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## **Influence of cationic ordering on the lattice dynamics of monoclinic $\text{Cu}_5\text{Sn}_2\text{S}_7$ and cubic $\text{Cu}_5\text{Sn}_2\text{S}_6.65\text{Cl}_{0.35}$ sulfides**

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# Influence of Cationic Ordering on the Lattice Dynamics of Monoclinic $\text{Cu}_5\text{Sn}_2\text{S}_7$ and Cubic $\text{Cu}_5\text{Sn}_2\text{S}_{6.65}\text{Cl}_{0.35}$ Sulfides

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**ABSTRACT:**  $\text{Cu}_2\text{SnS}_3$  is the parent compound of a series of phases in the  $\text{Cu}_{2+x}\text{Sn}_{1-x}\text{S}_3$  section ( $0 \leq x \leq 0.15$ ) of the ternary Cu–Sn–S phase diagram, the crystal structure of which can be controlled by varying the synthesis process and/or through a fine-tuning of the chemical composition. Despite being structurally close to the sphalerite structure, the thermal transport of these compounds is strongly dependent on the exact lattice symmetry and degree of atomic disorder. Here, we investigate the lattice dynamics of the monoclinic ordered  $\text{Cu}_5\text{Sn}_2\text{S}_7$  (space group  $C2$ ) and cubic disordered  $\text{Cu}_5\text{Sn}_2\text{S}_{6.65}\text{Cl}_{0.35}$  (space group  $F\bar{4}3m$ ) compounds by temperature-dependent powder inelastic neutron scattering (INS). In both cases, the INS spectra feature low-energy optical modes mostly weighed by the thermal motion of Cu atoms. The response of the INS spectra of  $\text{Cu}_5\text{Sn}_2\text{S}_{6.65}\text{Cl}_{0.35}$  to temperature variations is indicative of quasi-harmonic behavior. Combined with analyses of the low-temperature specific heat, these findings show that the significant lowering of the lattice thermal conductivity in cubic  $\text{Cu}_5\text{Sn}_2\text{S}_{6.65}\text{Cl}_{0.35}$  is due to a reduced phonon mean free path tied to the increased level of disorder in the unit cell. These results highlight how the stabilization of highly symmetric, yet strongly disordered crystal structures akin to those observed in high-entropy

alloys, can lead to a drastic reduction in the heat transport, offering an effective approach to design high-performance thermoelectric sulfides.

## 1. INTRODUCTION

Designing highly efficient thermoelectric materials, which enable to convert a temperature difference into electrical power and vice versa, requires to meet a subtle balance between electronic and thermal properties.<sup>1–5</sup> The unusual combination of good electronic and poor thermal properties that must be achieved is quantitatively captured by the dimensionless thermoelectric figure of merit  $ZT = \alpha^2 T / \rho (\kappa_{\text{el}} + \kappa_{\text{L}})$  where  $T$  is the absolute temperature,  $\alpha$  is the thermopower (or Seebeck coefficient),  $\rho$  is the electrical resistivity and  $\kappa_{\text{el}}$  and  $\kappa_{\text{L}}$  are the electronic and lattice thermal conductivity, respectively.<sup>1,2</sup> In addition to conventional doping, common strategies for the optimization of  $\alpha$ ,  $\rho$  and  $\kappa_{\text{el}}$ , all interdependent via the charge carrier concentration, usually relies on band structure engineering that notably includes resonant levels, band convergence, energy filtering effects or the insertion of magnetic ions.<sup>6–17</sup> Specific crystallographic characteristics, such as loosely bound atoms in oversized cages or tunnels,<sup>18–21</sup> rotational degrees of freedom of polyhedra or molecules,<sup>22–24</sup> lone-pair-driven atomic off-centering,<sup>25–30</sup> nanostructuring,<sup>31–33</sup> or formation of solid solutions,<sup>1,2</sup> are various approaches that have been demonstrated to be effective in lowering  $\kappa_{\text{L}}$  by either inducing dynamic disorder or enhancing static disorder. Copper-based sulfides, made of abundant and environmentally friendly elements, provide a prominent example of the latter approach where a fine control of the level of static disorder has been achieved through the optimization of the

sintering conditions or variations in the chemical composition.

34–38 Among them, the interest in the Cu–Sn–S system has been recently revitalized by the discovery of several phases, closely related to the mohite monoclinic phase  $\text{Cu}_2\text{SnS}_3$ .<sup>37–42</sup> The heterovalency of Cu–Sn substitution leads to various structural types derived from the sphalerite cubic structure. In the series  $\text{Cu}_{2+x}\text{Sn}_{1-x}\text{S}_3$ , cubic, tetragonal and monoclinic crystal structures have been reported,<sup>41–47</sup> wherein both the lattice symmetry and cationic disorder can be controlled by varying the Cu-to-Sn ratio. The change in the lattice symmetry by continuously increasing  $x$  up to 0.15 is accompanied by an increased metallic character of transport.<sup>41</sup> Recently, the partial substitution of Cl for S in monoclinic  $\text{Cu}_5\text{Sn}_2\text{S}_7$  was shown to stabilize a highly disordered cubic structure,<sup>48</sup> providing

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another strategy to maintain the conductive sphalerite network while concomitantly lowering  $\kappa_L$ . Interestingly, this cubic polymorph exhibits improved electronic properties due to optimized carrier concentration and, most remarkably, lower  $\kappa_L$  compared to its monoclinic parent compound.<sup>48</sup> Probing their lattice dynamics may thus help to determine whether the strong local chemical disorder in the unit cell of the Cl-doped compound is the main mechanism driving the reduction in the phonon transport. Here, we investigate the lattice dynamics of the monoclinic

ordered sulfide  $\text{Cu}_5\text{Sn}_2\text{S}_7$  and the cubic disordered polymorph  $\text{Cu}_5\text{Sn}_2\text{S}_{6.65}\text{Cl}_{0.35}$  by temperature-dependent powder inelastic neutron scattering (INS). The generalized vibrational density of states (GVDOS) inferred from these measurements is hardly influenced by the lattice symmetry. The temperature dependence of the GVDOS of the Cl-substituted polymorph follows a quasi-harmonic behavior, indicating that the distinct thermal transport between these two compounds is primarily tied to the strong degree of disorder in the cubic lattice, similar to what has been observed in colusites.<sup>49</sup> These observations confirm that controlling the disorder of the cationic sublattice in sulfides is an effective strategy to lower  $\kappa_{\text{ph}}$ , thereby contributing to improving their thermoelectric performance at high temperatures.

## 2. EXPERIMENTAL METHODS

### 2.1. Synthesis, Structural and Chemical Characterizations.

Polycrystalline samples of  $\text{Cu}_2\text{SnS}_3$ ,  $\text{Cu}_{5.133}\text{Sn}_{1.866}\text{S}_7$  and  $\text{Cu}_5\text{Sn}_2\text{S}_{6.65}\text{Cl}_{0.35}$  were prepared from pure elements Cu (99%), Sn (99.85%), S (99.5%) and CuCl (99%), all purchased from Alfa Aesar, in sealed silica tubes. All sample preparations and handlings were carried out in an Ar-filled glovebox.  $\text{Cu}_5\text{Sn}_2\text{S}_{6.65}\text{Cl}_{0.35}$  was synthesized from the precursor  $\text{Cu}_2\text{SnS}_3$ , prepared from stoichiometric quantities of powdered Cu, Sn and S that were cold-pressed into a cylindrical pellet. The pellet was sealed in an evacuated silica tube, heated to 1023 K at a rate of 50 K h<sup>-1</sup>, dwelt at that temperature for 48 h before being cooled to room temperature at the same rate. The as-prepared powder of  $\text{Cu}_2\text{SnS}_3$  was then used to prepare  $\text{Cu}_5\text{Sn}_2\text{S}_{6.65}\text{Cl}_{0.35}$  using additional amounts of Cu, Sn and CuCl to adjust the stoichiometry. The mixtures were cold-pressed

and then heated to 873 K for 24 h with an intermediate step at 673 K for 12 h. The obtained powders were ground and sieved down to 200  $\mu\text{m}$  to avoid the presence of large agglomerates.  $\text{Cu}_5\text{Sn}_2\text{S}_7$  was prepared by mechanical alloying following the route described in our prior study.<sup>41</sup> For transport properties and thermodynamic measurements, the powders were consolidated by spark plasma sintering (SPS, FCT HPD 25) in a graphite die of 10 mm diameter at 873 K for 30 min under a pressure of 64 MPa. The densities of the cylindrical dense pellets were higher than 99% of the theoretical densities calculated from X-ray diffraction data. X-ray powder diffraction (XRPD) data were collected at 300 K using a Bruker D8 advance Vario 1 two-circle diffractometer using the  $\text{Cu K}\alpha_1$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) and equipped with a Ge(111) monochromator (Johansson type) and a LynxEye detector. Rietveld refinements against the XRPD data were performed using the FullProf software.<sup>50</sup> For temperature-dependent XRPD, data has been acquired in Debye–Scherrer geometry on a D8 advance diffractometer equipped with a  $\text{Mo K}\alpha$  radiation (selected by a focusing multilayer mirror), a set of radial Soller slits and a LynxEye HE detector. For the experiment, sieved powder has been sealed in an evacuated silica capillary (diameter of 0.3 mm) in order to avoid oxidation at high temperatures. Data were collected every 25 K from 300 to 800 K in the angular range  $4^\circ \leq 2\theta \leq 35^\circ$  with a step size of  $0.0120^\circ$ . The analysis of the diffraction patterns was performed using a parametric approach as implemented in TOPAS-Academic code.<sup>51</sup> Transmission electron microscopy (TEM) experiments, including selected area electron diffraction (SAED), highangle

annular dark-field scanning TEM (HAADF-STEM), and energy-dispersive X-ray (EDX) STEM studies, were performed on a double aberration-corrected JEOL ARM200F cold FEG microscope operated at 200 kV and equipped with a CENTURIO large-angle EDX detector, an ORIUS CCD camera, and a Quantum GIF. Samples were prepared by crushing the materials in an agate mortar in ethanol and depositing the prepared suspension on a Ni holey carbon grid. The short-range ordering model was created using CristaKit software, and the simulation of the SAED pattern was performed using the MacTempas program.

## 2.2. Thermal Conductivity and Specific Heat Measurements.

Thermal conductivity was measured between 2 and 300 K using the thermal transport option of a physical property measurement system (PPMS, Quantum Design). Barshaped samples with typical dimensions  $2 \times 2 \times 8 \text{ mm}^3$  were cut from the consolidated pellets with a diamond-wire saw. Good electrical and thermal contacts were realized by attaching four copper leads onto the samples with a small amount of conductive silver epoxy. Specific heat  $C_p$  measurements were performed between 2 and 300 K on small pieces of the consolidated pellets using the dedicated option of the PPMS. Samples with a typical mass of 20 mg were mounted on the sample holder using a minute amount of Apiezon N grease, which gives rise to two small humps on the data between 200 and 300 K that correspond to the well-known phase transitions at  $\sim 215$  and  $\sim 289$  K. However, the use of this grease does not affect the accuracy of the data acquired at lower temperatures.

## 2.3. Inelastic Neutron Scattering Experiments.

INS experiments (ref 52) were performed at the cold neutron time-of-

flight spectrometer SHARP, operated by the Laboratoire Léon Brillouin (LLB, Saclay, France), at the Institut Laue Langevin (ILL, Grenoble, France). All measurements were carried out in a cryofurnace under helium atmosphere with an incident neutron wavelength of 4.14 Å. For each sample, about 15 g of powders were placed in a Nb cylindrical can. The data, collected at  $T \approx 150, 300,$  and 450 K, were corrected for empty sample holder scattering, for absorption, for frame overlap and self-attenuation and for different detector efficiencies of the multidetector bank using the Mantid software.<sup>53</sup> Due to differences in total scattering powers  $\sigma_t$  ( $\sigma_t = (\sigma_{\text{coh}} + \sigma_{\text{inc}})/M$  where  $\sigma_{\text{coh}}$  and  $\sigma_{\text{inc}}$  are the coherent and incoherent neutron cross sections expressed in barns, that is,  $10^{-24}$  cm<sup>2</sup> and  $M$  is the atomic mass) between Cu, Sn, S and Cl (0.126, 0.0412, 0.0320, and 0.474 barns/amu for Cu, Sn, S and Cl, respectively),<sup>54</sup> these measurements are more sensitive to Cu and Cl. The dynamic structure factors  $S(Q, \omega)$  were calculated as an average signal over the scattering angle. The GVDOS  $G(\omega)$  was derived within the incoherent approximation formalism.<sup>55–58</sup> All the spectra were normalized so that the integral of  $G(\omega)$  is equal to the total number of phonon modes, that is 18 modes, for both samples (based on the general chemical formula  $\text{Cu}_{2+x}\text{Sn}_{1-x}\text{S}_3$ ). Gaussian least-squares fits were used to approximate the position of the lowest-energy peak in  $G(\omega)$ . Only the inelastic signal at the anti-Stokes line was analyzed due to the limited energy range accessible at the Stokes line at SHARP.

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### 3. RESULTS AND DISCUSSION

3.1. Phase Purity and Crystal Structure. Crystal structure representations, XRPD patterns and HAADFSTEM images of ordered monoclinic sulfide  $\text{Cu}_5\text{Sn}_2\text{S}_7$  and its cubic disordered polymorph of nominal composition  $\text{Cu}_5\text{Sn}_2\text{S}_{6.65}\text{Cl}_{0.35}$  are summarized in Figure 1. Details on crystal structure analyses can be found in refs 41 and 48 for the  $\text{Cu}_5\text{Sn}_2\text{S}_7$  and  $\text{Cu}_5\text{Sn}_2\text{S}_{6.65}\text{Cl}_{0.35}$  compounds, respectively. These measurements confirm that  $\text{Cu}_5\text{Sn}_2\text{S}_7$  crystallizes in the monoclinic  $C2$  space group while the Cl-doped phase of nominal composition  $\text{Cu}_5\text{Sn}_2\text{S}_{6.65}\text{Cl}_{0.35}$  adopts a cubic sphalerite-type structure (space group  $F\bar{4}3m$ ) indicating a fully disordered cationic distribution in the sphalerite lattice and leading to a crystallographic chemical composition of  $\text{Cu}_{0.71}\text{Sn}_{0.29}\text{S}_{0.95}\text{Cl}_{0.05}$ . This composition-driven structural transition is further corroborated by HAADF-STEM images (see Figure 1) and their corresponding fast-Fourier transform patterns evidencing the disordered cubic crystal structure adopted by the Cl-doped compound. Traces of cubic

Figure 1. Crystal structure representations (left), XRPD patterns (center) and HAADF-STEM images with their corresponding electron diffraction pattern (right) of monoclinic ordered sulfide  $\text{Cu}_5\text{Sn}_2\text{S}_7$  (top) and its cubic disordered polymorph  $\text{Cu}_5\text{Sn}_2\text{S}_{6.65}\text{Cl}_{0.35}$  (bottom).

Figure 2. (a) GVDOS  $G(\omega)$  of monoclinic  $\text{Cu}_5\text{Sn}_2\text{S}_7$  and cubic  $\text{Cu}_5\text{Sn}_2\text{S}_{6.65}\text{Cl}_{0.35}$  determined from INS measurements at 300 K. For both compounds, the spectra were normalized so that the integral of  $G(\omega)$  corresponds to 18 phonon modes. (b) Debye plots  $G(\omega)/\omega^2$  for both samples that stress the low-energy region of the  $G(\omega)$  spectra.

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$\text{Cu}_{22}\text{Sn}_{10}\text{S}_{32}$  (space group  $P\bar{4}3n$ ) (ref 42) and orthorhombic  $\text{Cu}_2\text{-}\alpha\text{S}$  (space group  $P4_12_12$ ) (ref 59) are observed as secondary phases in the XRPD data of the  $\text{Cu}_5\text{Sn}_2\text{S}_7$  and

Cu<sub>5</sub>Sn<sub>2</sub>S<sub>6.65</sub>Cl<sub>0.35</sub> samples, respectively. Attempts to quantify the concentrations of these secondary phases are estimated to be ~8 wt % (that is, ~ 3.6 at. %) and ~1 wt %, respectively, according to Rietveld refinements. We note, however, that the crystal structure of cubic Cu<sub>22</sub>Sn<sub>10</sub>S<sub>32</sub> is very close to that of the main phase Cu<sub>5</sub>Sn<sub>2</sub>S<sub>7</sub> resulting in an important convolution of the main diffraction peaks. In the case of Cu<sub>2- $\alpha$</sub> S in the Cu<sub>5</sub>Sn<sub>2</sub>S<sub>6.65</sub>Cl<sub>0.35</sub> sample, the number and intensity of the observed diffraction peaks do not allow for an unambiguous determination of the structural model. For these reasons, the quantification of these impurities remains approximative and possibly overestimated in the case of Cu<sub>22</sub>Sn<sub>10</sub>S<sub>32</sub>. In any case, their presence is not expected to significantly affect the transport properties or the INS signal discussed hereafter. Temperature-dependent XRPD experiments further indicate the absence of structural phase transition between 300 and 800 K (Figure S1 in Supporting Information).

### 3.2. Powder Inelastic Neutron Scattering.

Figure 2a shows a comparison of the generalized densities of states  $G(\omega)$  of monoclinic Cu<sub>5</sub>Sn<sub>2</sub>S<sub>7</sub> and cubic Cu<sub>5</sub>Sn<sub>2</sub>S<sub>6.65</sub>Cl<sub>0.35</sub> inferred from INS measurements at 300 K. The measured  $G(\omega)$  are very similar, with pronounced low-energy peaks observed at 7.6 and 8.2 meV for Cu<sub>5</sub>Sn<sub>2</sub>S<sub>6.65</sub>Cl<sub>0.35</sub> and Cu<sub>5</sub>Sn<sub>2</sub>S<sub>7</sub>, respectively. These two peaks feature shoulders on either side, that are also visualized in the Debye plots  $G(\omega)/\omega^2$  (Figure 2b). A second block of peaks is observed around 15 meV. The inelastic signal becomes less structured beyond this peak and up to about 27 meV where the third and last block of peaks centered at ~31 meV can be distinguished. The phonon cutoff

energy of around 40 meV is consistent with lattice dynamics calculations predicting a cutoff frequency of ~10 THz (~41.3 meV).<sup>60</sup> For monoclinic Cu<sub>5</sub>Sn<sub>2</sub>S<sub>7</sub>, the spectral distribution of the peaks, their characteristic energies and their relative intensities are similar to those reported for monoclinic Cu<sub>2</sub>SnS<sub>3</sub> by lattice dynamics calculations.<sup>60</sup> The comparison of these calculations with  $G(\omega)$  indicates that the first two blocks are mostly weighed by Cu and Sn atoms while the peaks at higher energies mostly correspond to modes dominated by S atoms. A similar conclusion holds for cubic Cu<sub>5</sub>Sn<sub>2</sub>S<sub>6.65</sub>Cl<sub>0.35</sub>, with the presence of the small concentration of Cl hardly modifying the overall shape and characteristic energies of the first two blocks, while some differences can be observed above 20 meV. Optical modes mostly weighed by Cl are expected to dominate at high energies due to the similar molar mass of Cl with respect to S. The mode assignment and the presence of these low-energy peaks in both samples are consistent with nuclear inelastic scattering measurements of the partial GVDOS of Sn atoms performed on monoclinic CTS-based samples.<sup>60</sup> To shed light on the anharmonicity of the Cu and S-dominated low-energy peaks, temperature-dependent INS spectra were measured on Cu<sub>5</sub>Sn<sub>2</sub>S<sub>6.65</sub>Cl<sub>0.35</sub> (Figure 3). The experimental data collected at 150 K have been discarded above ~20 meV due to the strongly reduced intensity, which is scaled by the Bose–Einstein occupation factor. The weak shift of the entire spectrum upon heating is consistent with a quasiharmonic behavior, indicating the absence of significant anharmonicity beyond the cubic term associated with the thermal expansion of the crystal lattice.

This variation, equally observed for the colusites  $\text{Cu}_{26}\text{V}_2\text{Sn}_6\text{S}_{32}$ ,<sup>49</sup> contrasts with that reported for the tetrahedrites

$\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  (refs 61 and 62.) and aikinite  $\text{CuPbBiS}_3$  (ref

63) for which the lowest-energy peaks show the opposite

trend, that is a shift toward lower energy upon cooling,

characteristic of anharmonic behavior. The rate of change in

the characteristic energy of the main peaks can be well

accounted for by evaluating the volume dependence ( $V$ ) of the

phonon mode energy  $E_i$ , quantified through the mode-specific

Grüneisen parameter  $\gamma_i$  by the relation

$$\gamma_i = \left( \frac{E_i}{V} \right) \left( \frac{dV}{dT} \right) = \left( \frac{E_i}{V} \right) \left( \frac{dV}{dT} \right)$$

$E_i$   
 $V$   
 $T$   
 $E_i$   
 $V$   
 $T$   
 $\ln$   
 $\ln$   
 $i$   
 $i$

64 Within the quasiharmonic approximation, the thermodynamic averaged Grüneisen

parameter  $\bar{\gamma}$  for all modes can be assumed and is related to

Figure 3. (a) Temperature dependence of the GVDOS  $G(\omega)$  of cubic  $\text{Cu}_5\text{Sn}_2\text{S}_6.65\text{Cl}_{0.35}$ . (b) Corresponding Debye plots  $G(\omega)/\omega^2$ . The temperature- and color-coded symbols are reported in the figures.

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the average phonon energy  $\langle E \rangle$  via the relation  $\bar{\gamma} =$

$\frac{1}{V} \left( \frac{dV}{dT} \right) \left( \frac{d\langle E \rangle}{dT} \right)$   
 $\ln$   
 $\ln$   
 $E$   
 $V$   
 $G$   
 $V$   
 $0$

$\bar{\gamma}$  can be expressed in terms of thermodynamic quantities, experimentally accessible, according to the relation  $\bar{\gamma} =$

$\frac{C_V}{C_P} \left( \frac{B}{V} \right) \left( \frac{dV}{dT} \right)$   
 $G$   
 $C$   
 $V$   
 $V$

where  $V$  is the molar volume,  $C_V$  is the isochoric specific heat,  $B$  is the bulk modulus

and  $\alpha_V$  is the volumetric thermal expansion coefficient.<sup>64</sup>

$\bar{\gamma}$  has been calculated at 300 K using the measured  $C_P$  values and

the  $B$  values inferred from measurements of the longitudinal

and transverse sound velocities by a pulse-echo method (67

and 61 GPa for  $\text{Cu}_5\text{Sn}_2\text{S}_7$  and  $\text{Cu}_5\text{Sn}_2\text{S}_6.65\text{Cl}_{0.35}$ , respectively).

For cubic  $\text{Cu}_5\text{Sn}_2\text{S}_6.65\text{Cl}_{0.35}$ ,  $\alpha_V$  was determined from the linear

thermal expansion coefficient measured by dilatometry and

was found to be equal to  $20.4 \times 10^{-6} \text{ K}^{-1}$  at 300 K. For

monoclinic  $\text{Cu}_5\text{Sn}_2\text{S}_7$ ,  $\alpha_V$  was determined through lattice

parameter refinements of temperature-dependent XRPD

patterns collected up to 800 K (Figure S2 in Supporting

Information), yielding an average value of  $31.6 \times 10^{-6} \text{ K}^{-1}$

over the 300–500 K temperature range. Combining these

values results in  $\bar{\gamma}$  of 1.10 and 0.65 for  $\text{Cu}_5\text{Sn}_2\text{S}_7$  and  $\text{Cu}_5\text{Sn}_2\text{S}_6.65\text{Cl}_{0.35}$ , respectively. These two values are lower than

those inferred for the sulfur-based synthetic colusite

$\text{Cu}_{26}\text{V}_2\text{Sn}_6\text{S}_{32}$  ( $\bar{\gamma}$  1.5–2 depending on the synthesis route)<sup>49</sup> and several other strongly anharmonic compounds<sup>65–</sup>

<sup>69</sup> such as  $\text{AgSbTe}_2$  ( $\bar{\gamma}$  2.05),<sup>65</sup>  $\text{AgBi}_3\text{S}_5$  ( $\bar{\gamma}$  3.6,

averaged only over the acoustic dispersions along the  $a$ ,  $b$

and  $c$  crystallographic axes)<sup>66</sup> or  $\text{CsAg}_5\text{Te}_3$  ( $\bar{\gamma}$  4.2,

averaged only over the acoustic dispersions along the  $a$ ,  $b$

and  $c$  crystallographic axes),<sup>67</sup> indicating that both

$\text{Cu}_5\text{Sn}_2\text{S}_7$  and  $\text{Cu}_5\text{Sn}_2\text{S}_6.65\text{Cl}_{0.35}$  are weakly anharmonic. For

$\text{Cu}_5\text{Sn}_2\text{S}_6.65\text{Cl}_{0.35}$ , the quasiharmonic prediction of the temperature

dependence of the characteristic energy of the lowest-energy

peaks agrees reasonably well with that observed experimentally by INS

(Figure 4).

3.3. Specific Heat. Figure 5 shows the temperature dependence of the specific heat  $C_p$ , plotted as  $C_p/T$  versus

$T_2$ , of the  $\text{Cu}_5\text{Sn}_2\text{S}_7$  and  $\text{Cu}_5\text{Sn}_2\text{S}_6.65\text{Cl}_{0.35}$  samples. For

comparison, data measured on the parent compound  $\text{Cu}_2\text{SnS}_3$  (space group  $Cc$ ) and on the Cu-rich  $\text{Cu}_{5.133}\text{Sn}_{1.866}\text{S}_7$  composition (space group  $C2$ ) have been added. The low-temperature data were fitted to the conventional free-electron gas formula  $\gamma = \frac{1}{2} \frac{c}{T}$  where  $\gamma$  is the Sommerfeld coefficient corresponding to the electronic contribution and  $\beta T_2$  is the lattice contribution. The parameter  $\beta$  is related to the Debye temperature  $\vartheta_D$  by the relation  $\beta = \frac{12}{5} \frac{NR}{\vartheta_D^3}$  where  $R$  is the ideal gas constant and  $N$  is the number of atoms per formula unit. The best linear fit to the  $C_p/T$  versus  $T_2$  data yields a  $\gamma$  value indistinguishable from zero to within experimental uncertainty for  $\text{Cu}_2\text{SnS}_3$  and  $\gamma$  values of  $7.45 \pm 0.10$ ,  $7.00 \pm 0.10$  and  $5.00 \pm 0.10$   $\text{mJ mol}^{-1} \text{K}^{-2}$  for the  $\text{Cu}_5\text{Sn}_2\text{S}_7$ ,  $\text{Cu}_{5.133}\text{Sn}_{1.866}\text{S}_7$  and  $\text{Cu}_5\text{Sn}_2\text{S}_6\text{Cl}_{0.35}$  compounds, respectively. While the zero value of  $\text{Cu}_2\text{SnS}_3$  is consistent with its nearly intrinsic semiconducting nature,<sup>41</sup> the values inferred for these last three samples imply finite density of states at the Fermi level within a free-electron model, a finding consistent with the degenerate character of transport.<sup>41,48</sup> The  $\beta$  parameters correspond to Debye temperatures  $\vartheta_D$  of  $289 \pm 5$ ,  $268 \pm 5$ ,  $277 \pm 5$  and  $262 \pm 5$  K for  $\text{Cu}_2\text{SnS}_3$ ,  $\text{Cu}_5\text{Sn}_2\text{S}_7$ ,  $\text{Cu}_{5.133}\text{Sn}_{1.866}\text{S}_7$  and  $\text{Cu}_5\text{Sn}_2\text{S}_6\text{Cl}_{0.35}$ , respectively. For all samples, the lattice contribution to the specific heat,  $C_{ph}$ , determined by subtracting the electronic contribution to the  $C_p$  data, is characterized by a pronounced peak centered around 17 K, best visualized when the data are plotted as  $C_{ph}/T_3$  versus  $T$  (Figure 6). In cage-like compounds such as type-I clathrates and skutterudites,<sup>70–75</sup> this peak has been modeled

Figure 4. Temperature dependence of the characteristic energy (red filled circle symbols) of the low-energy peak near 7.5 meV for cubic  $\text{Cu}_5\text{Sn}_2\text{S}_6\text{Cl}_{0.35}$ , obtained from fits to the  $G(\omega)/\omega^2$  data with Gaussian functions. The black solid line corresponds to the quasiharmonic (QH) prediction of the temperature dependence of this peak using a thermodynamic average Grüneisen parameter  $G$  of 0.65.

Figure 5. Temperature dependence of the specific heat  $C_p$  of monoclinic  $\text{Cu}_2\text{SnS}_3$  (space group  $Cc$ ),  $\text{Cu}_5\text{Sn}_2\text{S}_7$  (space group  $C2$ ) and  $\text{Cu}_{5.133}\text{Sn}_{1.866}\text{S}_7$  (space group  $C2$ ) and cubic  $\text{Cu}_5\text{Sn}_2\text{S}_6\text{Cl}_{0.35}$  (space group  $F\bar{4}3m$ ). The solid black lines highlight the  $T_2$  range where the free-electron formula  $\gamma = \frac{1}{2} \frac{c}{T}$  is obeyed.

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by Einstein-like contributions reflecting the large thermal motion of encaged cations, providing a direct mean to extract the characteristic energies of the associated optical modes.

Herein, we tried to extend this model, which describes the specific heat as a linear combination of a Debye- and two Einstein-like contributions according to the relation  $C_p(T) = C_D(T) + C_{E1}(T) + C_{E2}(T)$  (1) where  $C_D(T)$  and  $C_{Ei}(T)$  are the lattice specific heat within the Debye approximation and the Einstein contribution of the localized oscillators  $i$ , respectively, given by

$$C = N R T x e^{-x} \left( \frac{9}{4} + \sum_{i=1}^3 \frac{e^{-x_i}}{x_i^3} \right)$$

(2)  
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 $z z z z$   
(3)

In these two expressions,  $\vartheta_D$  is the Debye temperature,  $R$  is the gas constant,  $N_D$  is the number of Debye oscillators per formula unit,  $p_i$  and  $N_{E_i}$  are the spectral weight and the number of the Einstein oscillators  $i$  characterized by the Einstein

temperature  $\vartheta_{E_i}$ . The best fits to the experimental  $C_{ph}$  data for  $Cu_2SnS_3$ ,  $Cu_5Sn_2S_7$ ,  $Cu_{5.133}Sn_{1.866}S_7$  and  $Cu_5Sn_2S_{6.65}Cl_{0.35}$  with

Figure 6. Lattice contribution to the specific heat  $C_{ph}$  plotted as  $C_{ph}/T^3$  versus temperature on a logarithmic scale for  $Cu_2SnS_3$ ,  $Cu_{5.133}Sn_{1.866}S_7$ ,  $Cu_5Sn_2S_7$  and  $Cu_5Sn_2S_{6.65}Cl_{0.35}$ . The solid, dashed, two-dashed and dotted lines are the best fit to the data according to the model described in the text.

Figure 7. Temperature dependence of the (a) total thermal conductivity  $\kappa$  and (b) lattice thermal conductivity  $\kappa_L$  for monoclinic  $Cu_2SnS_3$ ,  $Cu_5Sn_2S_7$ ,  $Cu_{5.133}Sn_{1.866}S_7$  and cubic  $Cu_5Sn_2S_{6.65}Cl_{0.35}$ .

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all the parameters allowed to vary are shown in Figure 6. For all the compounds, this simple model describes very well the experimental data and notably the peak at  $\sim 17$  K that is mostly determined by the Einstein contributions. For all compounds, the sum of the spectral weights deviates by at most 5% from the expected value of 6 corresponding to the number of atoms

per formula unit when considering the chemical formula

$Cu_{2+x}Sn_{1-x}S_3$ . While the value of  $\vartheta_{E2}$  of  $\sim 86$  K remains

practically equivalent for all samples, the  $\vartheta_{E1}$  value of 62 K for

$Cu_2SnS_3$  decreases to values ranging between 46 and 49 K for

the  $Cu_5Sn_2S_7$ ,  $Cu_{5.133}Sn_{1.866}S_7$  and  $Cu_5Sn_2S_{6.65}Cl_{0.35}$  compounds.

These values correspond fairly well to the onset of the optical continuum that was found to start near  $\sim 1.5$  THz

( $\sim 6.2$  meV,  $\sim 72$  K) and  $\sim 1.3$  THz ( $\sim 5.4$  meV,  $\sim 63$  K) in

ordered and disordered models of  $Cu_2SnS_3$ , respectively, by

lattice dynamics calculations and  $^{119}Sn$  nuclear inelastic

scattering measurements on ordered and disordered  $Cu_2SnS_3$

samples prepared by high-energy ball-milling.<sup>60</sup> The lower

values inferred for the disordered compounds may thus reflect

the tendency of the optical modes to shift toward lower

energies upon increasing the disorder in the unit cell.<sup>60</sup>

3.4. Thermal Transport. The total thermal conductivity  $\kappa$

of the monoclinic  $Cu_2SnS_3$ ,  $Cu_5Sn_2S_7$  and  $Cu_{5.133}Sn_{1.866}S_7$

samples and cubic  $Cu_5Sn_2S_{6.65}Cl_{0.35}$  differs significantly (Figure

7a). The pronounced Umklapp peak reaching  $\sim 30$   $W m^{-1} K^{-1}$

around 50 K in pristine  $Cu_2SnS_3$  is substantially reduced in

$Cu_5Sn_2S_7$  and no longer visible in  $Cu_{5.133}Sn_{1.866}S_7$  and  $Cu_5Sn_2S_{6.65}Cl_{0.35}$ . For  $Cu_5Sn_2S_7$ ,  $\kappa$  rapidly increases

upon heating to reach  $\sim 15$   $W m^{-1} K^{-1}$  around 50 K, before

monotonically decreasing to  $\sim 10$   $W m^{-1} K^{-1}$  at 300 K. In

contrast, the  $\kappa$  values of the cubic polymorph are significantly

lower, with a maximum of  $\sim 2.5$   $W m^{-1} K^{-1}$  that weakly varies

between 75 and 300 K. These observations hold true for the

lattice thermal conductivity  $\kappa_L = \kappa - \kappa_{el}$  determined by

subtracting the electronic thermal conductivity  $\kappa_{el}$  according to

the Wiedemann–Franz law  $\kappa_{el} = LT/\rho$ , where  $L$  is the Lorenz number assumed to be equal to the degenerate limit  $L_0 = 2.45 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$  due to the degenerate character of transport in  $\text{Cu}_{5.133}\text{Sn}_{1.866}\text{S}_7$ ,  $\text{Cu}_5\text{Sn}_2\text{S}_7$  and  $\text{Cu}_5\text{Sn}_2\text{S}_{6.65}\text{Cl}_{0.35}$ .<sup>41,48</sup> Because of the intrinsic semiconducting nature of  $\text{Cu}_2\text{SnS}_3$ , the heat transport is mainly mediated by phonons, making the approximation  $\kappa \approx \kappa_L$  quasi exact in the present case. The difference in  $\kappa_L$  between  $\text{Cu}_{5.133}\text{Sn}_{1.866}\text{S}_7$  and  $\text{Cu}_5\text{Sn}_2\text{S}_{6.65}\text{Cl}_{0.35}$  ( $\kappa_L \approx 3.8$  and  $1.5 \text{ W m}^{-1} \text{ K}^{-1}$ , respectively, at 300 K) cannot solely originate from mass fluctuations and size effects due to the similar molar masses and ionic radii of  $\text{Cl}^-$  and  $\text{S}^{2-}$  (181 and 184 pm, respectively). Rather, the strong decrease observed may be attributed to the scattering of acoustic phonons from force-constant fluctuations that accompany the strong local chemical disorder in the cubic unit cell of  $\text{Cu}_5\text{Sn}_2\text{S}_{6.65}\text{Cl}_{0.35}$  and significantly shorten acoustic phonon lifetimes. This mechanism is qualitatively equivalent to that observed in more complex materials such as type-I clathrates or high-entropy alloys, even though acoustic phonons have been shown to remain well-defined over a large part of the Brillouin zone.<sup>76–78</sup> In spite of the strong disorder-induced lowering of  $\kappa_L$ , none of the measured values approach the lower bound reached when the Ioffe-Regel limit for phonons is attained, that is, when the average phonon mean free path is nearly equivalent to the mean interatomic distance.<sup>79</sup> This lower bound can be estimated from the high-temperature limit of the formula derived by Cahill, Watson and Pohl for amorphous and strongly disordered compounds<sup>80</sup>

$$\kappa_{\text{glass}} = \frac{1}{3} k_B \frac{v_T}{V} + \frac{2}{3} k_B \frac{v_L}{V}$$

(2)

where  $V$  is the average volume per atom and  $v_T$  and  $v_L$  are the transverse and longitudinal sound velocity, respectively.  $v_T$  and  $v_L$ , measured at 300 K by a pulse-echo method, were found to be typically around 4550 and 2420  $\text{m s}^{-1}$  for the monoclinic compounds and equal to 4720 and 2470  $\text{m s}^{-1}$  for the cubic compound. These values lead to a lower bound of  $\kappa_{\text{glass}} \sim 0.2 \text{ W m}^{-1} \text{ K}^{-1}$  for the monoclinic and cubic polymorphs. Neither the ordered monoclinic nor the disordered cubic compounds approach this limit in this temperature range, suggesting room for further decreasing  $\kappa_L$  by enhancing mass fluctuations for instance.

#### 4. CONCLUSIONS

The lattice dynamics of the ordered monoclinic  $\text{Cu}_5\text{Sn}_2\text{S}_7$  and the disordered cubic  $\text{Cu}_5\text{Sn}_2\text{S}_{6.65}\text{Cl}_{0.35}$  sulfides has been investigated by means of low-temperature thermal conductivity and specific heat measurements and temperature-dependent powder INS experiments. The generalized phonon density of states measured by INS exhibit low-energy peaks that are assigned to phonon modes mostly weighed by Cu atoms. Upon cooling, the characteristic energy of the peaks of the INS spectrum shifts, following a rate of change mainly determined by the thermal expansion of the unit cell. The analysis of the low-temperature specific heat and lattice thermal conductivity suggests that the stabilization of the cubic unit cell upon Cl doping enhances the disorder on the cationic sublattice. This

high degree of disorder in  $\text{Cu}_5\text{Sn}_2\text{S}_6\text{Cl}_{0.35}$  appears to be the main ingredient that drives the significant reduction in the low-temperature thermal conductivity observed experimentally. Successfully growing single crystals of ordered and disordered  $\text{Cu}_2\text{SnS}_3$  would be of interest to verify experimentally the main trait of the phonon dynamics suggested by these results, that is, the disorder-induced shortening of acoustic phonon lifetimes. In this regard, one possibility to further reduce the lattice thermal conductivity in these disordered sulfides would be to consider substitutions on the cationic sublattice with more dissimilar elements to enhance the force-constant fluctuations between neighboring atomic species.

## ASSOCIATED CONTENT

\* Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.4c03489>.

Thermal expansion coefficients for a monoclinic lattice, high-temperature PXRD patterns of monoclinic  $\text{Cu}_5\text{Sn}_2\text{S}_7$ , temperature-dependent XRD data of monoclinic  $\text{Cu}_5\text{Sn}_2\text{S}_7$  (PDF)

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The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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