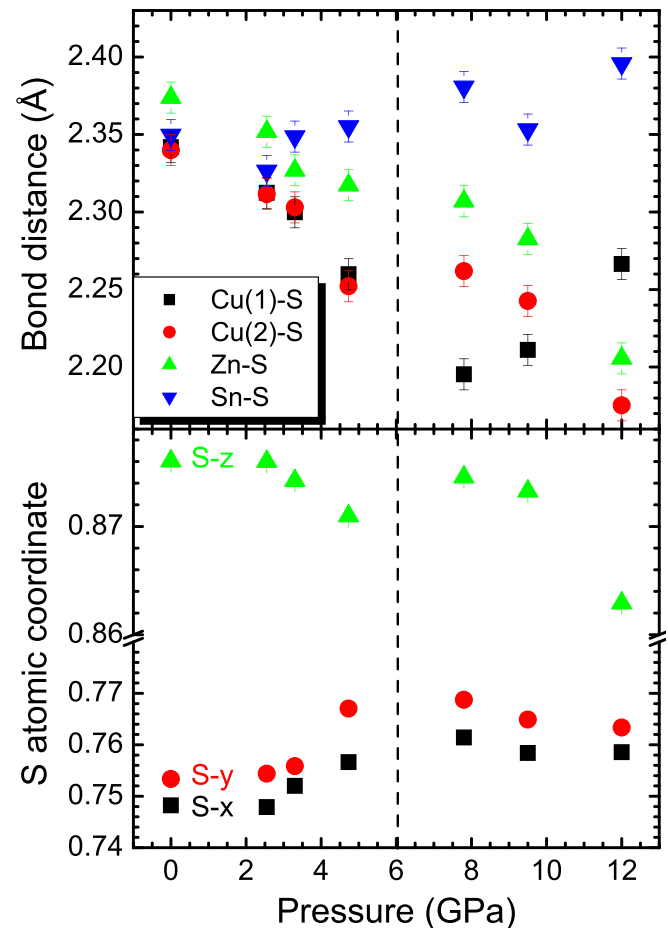


FIG. 4. Plot of the S atomic coordinates (bottom) and selected interatomic bond lengths (top) as a function of pressure for the KS $\text{Cu}_2\text{ZnSnS}_4$ phase, as extracted from the XRD measurements. The vertical dashed line depicts the onset of the pressure-induced changes (see the text).

$\text{Cu}_2\text{ZnSnS}_4$ phases by means of DFT. The results are displayed collectively in Fig. 5. As we can observe, the DKS phase *always* lies higher than the KS structure enthalpy-wise for all pressures investigated here. We remind here that the main structural difference between the tetragonal KS and DKS structures is the mixed occupancy between the Cu and Zn sites lying in the $z=1/4$ and $z=3/4$ cationic layers of DKS, which in turn is manifested as an expansion of the long c -axis.¹⁷ Considering that such a change is not supported by the present high-pressure XRD results (Fig. 2), as well as the finite KS and DKS enthalpy difference, we can safely conclude at this stage that the experimentally observed changes in the $F-f_E$ (Fig. 3) and interatomic parameters' pressure-induced evolution (Fig. 4) are most likely not originating from a KS \rightarrow DKS transition. Hence, which effects can account for these anomalies?

Before offering any reasoning, we should remind here that in the previous high-pressure Raman spectroscopic measurements on $\text{Cu}_2\text{ZnSnS}_4$ conducted with argon PTM, the emergence of a new D band at 335 cm^{-1} was detected at 1.2 GPa already,²⁴ far below the pressure-related subtle structural effects observed here (Figs. 3 and 4). This D band lies $\sim 3\text{ cm}^{-1}$ lower in terms of the Raman frequency shift compared to the most intense A band of the KS phase at 338 cm^{-1} (zero-pressure value); the latter is assigned to the sulfur S-S stretching vibrations along the KS c -axis (the metal cations are not involved in this vibration).^{61,62} Upon

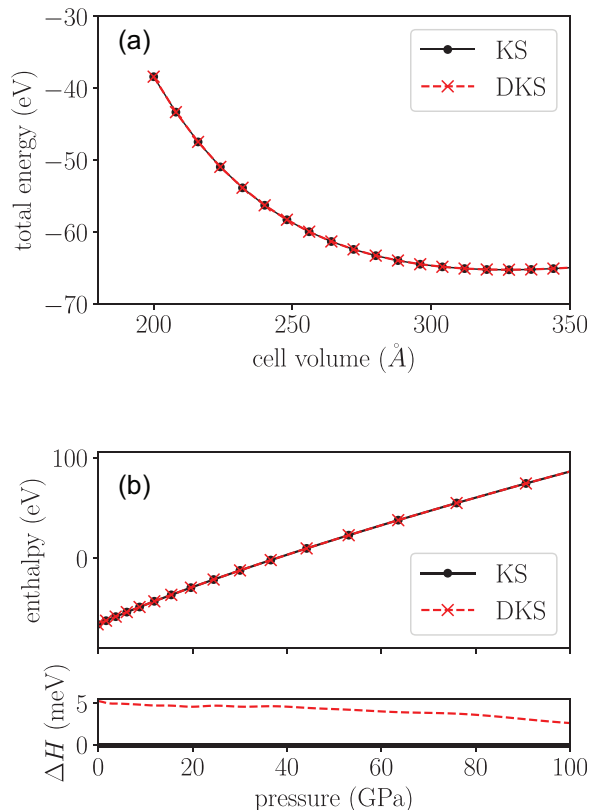


FIG. 5. (a) Volume-energy V - E plot for the KS (black circles) and DKS (red crosses) phases. (b) The calculated enthalpies of the KS and DKS phases as a function of pressure and the respective KS and DKS enthalpy difference ΔH with respect to pressure. Enthalpy H is defined as $H(P) = E + PV$, and a phase is stable if it has a lower value of H .

the increase in pressure, this D Raman feature becomes dominant intensity-wise at the expense of the KS A mode in the $\text{Cu}_2\text{ZnSnS}_4$ Raman spectra close to 9 GPa, whereas their $\sim 3\text{ cm}^{-1}$ frequency difference persisted throughout the investigated pressure range.²⁴

This D band has been commonly associated with the well-documented Cu-Zn anti-site cationic exchange in KS $\text{Cu}_2\text{ZnSnS}_4$,^{11,20,63} the presence of a stannite $\text{Cu}_2\text{ZnSnS}_4$ component,⁶⁴ or arising due to phonon confinement effects.⁶⁵ Among these possibilities, we can probably exclude the phonon confinement scenario due to the μm grain size of the investigated $\text{Cu}_2\text{ZnSnS}_4$ polycrystalline samples, as this model applies in nanocrystalline materials.⁶⁵ Moreover, the presence of a ST $\text{Cu}_2\text{ZnSnS}_4$ modification under these pressure conditions can also be excluded according to our DFT-PBE enthalpy calculations (Fig. S6 in the [supplementary material](#)). As for the Cu-Zn anti-site exchange possibility, given our aforementioned discussion, we can most likely exclude this scenario as well. The intensity-wise dominance of the D Raman band compared to the KS A mode above 9 GPa implies the existence of an almost fully (or at least partially) disordered $\text{Cu}_2\text{ZnSnS}_4$ phase, leading in turn to the adoption of a DKS phase. Such a type of disorder, however, should also be captured in the interatomic bond lengths to some extent since (a) the Cu-S and Zn-S bond distances are distinctly different in terms of values and (b) a pressure-induced averaging of these bond lengths due to the Cu-Zn anti-site exchange should yield characteristic changes in the respective interatomic bond distances;¹⁷ this picture cannot be verified unambiguously in our case, mainly due to the absence of any visible Zn-S bond-related anomalies (Fig. 4). Our XRD data clearly show that the anomalies are mainly related to the Cu(1)-S bond (Fig. 4). Regarding other well-documented intrinsic defect complexes in $\text{Cu}_2\text{ZnSnS}_4$, none is limited to the Cu(1) sites.^{15,66} Hence, we tend to exclude any type of pressure-induced cationic disorder or vacancy formation triggering either the presence and intensity enhancement of the Raman D band or the $F-f_E$ and Cu-S anomalies in KS $\text{Cu}_2\text{ZnSnS}_4$ (Figs. 3 and 4).

Regarding the former, we should remind here that B and E symmetry Raman-active modes may be present in the vicinity of the 338 cm^{-1} KS A mode.⁶¹⁻⁶⁴ The exact positions of these Raman-active vibrations may vary depending on the $\text{Cu}_2\text{ZnSnS}_4$ sample preparation method.⁶¹⁻⁶⁴ Hence, a simple explanation behind the presence of the Raman D band (even at low pressures) might be that it actually corresponds to a different B/E KS vibration, which becomes detectable in the $\text{Cu}_2\text{ZnSnS}_4$ Raman spectra upon moderate compression. The pressure-induced intensity enhancement of the D band on the other hand²⁴ may be connected with an increasing electronic polarizability of this mode compared to its adjacent A KS Raman peak under compression.

Another scenario accounting for both the observed $F-f_E$ and Cu-S anomalies, as well as the intensity enhancement of the Raman D band, might be that all these effects reflect pressure-induced electronic changes in $\text{Cu}_2\text{ZnSnS}_4$, e.g., a topological transition of the Cu-related electronic DOS under moderate compression. Such pressure-induced electronic topological transitions constitute a common motif for layered

materials and are evidenced by distinct compressibility and Raman intensity changes, without any alteration of the (average) crystalline symmetry.^{58,67–69} A thorough investigation of such a possibility, however, lies beyond the scope of the present paper.

B. Structural compression of $\text{Cu}_2\text{ZnSnS}_4$ up to 30 GPa with argon PTM

We turn now to the $\text{Cu}_2\text{ZnSnS}_4$ structural transition reported close to 15 GPa towards a disordered RS-type modification (Table I), where all the metal cations exhibit random/mixed occupancy of the cationic site.²⁴ The previous investigation was conducted up to ~ 18 GPa, with argon serving as PTM; here, we have expanded upon the previous high-pressure studies up to 30 GPa, again with argon as PTM for consistency.

The results are presented in Fig. 6. We can observe that the KS phase persists up to ~ 14 GPa; at this pressure, several new Bragg peaks appear in the XRD patterns, signifying a structural transition. The transition is completed at 15.8 GPa, in excellent agreement with the previous result.²⁴ The analysis of the measured XRD patterns reveals that the RS-type phase could reproduce the XRD diffractogram measured at 15.8 GPa; the following XRD pattern collected at 18.5 GPa, however, could not be fitted with the cubic RS-type structure satisfactorily. This prompted us to use a tetragonally distorted RS-type modification, noted here as the GeSb-type (SG $I4/mmm$, $Z=2$),⁷⁰ which resulted in a significantly improved XRD refinement (Fig. 6). We should point out here that the reason behind this unsuccessful RS-type structure indexing attempt involves the pressure-induced

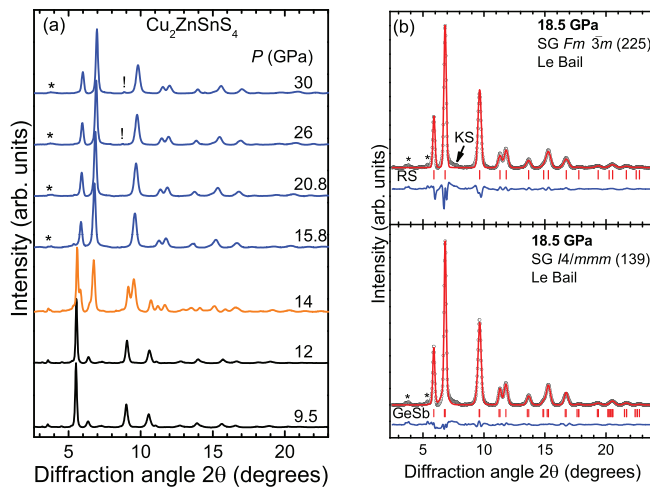


FIG. 6. (a) Selected XRD patterns of $\text{Cu}_2\text{ZnSnS}_4$ at various pressures with Ar PTM ($\lambda = 0.2913 \text{ \AA}$). The black, orange, and blue patterns indicate the KS, KS/GeSb coexistence, and GeSb-type phases, respectively (see the text). The background has been subtracted for clarity with Chebyshev polynomial functions. Asterisks and exclamation marks indicate the strongest Bragg peaks of the Cu_2S impurity phase and the argon PTM,^{36,37} respectively. (b) Examples of Le Bail refinements at 18.5 GPa, using both the RS-type (top) and the tetragonally distorted GeSb-type (bottom) modifications. The black circles and the red solid curves correspond to the measured and the calculated patterns, whereas their difference is depicted as blue curves. The starting structural parameters are taken from Ref. 24 (RS-type) and Ref. 70 (GeSb-type). The arrow indicates the KS phase residue, and asterisks mark the strongest Bragg peaks of the Cu_2S impurity.

evolution of the recorded Bragg peak positions, which do not follow the cubic RS-type structural trend (for more details, see Fig. S7 in the [supplementary material](#)).

Therefore, $\text{Cu}_2\text{ZnSnS}_4$ apparently adopts another disordered GeSb-type structure above ~ 18 GPa, again with a mixed/random occupancy of the cationic site by the Cu/Zn/Sn ions. This phase persists up to 30 GPa, where the highest pressure reached. A reasonable question which arises, however, is the following: does $\text{Cu}_2\text{ZnSnS}_4$ adopt the RS-type modification within a limited pressure range, i.e., between 15 and 18 GPa, or is the GeSb-type phase adopted from 15 GPa already? Considering the relevant theoretical results at our disposal, we tend to favor the second scenario. We will return to this point later below.

In Fig. 7, we plot the extracted structural parameters for the various phases of $\text{Cu}_2\text{ZnSnS}_4$ obtained with argon PTM (this run alone). As we can observe, the KS \rightarrow GeSb-type structural transition is accompanied by a $\sim 15\%$ volume change at the transition point. The latter volume drop results from the increase in the cationic coordination with respect to the S^{2-} anions from four to six (Fig. 1). The B-M EoS fitting results of the P - V data are listed in Table II.

In order to acquire certain insights into the aforementioned pressure-induced KS \rightarrow GeSb-type structural transition in $\text{Cu}_2\text{ZnSnS}_4$, we have calculated the enthalpies ($H(P) = E + PV$) for the starting KS phase and the disordered GeSb-type modification (Fig. 8). Additionally, we have calculated the enthalpies of several reported $\text{Cu}_2\text{ZnSnS}_4$ polymorphs, such as a modified wurtzite-type phase (WZ, SG $P2_1$), the aforementioned DKS modification (SG $P4$), the stannite-type structure (ST, SG $I42m$), and the primitive mixed Cu-Au phase (PMCA, SG $P42m$) (Fig. S6 in the [supplementary material](#)). As we can observe from the relative enthalpy difference between the KS and GeSb-type phases, the transition is predicted to take place at 16 GPa, in excellent agreement with the experimental transition pressure value between 14 and 16 GPa (Fig. 7). The respective lattice parameters and volumes for the KS and GeSb-type

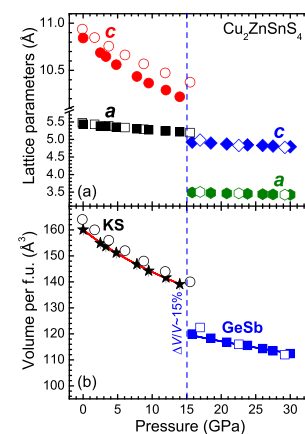


FIG. 7. Pressure-induced variation of the (a) lattice parameters and (b) volume per formula unit (f. u.) for the various phases of $\text{Cu}_2\text{ZnSnS}_4$ with argon serving as PTM. The solid curves through the P - V data correspond to fitted B-M EoS functions.^{38,39} The closed and open symbols correspond to experimental and DFT-PBE calculated data, respectively. The vertical dashed lines depict the onset of the KS \rightarrow GeSb-type structural transition. Error bars are smaller than the symbols.

TABLE II. Volume per formula unit $V/f.u.$, bulk modulus B , and bulk modulus pressure derivative B' for the various phases of $\text{Cu}_2\text{ZnSnS}_4$ at the respective reference pressure P , as obtained by Birch-Murnaghan EoS functions^{38,39} fitted to our measured and computed P - V data. The term “fixed” means that the corresponding parameters were not allowed to vary during the EoS fitting (N/A: not available).

$\text{Cu}_2\text{ZnSnS}_4$ phase	Method	P (GPa)	$V/f.u.$ (\AA^3)	B (GPa)	B' (GPa)
$\bar{1}\bar{4}$ (KS)	EXP	0.0	160.1 (fixed)	74(2)	4.4(4)
	GGA-PBE	0.0	163.75	68.64	4.64
	LDA ^a	0.0	150.7	89.4	N/A
	GGA ^b	0.0	164.61	63.94	N/A
$I4/mmm$ (GeSb-type)	EXP	15.8	119.4 (fixed)	213(4)	4.0 (fixed)
	GGA-PBE	16	120.75	298.53	2.03

^aOther results are from Ref. 61.

^bOther results are from Ref. 22.

$\text{Cu}_2\text{ZnSnS}_4$ structures are plotted alongside their experimental counterparts in Fig. 7. Generally, we can observe a very good agreement, with the exception of the KS c -axis, which is overestimated within the DFT-PBE approximation.⁷¹ We note that in our calculations performed up to 100 GPa, we could not observe a transition from the KS phase towards a stannite structure, or any of the other examined phases

(Fig. S6 in the [supplementary material](#)), in contrast to Zhao *et al.*²² The respective calculated volumes, bulk moduli, and bulk moduli derivatives for the KS and GeSb-type phases at the respective reference pressures P are listed in Table II.

Finally, upon full decompression, the GeSb-type structure transforms into a disordered sphalerite-type (ZB-type) phase (Figs. 1 and S8 in the [supplementary material](#)). This back-transformation indicates that even though the pressure-induced cationic coordination increase from four to six is reversible in $\text{Cu}_2\text{ZnSnS}_4$, the cationic disordering of the structure, i.e., the random occupation of the various Wyckoff sites by the Cu, Zn, and Sn constituent metals, can be quenched back to ambient pressure. This aspect of metastable structural disorder upon decompression appears to be a common trend among the relevant ternary chalcopyrite-type compounds.^{72–76} The adoption of a disordered ZB-type structure upon decompression is also consistent with the relevant Raman spectra collected upon decompression in the previous high-pressure Raman study conducted with argon PTM.²⁴ In particular, the Raman response of the recovered $\text{Cu}_2\text{ZnSnS}_4$ phase indicated strong signs of structural disorder, i.e., broad Raman features, whereas the Raman spectrum was reminiscent of the starting tetrahedrally coordinated KS phase, with two broad Raman bands located at $\sim 270 \text{ cm}^{-1}$ and at 330 cm^{-1} (the KS Raman spectrum is characterized by two intense Raman peaks at $\sim 291 \text{ cm}^{-1}$ and at 338 cm^{-1} at ambient conditions; see Fig. 2 in Ref. 24). This frequency downshift of the most significant Raman features in the ZB-type phase compared to the KS structure can be related to the cationic disorder present in the former phase. All in all, these Raman-related observations fully agree with the current XRD results.

C. Electronic properties of $\text{Cu}_2\text{ZnSnS}_4$ under pressure

We turn now to the calculated electronic DOS for the KS and GeSb-type $\text{Cu}_2\text{ZnSnS}_4$ structures (Fig. 9). As we can observe, the KS band structure below the Fermi level E_F is mainly dominated by the occupied Cu 3d and S 2p states, whereas the unoccupied S 3p and Sn 5p levels contribute mainly to the DOS above E_F . The calculated bandgap E_g of the KS phase is 1.18 eV at ambient pressure, in very good agreement with previous calculations^{23,77,78} and experimental results.^{1,79,80} The KS E_g value increases upon compression and reaches a value close to 2 eV at the KS \rightarrow GeSb-type (calculated) structural transition pressure of 16 GPa; this pressure-induced E_g shift is consistent with previous works.^{23,81}

Upon adopting the GeSb-type phase, the $\text{Cu}_2\text{ZnSnS}_4$ DOS changes drastically. In particular, the calculated electronic band structure reveals the presence of electronic states around E_F , thus indicating that the GeSb-type modification of $\text{Cu}_2\text{ZnSnS}_4$ shows metallic conductivity (Fig. 9). Given that pressure-induced structural transitions of binary and ternary compounds, which involve the cationic coordination increase from fourfold to sixfold, tend to exhibit concomitant insulator-to-metal transitions,⁸² our finding is in line with the established pressure-induced structural and electronic trends.

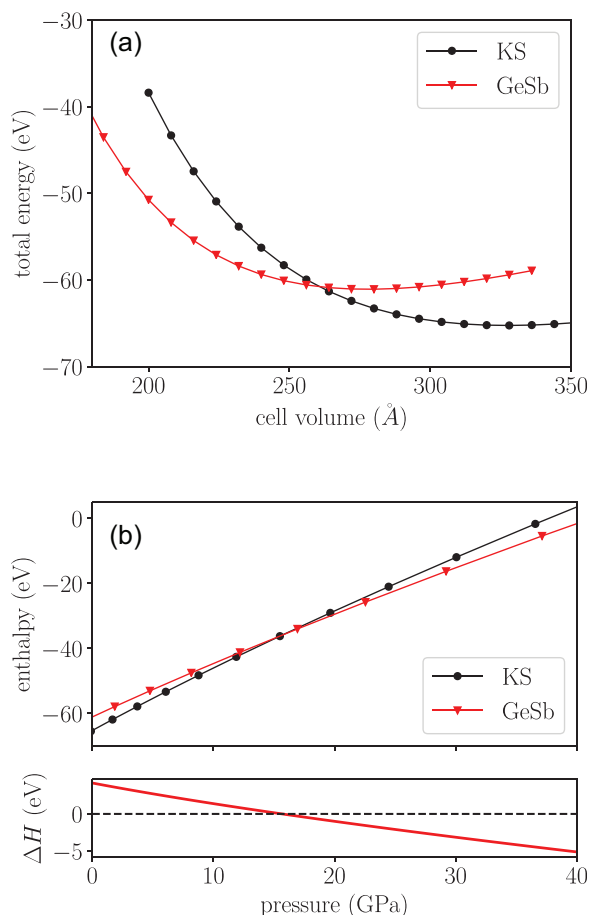


FIG. 8. (a) Volume-energy V - E plot for the KS (black circles) and GeSb-type (red triangles) phases. (b) Top panel: The calculated enthalpies of the KS and GeSb-type phases as a function of pressure. Bottom panel: The enthalpy difference between the KS and GeSb-type phases with respect to pressure. The enthalpy H is defined as $H(P) = E + PV$, and a phase is stable if it has a lower value of H .

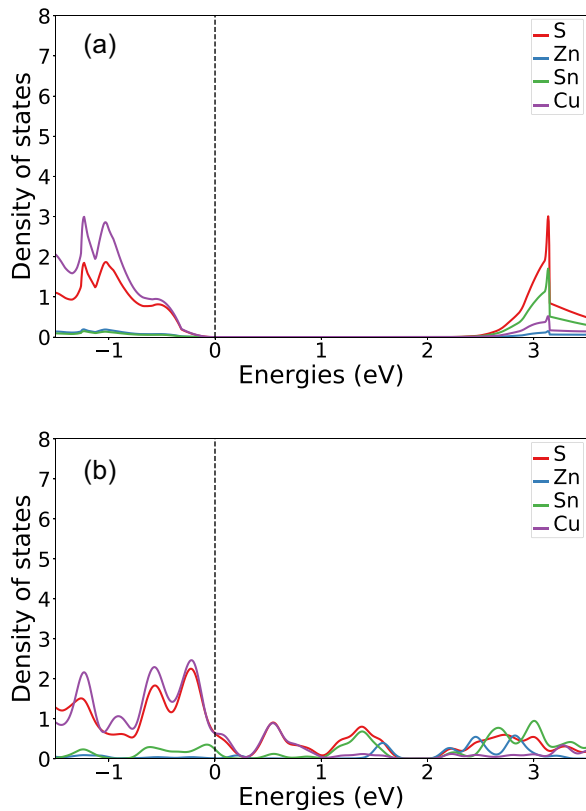


FIG. 9. DFT-HSE06 calculated density of states (DOS) for the $\text{Cu}_2\text{ZnSnS}_4$ (a) KS and (b) GeSb-type phases, both at the transition pressure of 16 GPa. The Fermi level E_F is set at zero.

D. Discussion

The disordered GeSb-type high-pressure modification of $\text{Cu}_2\text{ZnSnS}_4$ was shown to better index the experimental XRD diffractograms above 18 GPa, compared to the previously assigned disordered RS-type structure adopted at ~ 15 GPa (Ref. 24) (Fig. 6 and Fig. S7 in the [supplementary material](#)). Since the Le Bail refinements of the XRD patterns with either the RS-type or the GeSb-type structural models yield identical results within the 15–18 GPa pressure range, a clear conclusion over the exact pressure-induced structural path of $\text{Cu}_2\text{ZnSnS}_4$ cannot be drawn. For this reason, we turn to our DFT-PBE results. In Fig. 10, we plot the calculated

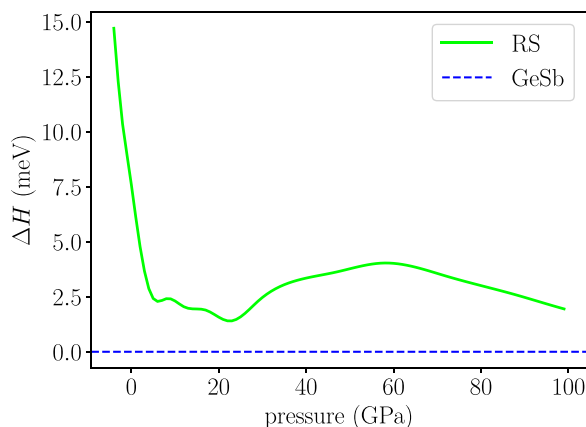


FIG. 10. Enthalpy difference between the RS-type and GeSb-type $\text{Cu}_2\text{ZnSnS}_4$ polymorphs with respect to pressure at 0 K.

enthalpy difference of the RS-type and GeSb-type $\text{Cu}_2\text{ZnSnS}_4$ modifications as a function of pressure. We can observe that the RS-type structure lies *always* higher than the GeSb-type one in terms of enthalpy for all the investigated pressures. Hence, our DFT-PBE results favor the existence of the GeSb-type phase as the high-pressure modification of $\text{Cu}_2\text{ZnSnS}_4$. Considering also that the high-pressure Raman spectra reported previously do not show any appreciable changes within the 15–18 GPa pressure range,²⁴ we conclude that the disordered tetragonal GeSb-type phase is the proper choice for describing the high-pressure structure of $\text{Cu}_2\text{ZnSnS}_4$ modification above 16 GPa (Fig. 6).

Since the KS phase is structurally related to the chalcopyrite structure, a comparison between the high-pressure behavior of these relevant chalcopyrite-type systems with $\text{Cu}_2\text{ZnSnS}_4$ is in order. Regarding the former, both the ternary chalcopyrite-type ABX_2 (SG $I\bar{4}2d$) and defect chalcopyrite AB_2X_4 (SG $I\bar{4}$) compounds exhibit similar structural and electronic trends. In particular, structural transitions from the starting tetragonal phases towards disordered RS-type structures have been reported for several chalcopyrite-based materials of varying chemical compositions.^{72–76,83–87} All these transitions are accompanied by electronic changes towards metallic states. Another interesting structural aspect is the fact that decompression does not lead to the recovery of either the starting chalcopyrite-type or the high-pressure RS-type modifications in these materials but rather towards disordered ZB-type phases.^{72–76}

Within this framework, the reported high-pressure behavior of KS $\text{Cu}_2\text{ZnSnS}_4$ (i.e., the KS \rightarrow disordered GeSb-type transition and the adoption of a disordered ZB-type modification upon decompression) is in agreement with the generic high-pressure structural and electronic trends of the structurally related chalcopyrite-type compounds.

IV. CONCLUSIONS

We have investigated the high-pressure structural and electronic properties of kesterite-type $\text{Cu}_2\text{ZnSnS}_4$, with a combination of XRD and first-principles methods. Our investigations indicate that the previously reported kesterite \rightarrow disordered kesterite structural transition between 7 and 9 GPa (Ref. 24) originated from the misinterpretation of specific XRD features. Nevertheless, subtle pressure-induced changes in the compressibility mechanism/behavior indeed take place in kesterite-type $\text{Cu}_2\text{ZnSnS}_4$ close to 6 GPa, as evidenced by distinct anomalies in the $F-f_E$ plots and in the pressure-induced evolution of the Cu(1)-S bond length, but without any change in the average crystalline symmetry; the exact origin of these subtle changes is unclear at this stage.

A further pressure increase to 16 GPa led to a transition towards a disordered GeSb-type polymorph with tetragonal symmetry. The cationic coordination increases from four to six upon the kesterite \rightarrow disordered GeSb-type transition. Our DFT-PBE calculations reproduced the experimental observations accurately, as (a) no sign of kesterite \rightarrow disordered kesterite transition was found and (b) the kesterite \rightarrow disordered GeSb-type transition was calculated to take place at 16 GPa. In addition, band structure calculations

revealed that the kesterite \rightarrow disordered GeSb-type structural transition is accompanied by a semiconductor-to-metal transition, in agreement with the available results on structurally similar materials.^{73,82} Finally, full decompression resulted in the adoption of a disordered sphalerite/zincblende structure, where the tetrahedrally coordinated cations retain mixed/random occupancies.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for relevant high-pressure XRD data, as well as for more details on our calculations (structures, band gaps, and P-V data).

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