Ultralow Thermal Conductivity of β -Cu₂Se by Atomic Fluidity and Structure Distortion

Hyoungchul Kim^{a,b,*}, Sedat Ballikaya^{c,d}, Hang Chi^c, Jae-Pyung Ahn^e,
Kiyong Ahn^b, Ctirad Uher^c, Massoud Kaviany^a

^a*Department of Mechanical Engineering, University of Michigan, Ann Arbor, MI 48109, USA*

^b*High-Temperature Energy Materials Research Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea*

^c*Department of Physics, University of Michigan, Ann Arbor, MI 48109, USA*

^d*Department of Physics, University of Istanbul, Vezneciler, Istanbul 34134, Turkey*

^e*Advanced Analysis Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea*

Abstract

We demonstrate a thermal evolution path prototype to liquid thermal conductivity in solids. Thermal evolution of β -Cu₂Se shows large interstitial displacement of constituent atoms marked with glass-like transitions and an asymptotic liquid thermal transport. With *ab-initio* molecular dynamics (AIMD), we identify these transitions, and with *in-situ* transmission electron microscopy and electron energy loss spectroscopy we confirm them. The thermal disorder of the Cu⁺ ions forms homopolar Cu-Cu bond under a rigid Se framework, and at yet higher temperatures the Se framework undergoes thermal distortion. The non-equilibrium AIMD prediction of lattice thermal conductivity shows significant suppression of the phonon transport, in agreement with experiments and molecular behavior.

Keywords: Structure evolution, Thermal conductivity, Thermophysical property, Thermoelectrics, Phonon engineering

*Corresponding author

Email address: hyoungchul@kist.re.kr (Hyoungchul Kim)

1. Introduction

Thermal structure evolution is ubiquitous in solids, including expansion, phase transformation, and melting, and aside from amorphous and crystalline, there are transitional superionics, macromolecules, and quasi-crystals. These have drawn interests with the premise to tune properties with structural anomalies. In thermoelectrics, structure evolution approaching liquid behavior has led to the '*phonon-glass electron-crystal*' paradigm.

Copper selenide, a chalcogenide, is a mixed conductor (electronic-ionic) with a phase transition [1, 2, 3, 4, 5, 6]. It undergoes a α - β transition (at $T_{tr,\alpha-\beta} \sim 410$ K) from the low-temperature monoclinic α -phase to the high-temperature β -phase [face-centered cubic (FCC) structure, $Fm\bar{3}m$; β -Cu₂Se] [1, 2, 3, 4, 5, 6]. Its critical electron and phonon scatterings during the second-order phase transition have been explored [7], however its relevant thermoelectric (TE) properties have suffered from structural instability and a narrow temperature domain. The β -phase also offers high TE figure-of-merit over unity, due to abnormal Cu migration reducing lattice thermal conductivity (κ_L) [6, 7]. Figures 1(a) and 1(b) show the β -Cu₂Se structure consisting of eight cations (Cu⁺) and four anions (Se²⁻) and several close-neighbor interstitial sites [3, 5, 8].

Figure 1: Crystal structure of β -Cu₂Se. (a) The β -Cu₂Se crystal structure (blue and green are Cu and Se atoms). (b) Multiple atomic sites for Cu⁺ and Se²⁻ ions, with designations. The Se atoms form a rigid framework (FCC site, 4a) and Cu⁺ ions readily drift among the different sites (octahedral, 4b; tetrahedral, 8c; trigonal site, 32f).

Since the crystallinity of FCC β -Cu₂Se is maintained for $T > T_{tr,\alpha-\beta}$ and the thermophysical properties are controlled by the Se framework, no significant property changes are expected. However, measurements show

dramatic changes, surprisingly without any distinct phase transitions. The β -Cu₂Se liquid-like behavior includes reduced specific heat (c_v) approaching the theoretical limit for liquid (i.e., $c_v = 2k_B$ per atom, where k_B is the Boltzmann constant) and a colossal linear thermal expansion coefficient (α_l) of $10.7 \times 10^{-5} \text{ K}^{-1}$ above 800 K [5]. Another anomaly has been associated with the significant scattering of lattice phonons, i.e., glassy behavior close the amorphous limit [5, 6, 9, 10], as desired in the '*phonon-glass electron-crystal*' of superior TE materials [11]. So far, clarifying the related physics and predicting the phonon transport have not been successful due to the theoretical and experimental (especially at high-temperatures) challenges.

We report the heterogeneous structure evolution of β -Cu₂Se at elevated temperatures, which explains the anomalous thermophysical properties and significant suppression of phonon transport, close to a liquid-state behavior, without any phase changes. Using the density-functional theory (DFT) including *ab-initio* molecular dynamics (AIMD) simulations, we predict the temperature-dependent lattice dynamics and thermal conductivity changes due to the atomic fluidity and homopolar Cu-Cu bond. We use *in-situ* transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) techniques to examine our theoretical predictions.

2. Methodology

2.1. Sample preparation

Cu₂Se was synthesized with a solid state reaction method by mixing Cu (99.9999% shot) and Se (99.999% powder), in their respective stoichiometric ratios in a glove box. The charge was then loaded into a carbon-coated quartz tube and sealed under vacuum of 10^{-3} torr. The quartz tube was placed in a furnace and heated to 1423 K at the rate of 1 K min^{-1} with a subsequent soak for 12 hours to ensure thorough mixing of the constituents. The temperature of the furnace was then decreased to 1073 K at the rate of 4 K min^{-1} and held for 10 days to complete the reaction. The furnace was finally turned off and cooled to room temperature. The resulting ingot was ground into a fine powder in a glove box and loaded into a cylindrical graphite die for Spark Plasma Sintering under a dynamic vacuum. The powders were first cold pressed under a pressure of 50 MPa then the pressure was reduced to 10 MPa. The samples were heated under this reduced load at the rate of 50 K min^{-1} to a final temperature of 823 K at which point the uniaxial pressure was increased to 50 MPa, with a subsequent isothermal/isobaric hold. The

ingot was cut by a diamond blade saw into disks for thermal diffusivity measurements and into rectangular bars for transport characterization.

2.2. Property measurements

The low and high temperature AC Hall effect measurements shown in Fig. 2(a) were performed to determine the carrier type, and concentration of the charge carriers and their mobility. The Hall coefficient (R_H) measurements were performed on a Hall bar with typical thickness of 1 mm in Magnetic Property Measurement System (2 to 300 K; Quantum Design) using silver epoxy contacts and/or in a customized air-bore superconducting magnet (300 to 850 K; Oxford) using pressure contacts. Signal was recorded using an AC resistance bridge (LR 700, Linear Research), where magnetic fields of ± 1 T were applied in order to eliminate probe misalignment. All high-temperature transport properties in Figs. 2(b) and (c) were observed under the dynamic flow of argon in the temperature range of 300 to 900 K. The electrical conductivity (σ_e) was measured using a home-built apparatus with a standard four probe potentiometric configuration, and the results are shown in Fig. 2(b). We have repeated the measurements for each sample at least twice and in each of these have repeated a heating-cooling cycle. After the first measurement, the sample was removed and all surfaces polished to make a new contact with new thermocouples. As shown in Fig. 2(b), the thermal hysteresis becomes negligible and there was no material losses. However, Brown *et al.* [12] report that under normal operating conditions material losses do occur (mostly due to vaporization of Se) and innovative methods should be developed to avoid them. The total thermal conductivity (κ) was calculated according to $\kappa = D\rho c_p$, where D is the thermal diffusivity, ρ is the bulk density, and c_p is the specific heat capacity at constant pressure. Thermal diffusivity was measured using a Flashline 5000 laser-based apparatus from Anter Corporation. Specific heat was measured by a differential scanning calorimeter (DSC 404 Pegasus, Netzsch) and density at room temperature, obtained from the Archimedes' method, indicated a value corresponding to 98% of the theoretical density. Linear thermal expansion was measured using a horizontal pushrod dilatometer (DIL 402E, Netzsch). The sample was heated with 5 K min^{-1} to 1143 K under argon atmosphere. For analysis of structural and electronic properties, a transmission electron microscope (Tecnai F20, FEI) operating at 200 kV and equipped with a CCD imaging system (GIF 866, Gatan) was used. Electron energy loss spectra were acquired with a dispersion of 0.05 eV/channel, a 2 mm GIF entrance aperture,

and parallel illumination.

Figure 2: Variations of the measured β -Cu₂Se properties with respect to temperature. (a) Hall coefficient, (b) electrical conductivity (including thermal hysteresis), and (c) total thermal conductivity. The electrical conductivity measurements were repeated during heating and cooling of the specimen, and these measurements were repeated twice, as marked.

2.3. First-principles calculations

We investigated the high-temperature electronic structure and the lattice dynamics of β -Cu₂Se using the DFT method (including equilibrium and non-equilibrium AIMD) implemented in the Vienna *ab-initio* Simulation Package (VASP) [13]. The PBE parameterization of the GGA for the exchange-correlated functional [14] and the PAW method for modeling core electrons (energy cutoff = 355.2 eV) [15, 16] were used. The high-temperature lattice dynamics were investigated by equilibrium AIMD. These simulations were performed on supercells consisting of 324 atoms ($3 \times 3 \times 3$ conventional cells). To consider the thermal expansion in the high-temperature simulations, we prepared supercells with the lattice parameter ($a = 5.864 \text{ \AA}$ at $T = 453 \text{ K}$) [5, 6] using our measured linear thermal expansion coefficient. The Brillouin zone is sampled at the gamma point. After constant-temperature simulations with the Nosé thermostat for 1 ps (0.5 fs time step) reaching equilibrium, we collect atomic trajectories for 20 ps (1 fs time step).

To predict the lattice thermal conductivity of β -Cu₂Se, we use the non-equilibrium *ab-initio* molecular dynamics (NEAIMD). Using the VASP code

modified to perform the NEAIMD-energy exchange [17, 18] as reported in the literature [19, 20]. Non-equilibrium method is one of the computational techniques to predict the lattice thermal conductivity. It is derived from the Fourier’s law, the time rate of heat transfer is proportional to the negative gradient in the temperature and to the area [21, 22]. The lattice thermal conductivity using NEAIMD simulations is computed as the ratio of an applied heat flux to the resulting temperature gradient [19, 20], i.e.,

$$\kappa_L = -[\overline{Q(t)}/A](\overline{dT/dz})^{-1}, \quad (1)$$

where the overbar indicates time average and $Q(t)$ is the heat flow rate. The heat flux is imposed by dividing the simulation cell into sections of equal width, and exchanging kinetic energy between hot and cold sections. The temperature gradient along the z axis is computed from the mean temperature of adjacent sections. Simulations were performed on supercells consisting of 192 ($4 \times 2 \times 2$ conventional cell), 288 ($6 \times 2 \times 2$), and 384 ($8 \times 2 \times 2$) atoms. Structure preparations were the same as the equilibrium AIMD simulations. We used the constant-temperature simulations with the Nosé thermostat for 1 ps (0.5 fs time step) and, after reaching equilibrium, non-equilibrium calculations were performed for 20 ps (1 fs time step). Because the exchange of kinetic energy results in non-Newtonian dynamics in the hot and cold sections, only the linear portion of the temperature gradient is considered in calculating the lattice thermal conductivity.

3. Results and discussion

3.1. Anomalies in thermophysical properties

From the various measurement shown in Figs. 2(a)-(c), we observe abrupt change in the transport properties resulting from the distinct structural transition between the α - and β -phase at $T_{tr,\alpha-\beta} \sim 410$ K. For the $T > T_{tr,\alpha-\beta}$ regime, the β -Cu₂Se has a stable thermophysical structure due to the rigid Se framework and the negligible anomalies in high-temperature transport properties. However, several anomalies in the thermophysical properties of the β -Cu₂Se (without any phase transition) are observed from the detailed experimental and computational analyses. Figure 3 presents the temperature dependence of thermophysical properties of β -Cu₂Se. The low-temperature linear thermal expansion coefficient is nearly constant and consistent with the reported value, 2.3×10^{-5} K⁻¹ for $T \sim 773$ K [5], while the high-temperature

Figure 3: Thermophysical properties of β -Cu₂Se as a function of temperature. (a) Measured lattice parameter and linear thermal expansion coefficient. (b) Measured density and the predicted bulk modulus. (c) Measured specific heat capacity at constant pressure, predicted specific heat capacity at constant volume and the Grüneisen parameter. The predicted glass transition temperatures, $T_{g,I}$ and $T_{g,II}$, are also shown. Shaded areas show temperature regimes.

results have two distinct peaks. Constructing tangent lines to the lattice parameter (a) curve, there are two distinct temperatures, ~ 800 and ~ 1000 K, where the tangents intersect. Such transition temperatures in the thermal expansion are commonly observed in the glass transitions of amorphous materials. While the glass transition theory generally applies to amorphous phases, the glass transition temperature (T_g) signifies the glass to rubber transition. Noting the β -Cu₂Se crystallinity (FCC for $T > T_{tr,\alpha-\beta}$) up to the melting point ($T_m \sim 1380$ K), here we suggest its glass transitions, i.e., thermal structure heterogeneity, at two distinct temperatures. Based on the measured thermal expansion coefficient and the specific heat capacity at con-

stant pressure, we use a lattice parameter relation ($a = a_o + a_o\alpha_l\Delta T$, where a_o is the reference lattice parameter of a sample at T_o), the bulk density ($\rho = m/a^3$, where m is sample mass), specific heat capacity at constant volume [$c_v = c_p - c(3\alpha_l)T/\rho$, where c is constant], bulk modulus [$B = \rho(c_p - c_v)/(3\alpha_l)^2T$], and the Grüneisen parameter ($\gamma_G = 3\alpha_l B/\rho c_v$), as shown in Figs. 3(a) to (c). Above the Debye temperature (~ 292 K [10]), B is obtained from the thermodynamic properties and the quasi-harmonic model, and its product with the volumetric thermal expansion is constant [23]. These thermophysical properties undergo noticeable changes at two distinct temperatures, without notable phase changes. Below $T = 800$ K, denoted as the '*first glass transition point*', B , c_v , and γ_G are nearly constant. For $800 < T < 1000$ K, B and c_v decrease, and the γ_G increases with temperature. Above $T = 1000$ K, the '*second transition point*', most properties reach a plateau. These three distinct regimes explain the structure-heterogeneity evolution, and the associated significant phonon scattering are discussed later.

Figure 4: Atomistic trajectories of β -Cu₂Se sampled with AIMD atomic trajectories for 3 ps, for four different temperatures: (a) 500 K, (b) 700 K, (c) 900 K, and (d) 1100 K.

3.2. Heterogeneous structure evolution

To elucidate this thermal structure evolution leading to heterogeneous glass transitions, we use the lattice dynamics analyses based on the DFT to reveal the unique vibrational behavior of β -Cu₂Se as a function of temperature (see calculation details in Methodology Section). Figure 4 shows the temperature-dependent atomic trajectories of Cu and Se atoms in β -Cu₂Se obtained from the equilibrium AIMD simulations. Unique lattice dynamics

Figure 5: Thermal evolution of β -Cu₂Se structure. (a) Temperature variations of three bond lengths (Cu-Cu, Cu-Se, and Se-Se) in disordered Cu₂Se from AIMD simulations. The vertical arrows demonstrates the extent of structural disorder. (b) Temperature-dependent partial and total structure factors. (c) The temperature dependence of the amplitude of the structure factor with a linear approximation between two glass transition points. Total and projected quantities are also shown. The straight dotted guide-line shows the general trend for each. Shaded areas shows temperature regimes.

features reported in the literature [5, 6, 7, 9, 10] are successfully reproduced: the Cu atoms are highly disordered, while the Se atoms nearly remain in their rigid framework. Based on these AIMD results, the temperature-dependent bond length (r) of various atoms in β -Cu₂Se atoms are calculated [Fig. 5(a)]. For the Cu atoms, the multiple interstitial sites are accessed, and their bond lengths are much reduced (at $T = 500$ K, $r_{\text{Cu-Cu}}$ is 2.94 and 2.60 Å for ideal symmetry and distorted structure, respectively) and decreases with temperature (at $T = 1100$ K, $r_{\text{Cu-Cu}}$ is 2.56 Å). This feature is also observed in another Cu related bond length, $r_{\text{Cu-Se}}$, while $r_{\text{Se-Se}}$ follows the pure thermal-expanded symmetrical structure. The atomic trajectories of Cu atoms become random and some migration among site occurs, but for the Se atoms below 900 K this is much limited (because of larger ion size and no notable interstitial sites). Such findings are consistent with the qualitative understanding of β -Cu₂Se lattice dynamics. Also, we expect formation of the homopolar Cu-Cu bond in high-temperature structural distortion because predicted $r_{\text{Cu-Cu}}$ is surprisingly in agreement with that of Cu metal [2.56 Å at 500 K [24], dash-dot line in Fig. 5(a)].

This supports the hypothesis we stated above, and will be verified with TEM-EELS studies in the following Section. Quantitatively, we also analyze

the structural transitions of β -Cu₂Se with the structure factor $S(\mathbf{q})$, i.e.,

$$S(\mathbf{q}) = \sum_{n=1}^{N_{\text{u.c.}}} f_n \exp(i\mathbf{q} \cdot \mathbf{r}_n), \quad (2)$$

where $\mathbf{q}$ is the wave vector, $\mathbf{r}$ is the position vector, and f is the atomic scattering factor, are calculated with equilibrium AIMD [Fig. 5(b)]. As expected, the $S(\mathbf{q})$ of a perfect crystal is represented as a series of sharp peaks at the designated wave vectors, while the thermal disordered structure gives broad and shifted (to lower $\mathbf{q}$) peaks. The peaks associated with Cu-Cu and Cu-Se bonds are observed at $3 \text{ \AA}^{-1}$, while Se-Se correlations give $\sim 1.9 \text{ \AA}^{-1}$. The second sharp diffraction peak (at $3 \text{ \AA}^{-1}$) in $S_{\text{Cu-Cu}}(\mathbf{q})$ and $S_{\text{Cu-Se}}(\mathbf{q})$ is reduced to unity close to its asymptotic limit. These changes suggest significant alteration of the spatial periodicity of Cu-related bonds in the β -Cu₂Se structure. We suggest marking this Cu thermal disorder, as $T_{g,\text{I}} \sim 800 \text{ K}$, observed in the expansion measurement and becomes more pronounced for $T > 700 \text{ K}$ [Cu-Cu panel in Fig. 5(b)]. The Se-Se correlations among the nearest neighbors persist in $S_{\text{Se-Se}}(\mathbf{q})$, and Se-Se framework is still persistent to 1000 K. Similarly, we find a close relation between the Se atoms thermal disorder and mark $T_{g,\text{II}} \sim 1000 \text{ K}$, by interpreting the peak transitions in Fig. 5(b) (Se-Se panel). Since the logarithm of the intensity of the diffraction peaks is proportional to the Debye-Waller factor and decreases linearly with temperature [25], we use the squared modulus of $S(\mathbf{q})$ to analyze this transition [26]

$$|S'_i(\mathbf{q})|^2 = \frac{1}{f_i^2 N^2} \left\{ \left[\sum_{n=1}^N f_i \cos(\mathbf{q} \cdot \mathbf{r}_n) \right]^2 + \left[\sum_{n=1}^N f_i \sin(\mathbf{q} \cdot \mathbf{r}_n) \right]^2 \right\}. \quad (3)$$

This structural amplitude is strictly unity only at 0 K and has a clear linearity in single-phase system, while it is close to zero for liquid phase and its linearity is deflected at the phase transition temperature. The thermal evolution of $|S'_i(\mathbf{q})|^2$ confirms the heterogeneous phase transition of β -Cu₂Se (for Cu- and Se-related bond, $T_g \sim 800$ and 1000 K), as observed in Fig. 5(c).

3.3. Chemical and electronic state analysis

The presence of these thermal structure heterogeneities are verified with chemical and electronic states analyses. These are done using (i) *in-situ* TEM

Figure 6: TEM-EELS experimental results on β -Cu₂Se. (a) The $\{111\}$ cubic plane showing a layered structure. (b) Inverse pole figure map showing the crystal orientation (parallel to the sample normal) of individual grains. The rolling direction of circled area is close to $\{221\}$, not exactly normal to $\{111\}$. (c) The *in-situ* TEM images taken at 300 and 773 K. (d) Temperature dependence of L_2 and L_3 core-loss edges in EELS for four temperatures. Distinct peak positions of each ionic state of Cu atom are shaded with dashed line and color.

with sample-temperature control and (ii) EELS. Before TEM-EELS characterization, the sample was a bulk slab, and its crystal orientation identified with electron back-scatter diffraction (EBSD) technique. The $\{111\}$ cubic plane, a layered structure owing to alternating segregation of Cu and Se atoms, is most relevant for the TEM-EELS analyses of β -Cu₂Se [see Fig. 6(a)]. The final EBSD mapping results shown in Fig. 6(b) provide crystal orientations of all grains. The circled blue region corresponds normal direction parallel to $\{111\}$ with an error of 12.5° . This region was milled with a focused ion beam to prepare for the *in-situ* TEM-EELS and Fig. 6(c) shows the images at two elevated temperatures. Other than carbon deposited on the ultra-thin sample edges, no significant physical change is observed, which is required to reduce uncertainties.

As we expected, Cu and its compounds show distinct EELS spectra [7, 27, 28]. Our EELS characterizations find changes in the L_2 and L_3 core-loss edges of β -Cu₂Se, as shown in Fig. 6(d). (i) As temperature increases, the EELS spectra above 980 eV have diminishing decay and reach a plateau for T

≥ 773 K. This abnormal decay can be associated with the multiple scattering of the high-temperature structure, while single scattering occurs in the low-temperature structure. (ii) Broader L_3 and L_2 peaks (or larger shoulder) are observed, while the L_3/L_2 magnitude ratio becomes smaller, with increase in temperature. (iii) The magnitude of Cu^0 peak (i.e., right edges of L_3 and L_2 shadow region) becomes stronger as temperature increases. Comparing these thermal evolutions with the conventional EELS observations of different Cu ionic states [27, 28], we draw close analogies between them. The fine structure of the low-temperature structure and the Cu ions (e.g., Cu^+ or Cu^{2+}) [7, 27, 28] result in relatively sharp edges for L_3 and L_2 , while the weak (or broad) L_3 and L_2 ionization edges appear in the high-temperature structure and Cu metal [27, 28]. The changes in Cu ionic states result in similar variations in the white-line ratio L_3/L_2 . From these analogies we conclude that the ionic states of Cu in $\beta\text{-Cu}_2\text{Se}$ depend on temperature and that $T \sim 773$ K (similar to $T_{g,I}$) is the threshold temperature for Cu disorder, i.e., presence of Cu^0 (Cu-Cu direct bond) for $T > T_{g,I}$, and Cu^+ for $T < T_{g,I}$.

3.4. Lattice thermal conductivity

The homopolar Cu-Cu bonds, two structural transitions, and related anomalous thermophysical properties of $\beta\text{-Cu}_2\text{Se}$ result in significant suppression of lattice thermal conductivity κ_L , reaching the limit of liquid thermal conductivity (κ_{liquid}). As noted in Methodology Section, we use the NEAIMD simulations and verify this observed suppression of lattice thermal conductivity. Computational details are presented in Methodology Section. Using three different simulation cell lengths l , we verify the expected size effect and extrapolate the lattice thermal conductivity for the infinite structure with the linear extrapolation of their reciprocal relation, $1/\kappa_L = 1/\kappa_{L,\infty} + c/l$, where c is constant [19]. Figure 7(a) shows the l dependence of the calculated κ_L and their extrapolation to very large l , for several temperatures. Due to the extensive computation time for NEAIMD simulations, we use limited cell volumes. The uncertainties associated with the linear extrapolation of the limited data sets are shown with error bars in Fig. 7(b).

The variations of the predicted lattice thermal conductivity, as a function of temperature, are shown in Fig. 7(b), and are in favorable agreement with experiments [5, 6, 9]. The predicted lattice thermal conductivity is constant for $T < T_{g,I}$, and decreases for $T > T_{g,I}$, while the bulk, homogeneous crystals is expected to be dominated by the interphonon scattering and follow the T^{-1} dependence [32]. The minimum (amorphous-solid) thermal conductivity κ_{min}

Figure 7: Predicted lattice thermal conductivity from NEAIMD simulations. (a) Variations of inverse of the predicted κ_L with respect to inverse of the supercell size, for three different temperatures. (b) The predicted κ_L variations with respect to temperature, and comparison with our and available experimental result [5], and with amorphous-solid minimum [29], liquid thermal conductivity [21, 30, 31], and the Slack relation [21]. All predictions use the relevant, temperature-dependent properties from our measurements and predictions in Fig. 3 and the literature [5, 10]. The $\kappa_{\min}$ is decomposed into the longitudinal (L) and transverse (T) components. The κ_{liquid} is $3k_B u_f / l_f^2$, where u_f is the sound speed $(B/\rho)^{1/2}$, l_f is the mean inter-molecular distance $(V_{\text{u.c.}}/4)^{1/3}$, and λ_p is $3l_f$ [21, 30, 31].

based on the phonon mean-free-path (λ_p) of one-half of its phonon wavelength [29] is also shown in Fig. 7(b), with its decomposition. The NEAIMD κ_L for $T < T_{g,I}$ is in general agreement with the total $\kappa_{\min}$, indicating significant Cu^+ disorder and homopolar Cu-Cu bond formation noted in the above. Despite stable Se framework, the interstitial random-distribution of Cu^+ ions and reduction in bond lengths reaching interatomic separation of metallic Cu result in large suppression of phonon transport, approaching $\kappa_{\min}$. Applying the Bridgman theory for κ_{liquid} based on liquid analogy to lattice [30, 31, 21], another lower limit to phonon transport is κ_{liquid} . As shown in Fig. 7(b), the κ_{liquid} model predicts a value slightly lower than $\kappa_{\min}$ for $T < T_{g,I}$ and close to $\kappa_{\min,L}$ for $T > T_{g,II}$. We consider this as an additional phonon suppression due to the atomic fluidity of $\beta\text{-Cu}_2\text{Se}$ beyond $T_{g,I}$. This is consistent with the principle of sound waves in fluids having longitudinal component only (not supporting shear stress). The NEAIMD results approach $\kappa_{\min,L}$ and κ_{liquid} and supports this fluidity limit. The suggested two glass transitions

of β -Cu₂Se, correlate well with the anomalous changes in lattice thermal conductivity toward these limits.

4. Conclusions

In summary, the temperature-dependent lattice dynamics and the measured thermal expansion of β -Cu₂Se show large interstitial displacement of the Cu⁺ ions and presence of two distinct glass transition temperatures associated with the two elements. These heterogeneous evolutions result in significant suppression of the phonon transport (i.e., temperature-independent lattice thermal conductivity approaching κ_{liquid}). These results provide new strategy and direction for achieving superior thermal insulators, thermal data storage devices, and TE materials.

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