Diverse lattice dynamics in ternary Cu-Sb-Se compounds

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Searching and designing materials with extremely low lattice thermal conductivity (LTC) has attracted considerable attention in material sciences. Here we systematically demonstrate the diverse lattice dynamics of the ternary Cu-Sb-Se compounds due to the different chemical-bond environments. For Cu3SbSe4 and CuSbSe2, the chemical bond strength is nearly equally distributed in crystalline bulk, and all the atoms are constrained to be around their equilibrium positions. Their thermal transport behaviors are well interpreted by the perturbative phonon-phonon interactions. While for Cu3SbSe3 with obvious chemical-bond hierarchy, one type of atoms is weakly bonded with surrounding atoms, which leads the structure to the part-crystalline state. The part-crystalline state makes a great contribution to the reduction of thermal conductivity that can only be effectively described by including a rattling-like scattering process in addition to the perturbative method. Current results may inspire new approaches to designing materials with low lattice thermal conductivities for high-performance thermoelectric conversion and thermal barrier coatings.

Designing novel and efficient energy-conversion materials has been of great importance in extricating the predicaments of global energy shortage and underutilization of energy resources. Thermoelectric (TE) materials are capable of converting waste heat directly into electricity1. The performance of a TE material is governed by the dimensionless figure of merit, defined as \( ZT = TS^2/\kappa \sigma \), where \( T \) is the absolute temperature, \( S \) the Seebeck coefficient, \( \sigma \) the electrical conductivity, and \( \kappa \) the thermal conductivity. The \( \kappa \) includes the lattice and the electronic components. One effective way to improve \( ZT \) is to reduce the \( \kappa \), especially the lattice thermal conductivity (LTC), via enhancing phonon scattering rates2-7. In our previous study8, a concept of part-crystalline part-liquid (PCPL) state was proposed. Materials in such a state, manifesting the coexistence of rigid crystalline sublattices and fluctuating noncrystalline substructures, are very likely to possess extremely low LTCs, which can be treated as potentially promising TE materials.

Investigating intrinsic crystal structures and corresponding lattice dynamic properties is conducive to understanding the differences between crystalline and PCPL materials. Ternary Cu-Sb-Se materials (Cu3SbSe4, CuSbSe2, and Cu3SbSe3) provide a suitable platform, as they are composed by the same elements but present distinct crystal structures, and consequently dissimilar thermal transport properties9. Their intrinsically low LTCs are gratifying for TE conversion, especially the extremely low LTC in Cu3SbSe310,11. The LTCs of Cu3SbSe4 and CuSbSe2 show a classical temperature dependence of \( T^{-1} \), while that of Cu3SbSe3 is nearly temperature-independent10. Such an abnormal thermal transport behavior has also been found in many other material systems, such as Cu3Se10,13, AgSbTe214-16 and \( \beta \)-K2Bi8Se1317. Different interpretations have been proposed to qualitatively explain these anomalous low intrinsic LTC, including strong anharmonicity18,19, lone \( s^2 \) pair interaction14,15,17, and complex compositions17,20. However, the physical origin of the low LTC is still a riddle in respect of lattice dynamics. Based on

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**Results and Discussion**

**Crystal structures and dynamic behaviors.** The calculated equilibrium lattice constants for Cu$_3$SbSe$_4$ ($a = b = 5.736$ Å and $c = 11.411$ Å), CuSbSe$_2$ ($a = 6.467$ Å, $b = 4.045$ Å, and $c = 15.048$ Å) and Cu$_3$SbSe$_3$ ($a = 8.099$ Å, $b = 10.672$ Å, and $c = 6.936$ Å) are in good agreement with the experimental data$^{21,22}$ and a previous study$^{10}$. The compounds Cu$_3$SbSe$_4$ and CuSbSe$_2$ have the diamond-like structures, as shown in Fig. 1(a,b), with Cu atoms occupied in the center of Se-formed tetrahedrons. As shown in Fig. 1(c), Cu$_3$SbSe$_3$ has an orthorhombic crystal structure with the $Pnma$ space group. The Cu atoms mainly locate in the Se-formed tetrahedrons; however, the intrinsic structural channel allows Cu1 atoms to vibrate with large amplitudes around their equilibrium positions, especially in the $z$ direction. The key structural difference between Cu$_3$SbSe$_4$ and CuSbSe$_2$ is that the Sb atoms are whether disengaged from the tetrahedrons and the crystal structure is whether twisted due to the lone pair $s^2$-induced redistribution in the former compound. Though the sublattices of Cu atoms look similar among the three compounds, there is no intrinsic structural channel in Cu$_3$SbSe$_4$ or CuSbSe$_2$.

Figure 2 shows the trajectories of atoms from MD simulations at 400 K. For Cu$_3$SbSe$_4$ and CuSbSe$_2$, both Fig. 2(a,b) illustrate that all the atoms are constrained around their equilibrium positions, indicating that they are in the crystalline state. However for Cu$_3$SbSe$_3$ (Fig. 2(c)), the part-liquid sublattice appears from the liquid-like random diffusion of Cu atoms, whereas the Se and Sb atoms are constrained around their equilibrium positions. The compound is thus in a mixed part-crystalline part-liquid state, containing one crystalline rigid part and the other liquid fluctuating sublattice$^8$. To gain a better understanding about the origin of differentiated dynamic behaviors in these ternary compounds, the chemical-bond strength should be investigated.

**Atomic displacement parameter (ADP),** which is defined as the mean-square amplitude of vibration of an atom around its equilibrium position, is calculated based on full phonon dispersions$^{8,23}$. A relatively larger ADP value generally means that the corresponding atom vibrates more about its equilibrium position than other atoms, physically implicating the weak restoring forces on the vibrating atoms due to the existence of the weak bonding$^{24,25}$. The ADPs of the atoms in Cu$_3$SbSe$_4$ and CuSbSe$_2$ are almost in the homogenous level ($<0.02$ Å$^2$), as shown in Fig. 3(a,b), respectively. None of the atoms in the two compounds is relatively weakly bonded, and consequently their melting points should be comparable.
due to the nonhierarchical chemical bonds, according to the classical Lindemann criterion of melting.\cite{26} However, as shown in Fig. 3(c), the calculated ADP data of Cu1 atoms in the z direction (Cu1_z) is at least twice larger than those for other species in Cu_3SbSe_3. The Cu1_z accordingly are weakly bonded, and thus the compound reveals bonding strength hierarchy and atomic-level inhomogeneity. The melting state firstly occurs in the Cu1_z-participated sublattice as the temperature increases. Similar behaviors can be observed in the Cu2 atoms due to their large ADP values along the x and z directions. In this regard, the appearance of the mixed PCPL state in Cu_3SbSe_3, as also represented in Fig. 2(c), is ascribed to the bonding strength hierarchy. Indeed, the experimental melting points of Cu_3SbSe_4 and CuSbSe_2 are about 730 K\textsuperscript{27} and 750 K\textsuperscript{28}, respectively, which demonstrates the typical crystalline character and homogeneous bonding strength in the two systems. Furthermore, the order-disorder transition of Cu atoms in Cu_3SbSe_3 was observed at finite temperatures.\textsuperscript{29,30} Bonding strength hierarchy thus becomes an indicator of the appearance of part-crystalline state.

**Harmonic and anharmonic properties.** Accordingly, investigating both harmonic and anharmonic phonon interactions at low temperatures can render deep understandings for different types of Cu-Sb-Se compounds. In the model adopted for calculating the LTC, three physical parameters (Debye temperatures, group velocities, and Grüneisen parameters) should be determined from several theoretical approximations, and the details are represented in Refs 8,10. For the three compounds, these parameters for each acoustic phonon mode were averaged by the weight of high-symmetry points, which are listed in Table 1. The CuSbSe\textsubscript{2} compound is a “transitional” structure, since it possesses the homogeneous bonding strength (or ADP values) similar to CuSbSe\textsubscript{3} and the lone pair s\textsuperscript{2} electrons similar to CuSbSe\textsubscript{4}. Harmonic properties, which are the reflections of the bonding stiffness including Debye temperatures and group velocities, of CuSbSe\textsubscript{2} correspondingly lie between those of CuSbSe\textsubscript{4} and CuSbSe\textsubscript{3}, as shown in Table 1.

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**Figure 2.** Trajectories of atoms from molecular dynamics simulations for (a) Cu\textsubscript{3}SbSe\textsubscript{4}, (b) CuSbSe\textsubscript{2}, and (c) Cu\textsubscript{3}SbSe\textsubscript{3} at 400 K.

**Figure 3.** Calculated atomic displacement parameters (ADP) for three compounds. For (c) Cu\textsubscript{3}SbSe\textsubscript{3}, the ADPs for Sb, Se, Cu2y, Cu1x, and Cu1y are within the belt region. The dashed line is for a guide for the eye.
The anharmonic properties, which cannot be characterized by either atomic trajectories or ADPs, are represented by the Grüneisen parameter ($\gamma$), which is related to the third-order (or even higher-order) anharmonic potential well. The intensity of phonon anharmonicity of CuSbSe$_2$ also lies between those of Cu$_3$SbSe$_4$ and Cu$_3$SbSe$_3$ (Table 1). To clarify the origins of phonon anharmonic interactions in Cu-Sb-Se compounds at low temperatures, partial Grüneisen parameters, describing the projected contributions from given atom types, are estimated by projecting the total Grüneisen parameter $\gamma(q, i)$ onto an atom type $\mu$ in the $\alpha$ direction as follows

$$\gamma_{\mu}^\alpha(q, i) = \sum_{\nu \in \mu} \gamma(q, i) \times |e_{\alpha}(q, i, \nu)|^2$$

(1)

where $e_{\alpha}(q, i, \nu)$ is the phonon polarization vector of a set of atoms $\nu$ derived from the dynamical matrix, $i$ the phonon mode, and $q$ the wave vector. The averaged partial Grüneisen parameters for transverse acoustic (TA with a lower group velocity and TA' with a higher one) and longitudinal acoustic (LA) modes are calculated by $\gamma^\alpha_{\mu} = \gamma^\alpha(q, i) = \frac{\omega^\alpha_{\mu}(q, i)}{\omega^\alpha_{\nu}(q, i)}$, where $\omega^\alpha_{\mu}(q, i)$ is the phonon frequency of the $\mu$-th atom type in the $\alpha$ direction and $\omega^\alpha_{\nu}(q, i)$ is the phonon frequency of the $\nu$-th atom type in the $\alpha$ direction. The expended volume of 105% for the strained phonon calculations was used.

Table 1. Debye temperature ($\theta$), group velocities ($v$), and averaged Grüneisen parameters ($\gamma$) for the three compounds. The average Grüneisen parameters are calculated by $\gamma = \sqrt{\frac{1}{\omega^2} \frac{\partial}{\partial \ln V} \ln \omega^2}$, where $\omega$ and $V$ are the wave vector and the equilibrium volume, respectively. The expended volume of 105% for the strained phonon calculations was used.

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overwhelmingly contributed by the $\varepsilon$ component, which is consistent with the abnormal large Cu$_1$z ADP and the liquid-like fluctuation behavior at finite temperatures.

**Lattice thermal conductivity.** By using the harmonic and anharmonic parameters given in Table 1 and the modified Debye-Callaway model, the LTCs can be estimated for the three compounds. Based on the aforementioned analysis, it should be rational to treat bond-homogenous Cu$_3$SbSe$_4$ and CuSbSe$_2$ compounds as traditional crystalline solids, and the corresponding thermal transport behaviors are expected to be described by the classical perturbation techniques. As shown in Fig. 5(a,b), the theoretical temperature dependences ($\sim T^{-1}$) show acceptable agreements with the experimental data by only considering the U and N processes for total phonon scattering rates. The slightly overestimation of the phonon-phonon interaction strength for the CuSbSe$_2$ compound should be attributed to the inaccurate estimates by using three-phonon processes for the higher-order nonlinear correction caused by the lone pair $s^2$ electrons. Generally, the well-fitted temperature dependence indicates that the anharmonic effect of the extra electrostatic repulsion given by unbonded electrons can still be described effectively by the U and N processes, which also corroborates the rationality of estimating LTCs of crystalline solids by the perturbative phonon-phonon interactions. For the hierarchically bonded Cu$_5$SbSe$_9$, the experimental LTC data (Fig. 5(c)) demonstrate a nearly-temperature-independent nature, which significantly deviates from the classical $T^{-1}$ relationship. A resonant-like phonon scattering rate ($\tau_\omega = 1/C\omega^2/(\omega_0^2 - \omega^2)^2 + \Delta^2$) (rattling-like frequency $\omega_0 = 1.0$ THz, effective width $\Delta = 0.2$ THz, and rattling-concentration-related parameter $C$), which approximately describes the rattling-like thermal damping in the PCPL Cu$_5$SbSe$_9$, should be considered in addition to the other phonon scattering processes, including perturbative phonon-phonon U and N processes. The calculated LTC (Fig. 5(c)) accordingly displays an excellent agreement with the experiment in a wide temperature range.

**Summary**

In summary, the three Cu-Sb-Se compounds exhibit significantly different lattice dynamic behaviors due to the different chemical-bond environments. Cu$_3$SbSe$_4$ and CuSbSe$_2$ compounds are both in the crystalline state due to the homogeneous bonding strength, while the Cu$_5$SbSe$_9$ compound with chemical-bond hierarchy is in the part-crystalline part-liquid hybrid state at elevated temperatures. Harmonic and anharmonic properties vary with respect to the different crystal structures among Cu$_3$SbSe$_4$, CuSbSe$_2$, and Cu$_5$SbSe$_9$ at low temperatures. For the close-packed diamond-like Cu$_5$SbSe$_9$, the phonon anharmonic interactions mainly originate from the Se atoms in the frameworks. While for CuSbSe$_2$, the Sb$^{3+}$ ions with lone pair $s^2$ electrons dominate the anharmonicity by introducing an extra electrostatic repulsion. The weakly bonded Cu atoms in Cu$_5$SbSe$_9$, especially the Cu$_1$ atoms, have a great influence on phonon-phonon anharmonic processes. For the description of thermal transport, traditional perturbative phonon-phonon interactions well depict LTCs of crystalline bulks (Cu$_3$SbSe$_4$ and CuSbSe$_2$), whereas a rattling-like effective approach should be adopted in addition to the total scattering rate for the PCPL Cu$_5$SbSe$_9$ compound. Our analyses reveal the diverse lattice dynamics in the crystalline and PCPL Cu-Sb-Se materials, which may inspire additional approaches to designing materials with low LTCs for high-performance TE conversion.

**Methods**

The first-principles calculations were performed in the framework of the density-functional theory using the plane wave basis VASP code, implementing the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) form. The interactions between the ions and electrons were described by the all-electron projector augmented wave (PAW) method with plane waves up to a cutoff energy of 600 eV. The atomic configurations 3d$^{10}$4s$^2$ for Cu, 5s$^2$5p$^3$ for Sb, and 4s$^2$4p$^4$ for Se atoms were treated as the valence electrons. The Brillouin-zone integrations were performed on the grid of Monkhorst-Pack.
procedure. For the unit cell of Cu₃SbSe₄, CuSbSe₂, and Cu₃SbSe₄, 4 × 3 × 4, 4 × 6 × 2, and 5 × 5 × 3 k-point meshes were used, respectively. To calculate the phonon dispersion curves, we used the direct ab initio force-constant approach, which is implemented in the PHONON software by Parlinski et al. Supercells with dimensions of 2 × 1 × 2, 2 × 3 × 1, and 2 × 2 × 1 were used for Cu₃SbSe₄, CuSbSe₂, and Cu₃SbSe₄, respectively. High-symmetry points in Brillouin zones (Γ (0, 0, 0), Z (0.5, 0, 0), N (0.5, 0, 0), P (0.25, 0.25, 0.25), X (0, 0.5, 0.5) for CuSbSe₂, Γ (0, 0, 0), Z (0, 0, 0.5), X (0.5, 0, 0), U (0.5, 0, 0.5), Y (0, 0.5, 0) for Cu₃SbSe₄, and Γ (0, 0, 0), R (0.5, 0.5, 0.5), S (0.5, 0.5, 0), T (0, 0.5, 0.5) for Cu₃SbSe₄) were considered in our phonon dispersion and Grüneisen parameter calculations. The ADP values are calculated based on the partial phonon density of states from DFT calculations. Molecular dynamics (MD) calculations were performed using the GGA of PBE form as implemented in the VASP code with the NVT ensemble. The PAW method was adopted, and supercells with 112 atoms (16.20 Å × 10.67 Å × 13.87 Å), 192 atoms (19.40 Å × 16.18 Å × 15.05 Å), and 64 atoms (11.47 Å × 11.47 Å × 11.41 Å) were used for Cu₃SbSe₄, CuSbSe₂, and Cu₃SbSe₄, respectively.

To calculate the LTC in nonlinear phonon scattering, the Debye-Callaway model modified by Asen-Palmer et al. was applied, which can be expressed as

$$\kappa_i = \frac{1}{3} \frac{k_B}{2\pi^2 v_i} \left( \frac{k_BT}{h} \right)^3 \int_0^{\theta_i} \frac{x^4 e^x}{(e^x - 1)^2} dx + \left[ \frac{2}{\tau_{\text{total}}^{\text{N}}} \frac{x^4 e^x}{(e^x - 1)^2} \right] \right| \int_0^{\theta_i} \frac{dx}{\tau_{\text{total}}^{\text{N}}} \frac{x^4 e^x}{(e^x - 1)^2} dx \right),$$

where $k_B$, $v_i$, $\theta_i$, and $\tau$ are the Boltzmann constant, phonon group velocity, Debye temperature and phonon relaxation time, respectively. Here $i$ corresponds to the TA, TA’, or LA mode, while $x = \hbar\omega/k_B T$. $U$ and $N$ stand for the phonon-phonon Umklapp and Normal processes, respectively, and further details of these expressions are included in Refs 8,40,41. In an ideal semiconductor, the scattering rates in the two processes are both considered to be proportional to $\gamma^2$ according to traditional theories, with $\gamma$ being the Grüneisen parameter.

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X.K., J.Y. and W.Z. designed research; W.Q., L.W. and X.K. performed research; W.Q., X.K. and W.Z. analyzed data; and X.K., J.Y. and W.Z. wrote the paper.

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