Thermal conductivity switch: Optimal semiconductor/metal melting transition

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Scrutinizing distinct solid/liquid (s/l) and solid/solid (s/s) phase transitions (passive transitions) for large change in bulk (and homogenous) thermal conductivity, we find the s/l semiconductor/metal (S/M) transition produces the largest dimensionless thermal conductivity switch (TCS) figure of merit Z_{TCS} (change in thermal conductivity divided by smaller conductivity). At melting temperature, the solid phonon and liquid molecular thermal conductivities are comparable and generally small, so the TCS requires localized electron solid and delocalized electron liquid states. For cyclic phase reversibility, the congruent phase transition (no change in composition) is as important as the thermal transport. We identify XSB and XAs (X = Al, Cd, Ga, In, Zn) and describe atomic-structural metrics for large Z_{TCS}, then show the superiority of S/M phonon- to electron-dominated transport melting transition. We use existing experimental results and theoretical and \textit{ab initio} calculations of the related properties for both phases (including the Kubo-Greenwood and Bridgman formulations of liquid conductivities). The 5p orbital of Sb contributes to the semiconductor behavior in the solid-phase band gap and upon disorder and bond-length changes in the liquid phase this changes to metallic, creating the large contrast in thermal conductivity. The charge density distribution, electronic localization function, and electron density of states are used to mark this S/M transition. For optimal TCS, we examine the elemental selection from the transition, basic, and semimetals and semiconductor groups. For CdSb, addition of residual Ag suppresses the bipolar conductivity and its Z_{TCS} is over 7, and for ZnSb$_2$ it is expected to be over 14, based on the structure and transport properties of the better-known \( \beta \)-Zn$_4$Sb$_5$. This is the highest Z_{TCS} identified. In addition to the metallic melting, the high Z_{TCS} is due to the electron-poor nature of II-V semiconductors, leading to the significantly low phonon conductivity.

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I. INTRODUCTION

The thermal conductivity switch (TCS) is the phenomenon of significant change in thermal conductivity at a distinct temperature, under an external field, or by other means. The TCS performance may be assessed by the ratio of this temperature, under an external field, or by other means. of significant change in thermal conductivity at a distinct

\[
\Delta k / k_{\text{min}} = Z_{\text{TCS}},
\]

which is called the TCS figure of merit here. The \( \Delta k \) mechanisms are classified in detail in Sec. II by thorough examination of the various thermal energy carriers, namely, phonon, electron (and hole), fluid particle and photon, and transitions. The phonon conductivity (\( k_p \)) in the solid phase increases as \( T^3 \) at low temperatures (<0.1 \( T_D \), Debye temperature) due to the increase in specific heat and decreases as \( T^{-1} \) at high temperatures, mainly due to dominant phonon-phonon scattering (mostly by the Umklapp processes) [1]. So, \( k_p \) becomes rather small near the melting temperature (\( T_{sl} \)). After melting, the fluid (liquid or melt) particles replaces the solid phonons with the fluid-particle thermal conductivity \( k_f \), which is lower but generally comparable to \( k_p \) at \( T_{sl} \), as the softened lattice turns into random structure of liquid.

The electronic thermal conductivity (\( k_e \)) increases from dielectrics to semiconductors to metals and for metals it becomes independent of temperature near \( T_D \) [1]; for intrinsic semiconductors it increases with temperature (increase in

The conduction electron density \( n_{e,c} \)) [2] unless the electron mobility \( \mu_e \) significantly decreases with temperature. The \( k_e \) for semiconductors is much smaller than that of metals, through the generally accepted (even for semiconductors) Wiedemann-Franz (W-F) law (\( k_e = N_L T \sigma_e \), where \( N_L \) is the Lorentz number and \( \sigma_e \) is the electrical conductivity), which is also applicable to liquids. So, we expect at melting TCS to have a large \( \Delta k \) when this change is dominated by \( \Delta k_e \) (i.e., \( \Delta \sigma_e \)) in the transition.

There is also thermal conductivity contribution from the bipolar (combined electron-hole) thermal conductivity (\( k_{e+h} \)) in the solid semiconductors, through bipolar diffusion of the thermally excited electron-hole pairs [3,4] transporting additional thermal energy [5]. The photon conductivity becomes important at high temperatures and when the photon absorption coefficient is not small, but generally the conduction electrons absorb photons and here we assume the absorption coefficient is large and \( k_{ph} \) is negligible. So, the total thermal conductivity in solid is \( k(s) = k_p + k_e + k_{e+h} \) and for liquid is \( k(l) = k_f + k_e \). Since \( k_{e+h} \) is band-gap and temperature dependent, it is negligible at low temperatures and then has an exponential temperature dependence [4,5]. So, \( Z_{TCS} \) can be limited through \( k_{\text{min}} = k(s) \) with non-negligible \( k_{e+h} \).

Here we review and classify the identified and the potential TCS materials and give some example of each. Then we seek optimal (high \( Z_{TCS} \)) materials, based on the thermal energy transport mechanisms mentioned above, and use \textit{ab initio} calculations and theoretical treatments to predict these transport properties and introduce the some high \( Z_{TCS} \) compounds based on melting transition.

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II. THERMAL CONDUCTIVITY SWITCHES (TCSs)

The $Z_{TCS}$ combines $\Delta k$ at a distinct temperature with large contrast before and after transition through the low $k_{\text{min}}$; i.e.,

$$Z_{TCS} = \frac{\Delta k}{k_{\text{min}}}, \text{ TCS figure of merit.} \quad (1)$$

The broad classification of the TCSs is shown in Fig. 1, and thermal conductivity changes and $Z_{TCS}$ for some notable materials with different transitions and mechanisms are shown in Fig. 2 at their distinct transition temperatures. Figure 2 gives the change in thermal conductivity (left axis) as well as $Z_{TCS}$ (right axis) and transition temperature (lower axis) for a range of materials. The TCSs are divided into passive or active based on the lack or existence of external forces or actions exerted on materials. For active, a distant force or mechanism causes the thermal conductivity jump. External forces, electric and magnetic fields, and stress can change the thermal conductivity of materials. Change in thermal conductivity has been observed under electric field in the bees wax during its solidifying [6]. The thermal conductivity of SrTiO3 increases by an applied electric field only below 50 K [7], because the transverse optical (TO) phonon mode degenerated with the longitudinal acoustic (LA) phonon mode is shifted upward by the electric field, weakening the TO-LA interaction, thus increasing the thermal conductivity. The orientation of a uniaxially aligned nematic liquid crystal (cyanobiphenyl, 5CB) changes due to an ac electric field [8] and because its thermal conductivity (albeit small) depends on its molecular orientation [9], it can act at TCSs.

The thermal conductivity of Cu wire is affected by magnetic field, with experiment at 4.2 K recording thermal conductivity decrease and in proportionality under such fields (and the W-F law holding) [10]. They also mentioned negligible field effect on resin, because of the phonon transport dominance (insulator). However, Jin et al. [11] have shown that phonons are also affected by magnetic field. They measured thermal conductivities of InSb around 3 K–10 K with and without magnetic field (7 T), concluding that the decrease in thermal conductivity (up to 12% at 5.2 K) is due the anharmonicity of the interatomic bonds under magnetic field. They hypothesize that only the Grüneisen parameter is affected by the field (verified by the ab initio calculations). Note that the effect disappears above 9 K.

Simulations have revealed that the thermal conductivity of a ferroic-twinned thin film can be controlled reversibly by mechanical stress [12]. The shear deformation induces the vertical (perpendicular to the heat-flow direction) twin boundaries between the fixed two horizontal twin boundaries in the plastic regime and the emerged boundaries hinder the heat flow by acting as phonon barriers, and the density of the boundaries can be controlled by the magnitude and direction of applied field.

The thermal conductivity of boron nanoribbon is changed at room temperature by wetting the interface with variable solutions [13,14]. Yang et al. [14] show that the thermal conductivity of double boron nanoribbon prepared with a mixture of reagent alcohol and deionized water increases, while that with isopropyl alcohol remains the same as that of single boron nanoribbon. To enhance the heat transfer in the film boiling regime, where the heat transfer rate is significantly reduced due to the Leidenfrost effect, it is suggested to attract the slightly levitated liquid (conducting) droplet by a concentrated electric in the gap and decreasing the vapor gap thermal resistance [15]. For thermal controller in small satellites, a MicroElectroMechanical System (MEMS) thermal switch radiator is suggested [16] using a suspended thin membrane with a high emittance coating which contacts with the substrate when a sufficient electric field is applied (heat is emitted into space through the membrane while it is on). Also, Jia et al. [17,18] suggest microdevices of liquid-solid thermal

![Thermal Conductivity Switch (TCS)](image)

FIG. 1. Classification of thermal conductivity switches (TCSs) with some example materials. The active switches require an external force field or action and are divided based on that mechanism. In passive switches, rectification presents solid-state devices, while others are classified based on the phase transition and the mechanisms of the thermal conductivity jump.
FIG. 2. Thermal conductivity switch (change) $|\Delta k|$ (left axis, blue) and TCS figure of merit $|Z_{TCS}|$ (right axis, red) for some materials at distinct temperatures. The TCS mechanisms and the phase transitions are also shown. D is for dielectric, S is for semiconductor, M is for metal, s is for solid, and l is for liquid. The negative $Z_{TCS}$ indicates the decrease in thermal conductivity upon melting. Two of the highest $Z_{TCS}$ materials, namely, the Ag-added CdSb and Zn$_3$Sb$_2$, are marked (yellow). The four bond classifications are also shown.

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for a VO₂ beam was tested and the nanoscale asymmetric VO₂ beam, which has one narrow end width and the other wider with a uniform thickness, showed that a difference of the thermal conductance with respect to the heat transfer direction of up to 28%, below the transition temperature (340 K), while there is no difference above that temperature [25]. This temperature-gated thermal rectification for the active heat-flow control has been the highest rectification. A macroscopic thermal diode based on switchable thermal clocking can also control the thermal flow [26]. This device, which consists of alternating layers of copper and expanded polystyrene, blocks the heat in one direction whereas it conducts well in the opposite direction; thus, it acts as an electronic diode.

The s/s transitions are accompanied by atomic structure changes; for example, the structure of NbO₂ is changed from a distorted rutile structure under temperature transition (1080 K) to a undistorted rutile structure, and the thermal conductivity increases [27,28]. Also, VO₂ has a monoclinic structure at low temperature under 340 K, while it is tetragonal at higher temperatures [29,30]. During the structural transition of NbO₂ and VO₂, their σₑ increase undergoing semiconductor/metal (S/M) transition, increasing thermal conductivities as shown in Fig. 2. Liquid crystals have directional thermal conductivities and cyanobiphenyl (nCB) has s/s transition temperature (nematic below and isotropic above about 300 K) as the molecular arrangement changes [9]. It was found that the thermal conductivities of samples with a homeotropic orientation decrease at transition during heating, whereas those with a planar orientation increase, for n = 5–9 (ΔZ₁TCS < 0.5). Also, the highly drawn crystalline (C₆H₄)n (polyethylene) is predicted (classical molecular dynamics) to decrease distinctly in thermal conductivity at 397 K [31] and is a dielectric/dielectric (D/D) transition.

The s/l phase transition (melting/solidification) can change the thermal conductivity though Δkₑ and kₚ/kₙ due to the absence of distinct lattice in liquid atomic structures (more pronounced than the s/s transitions). Although the kₚ and the kₙ contribute to the Δkₑ, the Δkₑ can be much more effective, so s/l phase transition is classified as D/D, S/S, S/M, and M/M. This is only the electronic mechanism, but it shows the lattice contribution as well as characteristics of each transition. For example, all the TCS with D/D and S/S in Fig. 2 possess negative Z₁TCS; i.e., kₚ > kₙ and without the significant increase in σₑ. However, all the S/M TCS (including the s/s transitions, e.g., NbO₂ and VO₂) possess positive Z₁TCS resulting from the substantial, positive Δkₑ, which overcomes kₚ > kₙ, due to the melting into metal. The elemental metals show M/M transition upon melting and have negative Z₁TCS (except Bi [33]) because the electron mobility decreases significantly upon melting.

### III. HIGH Z₁TCS WITH SEMICONDUCTOR/METAL (S/M) CONGRUENT MELTING TRANSITION

While large change in the thermal conductivity at a distinct temperature is important, it is also important for the TCS materials to have large contrast in conductivity, i.e., high ratio of thermal conductivity so the heat flux undergoes major change upon transition. So, it is required to have low kₘₐₓ. The s/l TCS should have congruent melting composition to ensure the reversibility for the cyclic melting/solidification. Here, to achieve the highest Z₁TCS, we consider the passive switch with bulk material (no size effects) and examine each mechanism within this area for the best TCS.

The s/s transitions present a rather small change in the thermal conductivity (small Z₁TCS), i.e., the increase in kₑ due to solid-state atomic structure transition does not notably affect to the thermal conductivity. Also, although the predicted high-draw-ratio crystalline (C₆H₄)n (polyethylene) shows high Z₁TCS [31], the conventional polyethylene has a very low thermal conductivity (0.5 W/mK) [58]. Therefore, in general, it appears that the s/s transitions cannot yield high Z₁TCS, although it should be mentioned that the high Z₁TCS s/l transitions seem to be limited to high Tₛₜ; thus, some materials with these s/s transitions may be attractive.

Among the s/l transitions, the D/D and S/S transitions yield rather small change in thermal conductivity, as shown in Fig. 2. Although some of the examples show relatively large Z₁TCS, it is due to the rather small kₘₐₓ, so their kₑ (kₘₐₓ + Δkₑ) does not exceed a few W/mK. The transition temperature depends on the bond type (molecular, ionic, metallic, or covalent), and those are shown below the graph (Fig. 2). The ionic solids which have high Tₛₜ lack significant free electrons and so are poor conductors, e.g., NaF with relatively high Z₁TCS among ionic solids. The molecular solids have strong intramolecular forces and thus are electric insulators, but have low Tₛₜ due to weak intermolecular forces. The organic compounds and halogens are examples of molecular solids. The σₑ of ionic solids increases during melting, but is <10(Ω cm)⁻¹ [39], so kₑ gives negligible contribution. The Z₁TCS of molecular and ionic solids are not high [39,59] and are generally negative, as mentioned before.

From the kinetic theory, for molecular solids with a D/D mechanism (negligible kₚ contribution), the ratio of the kₚ to kₙ at Tₛₜ can be approximated as the ratio of the speed of sound in solid and liquid, considering that their the density, specific heat, and mean free path remain the same [59],

$$\frac{kₚ}{kₙ} \approx \frac{\omega_p}{\omega_f} \approx \frac{1}{\Delta \Omega^{1/3}} \exp \left( \frac{ΔS_m}{3k_B} \right).$$

where \(ω = u/d\) (u is the mechanical wave speed and d is the mean atomic space), \(Ω\) is ordering factor to show the difference in the degree of ordering between phases, \(S_m\) is entropy of melting, and \(kB\) is the Boltzmann constant. So, Z₁TCS for molecular solids is related to ratio of the speed of sound in solid and liquid at Tₛₜ.

InSe has the highest Z₁TCS among the D/D and S/S transitions, i.e., 3.9. This is due to change between kₚ and kₙ, because the σₑ is low [60] and continuous across Tₛₜ [61]. Its solid σₑ increases with temperature and then decreases from 823 K up to the Tₛₜ (873 K). The phase diagram of the In-Se system [62] and the measured properties [63] show that a peritectic melting temperature (incongruent; a different solid phase occurs) of In₄Se₃ marks this transition (823 K). Also, InSe undergoes a peritectic melting at 873 K and passes the liquidus curve near 900 K (the melting and liquidus points may vary) [62–64]. Therefore, InSe is not a good TCS material due to its irreversibility (noncyclic) during the melting and solidifying.
congruently at 729 K \[62\]. The Ge, because the liquid (green curve in Fig. 3). The results show that the thermal conductivity (by 0.8 W

\( T \) causes a large increase in electronic thermal conductivity. Addition

\( T \) gives high thermal conductivity than its elements. It can be expected that the thermal conductivity is correlated with several properties which are also related to each other; thus, it is important to understand and find the relations of thermal conductivity and fundamental properties. Figure 4 renders such metrics of high \( Z_{\text{TCS}} \). For semiconductors the charge effective mass \( m_{i,e} \) (i = e or h: electron or hole) is proportional to the band gap \( (\Delta E_{e,g}) \) and the alloy composition, the static dielectric constant \( (\varepsilon_{e,g}) \) decreases linearly with \( \Delta E_{e,g} \), and \( \Delta E_{e,g}(T) \) is linear \((T > 150 K)\) with generally negative slope \[65\]. The effective mass influence the intrinsic charge carrier density \((n_1 \propto m_{i,e}^{-2/3})\) and mobility \((\mu_1 \propto m_{i,e}^{-1})\) \[2\].

A low \( T_D \) is preferred for TCS (low phonon conductivity), but the covalent bond needed for solid semiconductor means high \( T_{sl} \), which is proportional to the square of \( T_D \) \((T_D = C(M)T_{sl}^2)\), the Lindemann relation \[66\] for melting, where \( C(M) \) is the average atomic mass, \( d^3 = V_o \) is average volume per atom, and \( C \) is a constant) \[67\]. The strong bond leads to the high \( T_{sl} \) \[67\] and large \( \Delta E_{e,g} \) \[68\]. In the report \[68\], 18 III-V and II- VI compounds show that increase in the atomic number decreases \( T_{sl} \) and\( \Delta E_{e,g} \) due to expansion of the overlapped atomic potentials leading to the close coupling of the atoms (also, the higher is \( T_{sl} \), the larger is \( \Delta E_{e,g} \)).

Low \( k(s) \) leads to high \( Z_{\text{TCS}} \), and \( k_p \) increases with \( T_{sl} \) and decreases with increase in atomic-mass ratio of the constituents \[69\]. So, compounds with moderate and heavy elements result in high \( Z_{\text{TCS}} \). While large \( \Delta E_{e,g} \) gives small intrinsic \( k_e \), moderate \( \Delta E_{e,g} \) is sought to avoid high \( T_{sl} \). CdSb has \( \Delta E_{e,g} \) of 0.5 eV. However, the moderate \( \Delta E_{e,g} \) can result in significant \( k_{e+h} \) at high temperatures. So, intervention is needed to suppress \( k_{e+h} \). Although large \( \Delta E_{e,g} \) can give high \( Z_{\text{TCS}} \), but larger than 4.0 (AlSb in Fig. 5) may not be possible due to very large \( k_p \).

The simple estimation of the \( k_{e+h} \) is \[[70]\]

\[ k_{e+h} = A \exp \left( \frac{-E_{e,g}^*}{2k_B T} \right), \]

where \( A \) is a constant and \( E_{e,g}^* \) is the band gap for the bipolar diffusion. The relation shows that the \( k_{e+h} \) will not be negligible if the temperature is sufficiently high, so the \( k_{e+h} \) can be suppressed by increasing the band gap \[4,5\]. However, this increases \( T_{sl} \) and \( T_D \), increasing solid thermal conductivity. Rather, it is preferred for \( \Delta E_{e,g} \) to have a weak dependence on temperature (unlike CdSb) so that \( k_{e+h} \) can be less effective (less thermal excitation of electrons) at high temperature, but having the S/M transition upon melting. Also, \( k_{e+h} \) can be suppressed with the size effect \[71\]; the nano-PbS suppresses the \( k_e \) and \( k_{e+h} \) due to the electron scattering at high-density grain boundaries \[72\], but here

\[ \text{FIG. 3. Measured thermal conductivities of pure CdSb as a} \]

\[ \text{function of temperature. The semiconductor/metal transition at} \]

\[ T_{sl} \text{ causes a large increase in electronic thermal conductivity. Addition} \]

\[ \text{of 0.1% Ag to CdSb in the solid phase lowers the total thermal} \]

\[ \text{conductivity (by 0.8 W/mK at} \]

\[ T_o \text{).} \]
we remain with bulk homogeneous materials. In addition to the CdSb, small addition of Ag to PbSe reduces \( k_p \) by the point-defect scattering and electron-phonon coupling and \( k_{e+h} \) by increasing the hole (majority) density, leading to a decrease in the Seebeck coefficient \([48,73]\). This can be interpreted with the fact that the \( k_{e+h} \) is maximized when the \( \sigma_i \) contributions from electrons and holes are equal \([3]\); thus, the unbalancing \( \sigma_i \) can reduce the \( k_{e+h} \). Though, suppressing of \( k_{e+h} \) is effective with minority-carrier manipulation \([74]\); decrease in \( m_{i,c} \) (by doping) and \( \mu_i \) (by microstructure refinement or interface modification) of minority carriers reduces it \([5]\).

These show that \( k_{e+h} \) is minimized when the minority carriers are hindered from participating in conduction \([75]\). In the report \([75]\), band engineering with heterostructure barriers is suggested as a barrier for minority carriers, while the effect on majority carriers is negligible. So, doping for the unbalance by decreasing \( m_{i,e} \), \( \mu_i \), and \( n_{i,c} \) of the minority carrier and lowering the temperature dependence of \( \Delta E_{i,c} \) is effective in suppressing the \( k_{e+h} \), with the additional advantage to reducing \( k_p \) by the point-defect scattering.

The large change in \( \sigma_e \) at \( T_{sl} \) occurs when solid semiconductors makes a metal transition upon melting. This electron delocalization has history back in Wigner in 1938 suggesting that a free-electron gas should crystallize at low densities (localized in a nonconducting state), and Mott in 1949 discussed this transition (so-called Mott transition) with a crystalline array of monovalent atoms such that the array must be an insulator for large values of lattice parameter and a metal when it reaches a critical value \([76]\). According to the Mott transition \([76]\), the transition must be discontinuous because electron-hole pair can form because of their Coulomb attraction, \(-e^2/\epsilon_{e+h}r_{eh}\), where \( \epsilon_{e+h} \) is the background dielectric constant and \( r_{eh} \) is distance, and the binding energy of order \( m_e\epsilon^2/\hbar^2\epsilon_{e+h}^2 \), where \( m_e \) is the electron mass and \( \hbar \) is the reduced Planck constant. The transition occurs when \( n_{e,c}^{1/3}R_B \approx 0.2 \), where \( R_B = 0.53\epsilon_e/(m_{e,c}/m_e) \) is the Bohr radius. It shows that the transition occurs when the \( n_{e,c} \) and \( \epsilon_e \) is large or the \( m_{e,c} \) is small. However, large solid \( n_{e,c} \) (large \( k_{e+h} \)) is not desired, and the \( m_{i,c} \) should be tuned so that both \( k_e \) and \( k_{e+h} \) are reduced. So, \( \epsilon_e \) is key in the binding of the electron-hole and is worth examining near the transition \([77]\).

Although Mott mentioned that the transition is not always discontinuous \([76]\), Mott and Davis \([76,78]\) argued that the transition of semiconductors is a Mott transition, taking account of the disorder of a random array of atoms and \( \epsilon_e \) tending to infinity at transition. From Adachi \([65]\), the \( \epsilon_e \) semiconductors increases as \( \Delta E_{i,c} \) decreases, then \( \epsilon_e \) of CdSb will increase with temperature \([79]\) and tends to infinity as \( \Delta E_{i,c} \) vanishes upon melting, leading to significant dielectric screening of the Coulomb attraction of the electron-hole pair. Also, the transition should be discontinuous, because solid \( \Delta E_{i,c} \), which is about 0.2 eV at \( T_{sl} \) for CdSb, suddenly disappears (metallic liquid). Therefore, the CdSb undergoes the Mott transition upon melting, and this is expected for other S/M transition TCS materials.

The other theory describing the criteria for the insulator-metal transition of many liquid alloys is the Ioffe-Regel limit. The scattering of electrons becomes weak due to the screening of the ionic potentials when the \( n_{e,c} \) is sufficiently large [nearly free-electron (NFE) metals], and there is a limit where the scattering becomes strong \([80]\). The electrical conductivity limit \( (\sigma_{lim}) \) at this point is about 3000 (\( \Omega \) cm)\(^{-1} \) for typical liquids and the \( \sigma_e \) follows \( \sigma_{lim}/\eta \), where \( \eta \) is the Körringa enhancement (\( \eta > 1 \)) under the Ioffe-Regel limit (\( \sigma_e < \sigma_{lim} \)), where the transport becomes diffusive. Therefore, the \( \sigma_{lim} \) can be considered as the metallic liquid regime for the S/M transition, and favorable TCS materials will have the \( \sigma_e \) higher than \( \sigma_{lim} \). It should be noted that this theory may not sufficiently consider the remaining short-range order clusters in the metallic liquid; it is expected from this theory that the
liquid alloys with $\sigma > \sigma_{\text{limit}}$ are NFE metals (ideal metallic behavior), but the liquid CdSb has a semiconductor behavior of the $\sigma_e$, even though $\sigma_e > \sigma_{\text{limit}}$ [47].

The electronic localization function (ELF) and the charge density distribution present clues for evaluating the behavior of valence electrons of materials in terms of the localization/delocalization. As shown in Fig. 4, the localized electrons (due to the nature of orbitals and its contribution to the bonding). As shown in Figs. 11 and 12, the S/M transition of CdSb is mainly due to the $p$ orbital of Sb atom, the same as the semimetal/transition of elemental Sb (see Sec. VI). Considering binary semiconductor compounds including CdSb, it is expected that the combinations of metal and semimetal/semiconductor elements provide the $p$ orbital (S/M transition) for high ZTC. Investigation for existing materials shows six compounds with the $Z_{\text{TCS}} \geq 1.8$, i.e., elemental Ge and Si; CdSb, InSb, Ge$_2$Sb$_2$Te$_5$, GaSb, and AlSb, in Fig. 2. The most interesting feature is that all the compounds possess Sb as a base element. Also, all of them except Ge$_2$Sb$_2$Te$_5$ are the binary Sb compounds with metallic elements. Therefore, it is believed that Sb is one of the most promising semimetal/semiconductor elements for binary TCS materials, and we call such elements the TCS base element.

To determine possible TCS base elements, the metalloid elements (B, Si, Ge, As, Sb, and Te) are searched for large $\Delta \lambda$ upon melting. The usual Boron-based semiconductors are III-V compounds (BN, BP, BAs, and BSB) with significantly high $k_p^*$, the $ab$ initio calculation result [81] shows that their $k_p^*$'s are higher than 500 W/m K at room temperature and that of BAs is comparable to that of diamond, due to their strong bond, which yields large $T_{sl}$ and $T_D$. So, they cannot possess high ZT$_{TCS}$. The available data show that Se and Te are not suitable since the highest liquid $\sigma_e$ among most telluride and some selenide semiconductors is less than 3000 (\Omega cm)$^{-1}$, and many selenide compounds remain semiconductors upon melting [60]. In the report [60], it is mentioned that the chemical binding remains strong and they cannot be considered as the system of free-electron model, similar to CdSb but with much lower $\sigma_e$. So, selenides and tellurides do not have a large $\sigma_e$ jump upon melting. The common binary semiconductor compounds of Si or Ge are SiSe, SiSe$_2$, GeSe, GeSe$_2$, and GeTe. As discussed, the GeSe is a liquid semiconductor and the highest liquid $\sigma_e$ of GeTe is $< 3000$ (\Omega cm)$^{-1}$ [60]. The $\sigma_e$ of Ge-Se system decreases as the Se composition increases [82], so GeSe$_2$ is also a liquid semiconductor. Also, the liquid $\sigma_e$ of the SiSe and SiSe$_2$ are almost close to those of the GeSe and GeSe$_2$, respectively, which implies that the SiSe and SiSe$_2$ are also semiconductors [83]. There is no congruent melting composition for the binary compounds of Si or Ge with metal elements in groups 12–15 [84]. Therefore, the Si and Ge can be excluded from the TCS base elements. The remaining metalloid elements are the As and Sb, and they do not make a distinct binary compounds with congruent melting [84]. It is expected that As would be TCS base element, the same as Sb since both are semimetals in group 15.

Figure 5 lists properties of binary compounds (with congruent melting) based on the As and Sb. The incongruent melting compounds are excluded. The TCS-related properties of the compounds are listed. There are periodic trends for properties and CdSb and ZnSb stand out. The As compound data are rare due to their reactivity and toxicity.
of GaSb. So, the electron contribution to the $k_\beta(s)$ decreases, whereas the lattice contribution increases. However, the liquid $\sigma_e$ increases due to the same trend as the solid and liquid $\sigma_e$ of each pure element ($\sigma_e_{\text{Al}} > \sigma_e_{\text{Ga}} > \sigma_e_{\text{In}}$) [53], and the liquid $k_\beta$ increases notably since the $T_{sl}$ also increases (W-F law). Because $k_\beta$ is negligibly small, dominant contribution to $k(l)$ is $k_\sigma$. So, AlSb has a high $Z_{TCS}$ about 4.0, although it has a significantly large contribution from $k_\sigma$ and high $T_{sl}$. The reason for the lowest $Z_{TCS}$ of GaSb among them is that both $k_\sigma$ and $k_\beta$ are not negligible, so $k(s)$ is almost the same as that of AlSb.

The group 13-As compounds have the same trends for properties as those of the 13-Sb compounds: increasing $T_{sl}$ and band gap and the decreasing $\epsilon_e$. Also, the solid $\sigma_e$ decreases and the liquid $\sigma_e$ increases (no data for AlAs). These uniform trends are due to the same composition with some elemental group 13-As at liquid are lower than those of 13-Sb (the solid $\sigma_e$ is lower or similar) due to higher liquid $\sigma_e$ of elemental Sb compared to that of As [53,90]. So, it is expected that the $k(s)$ of AlAs is higher than that of GaAs due to increase in $k_\sigma$ (but negligible decrease in $k_\beta$) and a liquid $\sigma_e$ much lower than AlSb, so $Z_{TCS}$ not higher than AlSb (4.0). The reason for the higher $Z_{TCS}$ of GaAs compared to InAs (no the same trend as the 13-Sb) is a much lower electrical contribution to $k(s)$ for GaAs (low solid $\sigma_e$), so they have similar $k(s)$. Therefore, the highest $Z_{TCS}$ material in group 13 is the AlSb, the same $Z_{TCS}$ as pure CdSb.

The CdAs$_2$ is a possible TCS in the Cd-As system, but its predicted $k(s)$ is slightly larger than CdSb, and it is expected that its liquid $\sigma_e$ is lower than CdSb (due to high As content and higher $\sigma_e$ for antimonides compared to arsenides). So $Z_{TCS}$ of CdAs$_2$ should be lower than CdSb (the data for CdAs$_2$ is limited). Also, CdSb can have higher $Z_{TCS}$ with Ag addition, as discussed. Similarly, liquid $\sigma_e$ of Zn$_3$As$_2$ will be smaller than Zn$_3$Sb$_2$. However, most of Zn$_3$Sb$_2$ properties are not known [91,92]. Since $k(s)$ of $\beta$-Zn$_3$Sb$_2$ [93] is much smaller than Zn$_3$As$_2$ and $k(s)$ of Zn$_3$Sb$_2$ is not expected to be higher (see below), $Z_{TCS}$ of Zn$_3$As$_2$ is smaller than Zn$_3$Sb$_2$. The reason for the low $k(s)$ of CdSb and $\beta$-Zn$_3$Sb$_2$ (essential to the high $Z_{TCS}$) is their electron-poor nature [48,91]. Since there are 3.5 electrons per atom, the weak multicenter bonds are formed in CdSb to make up for this, leading to nonuniform atomic bonds and the strong anharmonicity [48,94]. The main structure of $\beta$-Zn$_3$Sb$_2$ is the rhombohedral Zn$_{30}$Sb$_{10}$ with an electron deficiency, so the balance is corrected by the interstitial Zn atoms which yield disorder as defects and the soft and anharmonic bonding [91,95,96]. Therefore, the $k(s)$ of CdSb and $\beta$-Zn$_3$Sb$_2$ are rather low. Similarity is expected between $\beta$-Zn$_3$As$_2$ and Zn$_3$Sb$_2$. Whereas $\beta$-Zn$_3$Sb$_2$ has three interstitial Zn atom sites (36 available positions for each site) in the unit cell [95], there are 18 Zn atom sites (8 available positions for each site) in Zn$_3$Sb$_2$ (with larger unit cell) and only one of them has the full occupancy [97]. So, a more disordered structure with a stronger anharmonic bonding is expected for the Zn$_3$Sb$_2$, and thus the $k(s)$ of Zn$_3$Sb$_2$ should not be higher than $\beta$-Zn$_3$Sb$_2$.

From the discussions above, Sb is the best TCS base element due to its anharmonic bonding characteristics with group 12 elements, and higher liquid $\sigma_e$ of antimonides than arsenides, leading to high $Z_{TCS}$. Among antimonides, Zn$_3$Sb$_2$ and CdSb have high $Z_{TCS}$. We discuss and analyze related properties of CdSb in Sec. VI and Zn$_3$Sb$_2$/\beta-Zn$_3$Sb$_3$ in Sec. VII.

V. AB INITIO CALCULATION METHOD

The ab initio calculations are implemented by the Vienna ab initio Simulation Package (VASP) [105] and the ABINIT packages [106,107]. The VASP is used for the relaxation of atomic structures, electron density of states ($D_e$) and band structures, ELF, ab initio molecular dynamics (AIMD), and bulk modulus. The Perdew-Burke-Ernzerhof (PBE) [108] exchange-correlation functional is used along with the projector augmented wave (PAW) method [109,110] with 300-eV cutoff energy. The DFT-D3 method [111,112] with the Becke-Johnson damping for the van der Waals correction is adopted to obtain accurate results, since the cleavage planes inside CdSb are interconnected by the van der Waals interaction [48]. The usual density functionals are unable to describe the van der Waals correctly [113], and the calculations can be improved drastically with the van der Waals density functional [114]. In the $D_e$ and band structure calculation, the modified Becke-Johnson (mBJ) exchange potential [115,116] is included with nonspherical contributions from the gradient corrections inside PAW spheres (LASPH = TRUE., in the VASP tag), since the mBJ often results in aspherical charge densities [113]. Our predicted band-gap energy for CdSb only with PBE functional was very poor, less than 0.1 eV significantly different to the experimental results (about 0.5 eV), and the previous reports [48,94] show that the mBJ can predict the correct $D_e$ and band structure.

For CdSb, the $\Gamma$-centered grids with $8 \times 6 \times 6$ $k$ points are used for the relaxation of the atomic structure, and the relaxed structure is used to calculate the $D_e$ with expanded $30 \times 24 \times 24$ $k$ points for accuracy and the band structure with $k$ points along the Brillouin zone edges, but $4 \times 3 \times 3$ $k$ points are used for $D_e$ calculations with a supercell, considering that $D_e$ results for the CdSb supercell do not vary with larger number of $k$ points. For pure Sb, the $\Gamma$-centered grids with $13 \times 13 \times 5$ and $33 \times 33 \times 13$ $k$ points are used for the relaxation and the $D_e$ of the solid unit cell and $8 \times 8 \times 3$ $k$ points for the $D_e$ of the liquid supercell. Also, for pure Cd, the $\Gamma$-centered grids with $25 \times 25 \times 13$ $k$ points are used for the relaxation of the solid unit cell and $7 \times 7 \times 6$ $k$ points for the $D_e$ of the liquid supercell. For $\beta$-Zn$_3$Sb$_2$, the $\Gamma$-centered grids with $3 \times 3 \times 3$ $k$ points are used for the structure relaxation, considering the large unit cell size and the fact that the relaxed structure with larger number of $k$ points is almost the same.

The AIMD calculation is implemented with canonical ensemble (NVT) under the Nosé-Hoover thermostat at prescribed temperature and a 1-fs time step is used. The Fermi-smearing method is adopted with the smearing width corresponding to the energy at prescribed temperatures. The only $\Gamma$ point is used for the AIMD [117,118], and four snapshots are collected from the AIMD results at every 1 ps after reaching equilibrium (3 ps) to calculate properties of liquid phase [118,119]. The thermodynamic relation of the bulk modulus is $E_p = V_p(dP/dV)$, where $V_p$ is the zero-pressure volume. The pressure data from the AIMD calculations for various volumes are used to obtain the $V_p$ and the derivative of $P$ with respect to
V and to calculate the \( E_p \), by following the method suggested [120].

The ABINIT package with CONDUCTI code [121,122] embedded in the package is used to predict the real part of the \( \sigma_e \) for liquid CdSb by calculating the Kubo-Greenwood (K-G) formula [123,124] written as [118]

\[
\sigma_e = \frac{\hbar e^2}{V} \sum_{k'k} \lim_{\varepsilon \to 0} \frac{f(E_{k'}) - f(E_k)}{E} \delta (E_k - E_{k'} - E) \langle \psi_k | \hat{\nabla} | \psi_k \rangle \langle \psi_k | \hat{\nabla} | \psi_k \rangle,
\]

where \( h \) is the Planck constant, \( E_k \) is energy (eigenvalue) of eigenstate \( k \), \( f(E_k) \) is Fermi-Dirac occupancy function, \( \psi_k \) is wave function of eigenstate \( k \), and \( \langle \psi_k | \hat{\nabla} | \psi_k \rangle \) is velocity matrix elements. The \( \delta \) function ensures the energy conservation of electrons, and the \( \hat{\nabla} \) can be expressed by Hamiltonian gradient as [118]

\[
\hat{\nabla} = \frac{1}{\hbar} \frac{\partial}{\partial k}.
\]

The calculations are implemented with snapshots obtained by the VASP AIMD calculations for each temperature. The PBE exchange-correlation functional is used along with PAW method, with 408 eV (15 Hartree) cutoff energy and 2 \( \times 2 \times 2 \) \( k \) points of a Monkhorst-Pack grid. Our tests showed that results were not affected by further increases in cutoff energy and \( k \) points. The \( \delta \) function is treated by the Gaussian function with the broadening width of 0.03 Hz following the suggested method [125], and the well-converged \( \sigma_e \) can be obtained without any unphysical fluctuations along frequencies.

VI. HIGH \( \zeta_{\text{cs}} \) CdSb

A. Atomic structure of CdSb

Solid CdSb has a small \( \Delta E_{\text{cs}} \) (0.5 eV) [94], very low phonon cutoff energy (21 meV) [48,126], and its orthorhombic unit cell consist of 8 Cd and Sb atoms each having five neighbors, whereas there are only two Cd-Sb bonds for Cd atoms and two Cd-Sb and one Sb-Sb bond for Sb atoms within the sum of covalent radii for Cd (1.44 Å) and Sb (1.39 Å), respectively [48,127]. The \( sp^3 \) hybridization has been suggested, but Ashcheulov et al. [128] claims inequivalent hybrid orbitals as linear combinations of \( s \) and \( p \) orbitals. Using the electron-localizability indicator (ELI-D), Wang et al. [48] show there are a collection of three covalent bonds (two-center bonds) and one three-center interaction (Cd-Sb-Cd), i.e., a shared lone electron pair and inducing the interlayered structure with anisotropic properties. They explained the existence of the three-center interaction is from the deficiency of valence electrons (3.5 electrons per atom).

The \textit{ab initio} calculated structure is presented in Fig. 6, showing nonuniform atomic bonds and angles and anisotropy more accurately than previous reports [48,94] because the van der Waals interactions are included (Table I). Figure 6(a) shows that the contours of charge density distribution around Sb atoms is distorted (rounded triangular or tetrahedron), but around Cd it is spherical (slightly distorted) and Cd and Sb contours overlap due to the Cd-Sb covalent bonds. Figure 7 shows the structures of Cd and Sb, where the charge density distribution around Cd is spherical and around Sb is also spherical but linked between atoms. The bond length of Cd and Sb is 2.96 and 2.93 Å, respectively, larger than the covalent bonds. Considering the charge density distributions and bond lengths, these imply that valence electrons of Cd are localized with those of Sb forming covalent bonds.

CdSb is the only stable one in the Cd-Sb system under phase transition [128], i.e., congruent melting (\( T_{\text{cl}} = 729 \) K). In the melt CdSb, clusters of short-range order remain [130], consisting of Cd\(_x\)Sb\(_y\), implying strong interactions (Cd-Cd or Sb-Sb clusters are not possible [130]). The softening effect by melting is weak and the difference between the \( k_p \) and the \( k_f \) will be small. The liquid CdSb is rather isotropic with free-electron-like transport properties [60,131,132]. Some bonds (especially shared electron pairs and Sb-Sb) dissociate upon melting and some unbound valence electrons become delocalized and wander, i.e., metal-like.

AIMD calculations verify the liquid properties at 800 K, using a \( 2 \times 2 \times 2 \) supercell (128 atoms) and the density of the liquid supercell is set the same as solid (actual 1% density difference [103,133] is comparable to relaxation error in Table I). Figure 8 is a snapshot of liquid CdSb at 800 K.

### TABLE I. Atomic structure properties of CdSb predicted by \textit{ab initio} calculations and compared with experiments [48,129]. The maximum difference is 1.1%.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>\textit{Ab initio}</th>
<th>Previous reports</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constants (Å)</td>
<td>( a = 6.473 )</td>
<td>( a = 6.469 )</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>( b = 8.308 )</td>
<td>( b = 8.251 )</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td>( c = 8.551 )</td>
<td>( c = 8.522 )</td>
<td>0.34</td>
</tr>
<tr>
<td>Bond length, Cd-Sb (Å)</td>
<td>2.805</td>
<td>2.793</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>2.838</td>
<td>2.824</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>2.892</td>
<td>2.882</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>3.124</td>
<td>3.127</td>
<td>0.10</td>
</tr>
<tr>
<td>Bond length, Sb-Sb (Å)</td>
<td>2.841</td>
<td>2.810</td>
<td>1.10</td>
</tr>
<tr>
<td>Bond length, Cd-Cd (Å)</td>
<td>3.132</td>
<td>3.136</td>
<td>0.13</td>
</tr>
<tr>
<td>Angle, Cd-Sb-Cd (deg.)</td>
<td>( \alpha = 103.3 )</td>
<td>( \alpha = 103.9 )</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>( \beta = 111.3 )</td>
<td>( \beta = 110.4 )</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>( \gamma = 141.7 )</td>
<td>( \gamma = 141.4 )</td>
<td>0.21</td>
</tr>
</tbody>
</table>
with charge density distribution and most Cd show spherical distribution without overlaps, indicating metallic bonding and properties [134]. The charge density distribution around Sb is less distorted and most of its covalent bonds are dissociated, so its delocalized electrons contribute to transport.

### B. Electronic structure of CdSb

The S/M transition features are described by the charge density distributions combined with the ELF, which suggests classification of bonding based on the topological analysis [135]. The value of ELF is between 0 and 1, where 1 and 0.5 correspond to perfect localization and uniform electron gas [135,136]. The localization attractors are defined by the local maxima of local functions related to the Pauli exclusion principle and there are bonding and nonbonding attractors. The bonding attractors have point or circular shapes and indicate that the localized electrons are involved in bonds, whereas the nonbonding attractors have ring shapes. The metallic bonds form a three-dimensional (3D) network (trajectories) connecting all attractors as the ELF level decreases [135]. The metallicity identification may not always be reliable using the ELF; diamond carbon [136] and lithium [135] both show bond attractors at high ELF levels and a network of channels at low ELF levels. Here, with focus of the TCS on the S/M transition upon melting, there is almost no bond attractor in metallic liquids, so the discussion regarding metallicity of the liquid phases using the ELF is rather valid (see the CdSb as an example below). Although the solid CdSb does not show a network of channels, it is possible that the solid phases of other notable TCS materials do. In that case, the density of states (DOS) should also be examined to confirm a nonmetallicity.

Figure 9 shows the ELF contours for solid CdSb, and the reducible localization domain, where the attractors merged within two neighboring Sb, is seen in Fig. 9(a). The network is formed within only one Sb-Sb bond, indicating that CdSb cannot be metallic. As the ELF level increases, the bifurcations of attractors occur at a critical value [135], and Sb-Sb bond attractor begins to separate at the critical level of 0.74. The Sb-Sb bond attractor is located in the middle point of Sb-Sb bond, suggesting that electrons forming a covalent bond are localized [Fig. 9(b)]. The attractors for Cd-Sb bonds and Cd-Sb-Cd interaction (van der Waals) are fully separated at the ELF level of 0.835 [Fig. 9(c)]. All attractors are located on the bonding line [135] and are much close to Sb [128], since the electronegativity of Sb (2.05) [1] is larger than Cd (1.69) [1] (electrons localized close to Sb). Two van der Waals attractors are very close to each other and facing partner (Cd), but contours are nonuniform; the van der Waals attractor with shorter interaction distance (2.892 Å) is much larger than the longer distance (3.124 Å). The shared lone electron pair in Cd-Sb-Cd interaction is more probable to be located near a Cd, leading to stronger van der Waals interaction and a closer, shorter bond.

Contrary to solid bond characteristics, the liquid attractors [Fig. 10(a)] around Sb are ring type (not intact due to disorder), similar to nonbonding ring attractor [135]. There is no attractor between Sb-Sb pairs with bond length 2.647 Å [smaller than two times covalent radius of Sb (2.78 Å)] in Fig. 10(a). There are Cd, Sb clusters in liquid; the Cd-Sb pair with long bond length 3.082 Å forms the bond attractor between them (close to Sb). Based on the length, it may not be a covalent bond, but shows Cd-Sb interaction [130]. Figure 10(b) shows the liquid metallic behavior with a 3D network connecting all attractors around Sb [135]. The ELF contours around the Sb-Sb pair with bond length 2.647 Å [Fig. 10(a)] become closer as the ELF level decreases and finally merge each [Fig. 10(b)], but the bonding attractor between them is never formed. The ELF results suggest that liquid CdSb is metallic.

The band structure and solid and liquid $D_e$ from *ab initio* calculations are shown in Fig. 11. The highest-edge valence and lowest-edge conduction band are near the X and Z
points, and the solid band gap of 0.49 eV is consistent with experiments/predictions \([48,94]\). The solid \(D_e\) shows that the 4\(d\) of Cd is intensely overlapped with 5\(s\) orbital of Sb, within deep electron energy states (−11 to −7 eV), similar to liquid Hg \([137]\) (group 12 feature). These states consist of four narrow energy bands with high peaks and some narrow band gaps between them, and the band with the largest peak is significantly contributed to Cd 4\(d\) (near −9 eV). So, these four peaks originate from Cd-Sb and Cd-Cd interactions and related electrons are localized in these deep bands. Many valence electrons are from Cd 4\(d\), so the band with the Cd-Cd interaction has the highest peak.

There are two wide conduction and valence bands up and down from both gap ends and the Sb 5\(p\) makes the largest contribution to these bands, especially to upper side of the valence band, and also contributions of Cd 5\(s\) and 5\(p\) to those bands can be seen \([48]\). These bands are mainly originated from the Sb-Sb bond, but the couplings of the Sb 5\(p\) with the Cd 5\(s\) and 5\(p\) through Cd-Sb also affect to the formation of valence and conduction bands, especially the Cd 5\(s\) for lower parts of valence and conduction bands and the Cd 5\(p\) for upper parts. The interactions between Sb-Sb and Cd-Sb contribute to the prohibited band-energy region, but not the interaction between Cd atoms.

The liquid CdSb \(D_e\) at 800 K in Fig. 11(b) is obtained by averaging of the snapshot results and shows that the valence and conduction bands merged and the band gap disappears (metallic). The highest contribution near the Fermi level is the Sb 5\(p\); the valley of partial Sb 5\(p\) \(D_e\) is fully represented to total \(D_e\). Figures 12(a) and 12(b) show solid and liquid (950 K) Sb \(D_e\), with the main contribution to the metallic transition upon melting from the 5\(p\) orbital and the partial \(D_e\) of other orbitals barely changing. The phenomenon is similar to the changes in partial Sb \(D_e\) in CdSb upon melting. Also, the valley in Fig. 11(b) is observed in Fig. 12(b). The valence electrons of the Sb 5\(p\) orbital, once localized in the solid state by the interactions with the Cd 5\(s\) and 5\(p\) orbitals and the 5\(p\) orbital of other Sb atoms, are delocalized, and these electrons contribute to the metallic behavior of the liquid. Also, the Cd partial \(D_e\)'s in liquid CdSb are similar to those of liquid Cd [Fig. 12(c)], confirming that sole Cd contributes to the liquid metallic properties. Although gradual increase in 5\(s\) and decrease in 5\(p\) partial \(D_e\) of liquid Cd are observed, the shallow valleys in the partial \(D_e\) of Cd 5\(s\) and 5\(p\) can be found in compound [Fig. 11(b)]. This implies that not all Cds behave like liquid but some of them are engaged in Cd, Sb, clusters.

### C. Transport properties of CdSb

The CdSb \(k(s)\) decreases up to 425 K, then increases, as reviewed in Fig. 3 \([48,138]\). Following the Slack relation \((T^{-1})\) \([1]\), this increase is due to \(k_e\) and/or \(k_{e+B}\); however, \(k_e\) is very small (about 0.2 W/m K \([48]\)), so this is due to \(k_{e+B}\). The thermal conductivities of the solid and liquid CdSb are obtained by the theoretical treatments, and each contribution is shown in Fig. 13. The \(k_f\) is derived from the kinetic
theory [1]

\[ k_f = \frac{1}{2} \rho_f c_{v,f} a_f \lambda_f, \]

where \( \rho_f \) is the fluid density, \( c_{v,f} \) is specific heat at constant volume, \( a_f \) is speed of sound in liquid, and \( \lambda_f \) is mean free path of fluid molecules. The Bridgman theory treats liquid as a simple cubic arrangement of atoms with its mean free path equal to the three times of mean atomic spacing, i.e. [1],

\[ k_f = \rho_f \frac{3 R_g}{M} a_f \left( \frac{M}{\rho_f N_A} \right)^{1/3} = \frac{3 R_g}{N_A} \frac{\rho_f^{1/6}}{M^{2/3}} \left( \frac{c_{p,f}}{c_{v,f}} \right)^{1/2} (e_p E_p) \]

where \( R_g \) is the gas constant, \( M \) is molecular weight (here in molar base), \( N_A \) is Avogadro number, and \( c_{p,f} \) is specific heat at constant pressure (usually \( c_{p,f} \approx c_{v,f} \) for liquid). The \( k_f \) of liquid CdSb estimated as 0.49 W/m K at \( T_{D,f} \), with \( M = 234.17 \) g/mol, \( a_f = 1748 \) m/s, and \( \rho_f = 6.857 \) g/cm\(^3\) [103], so in TCS, \( k_f \) is small, making negligible contribution compared to \( k_e \).

The Slack relation \( k_{p,s} \), which is extended from the Leibfried and Schlömann equation for complex lattices [139], is [1]

\[ k_{p,s} = \frac{3.1 \times 10^4 (M)V_a^{1/3}T_D^{3}}{T_0^{1/3} N_a^{1/3} N_c^{1/3}}, \]

where \( T_D^{\infty} \) is the high-temperature Debye temperature, \( \langle \gamma_G \rangle \) is mode averaged square of the dimensionless Grüneisen parameter at high temperature, and \( N_a \) is number of atoms in the primitive cell. The \( T_D^{\infty} \) and \( \langle \gamma_G \rangle \) can be replaced with \( T_D \) and \( \langle \gamma_G \rangle^2 \), respectively. The properties \( M = 117.058 \) g/mol, \( V_a = 1/n \ (n = N_a/abc) \), where \( a = 6.469 \) Å, \( b = 8.251 \) Å, and \( c = 8.522 \) Å are lattice constants from the experiment [129] and \( N_a = 16 \), \( T_D^{\infty} = 180 \) K, and \( \langle \gamma_G \rangle = 1.82 \) are used [94,140]. The \( k_p \) within 300 K–400 K is coincident with \( k(s) \) from the experiment due to negligible \( k_e \) and \( k_{e,th} \) at low temperatures. Though the Slack relation underestimates \( k_p \) at high temperatures due to its simplicity \((T^{-1})\), \( k_f > k_p \) (0.42 W/m K) at \( T_{D,f} \). Therefore, the actual decreasing rate of \( k_p \) with temperature is slightly lower than the Slack result.

The minimum \( k_p \) can be obtained from the Cahill-Pohl model with assumptions of a mean free path of phonon equal to one half of wavelength, no phonon dispersion, and dominant short length-scale interactions [1], i.e.,

\[
\begin{align*}
    k_{p,c-p} &= \left( \frac{\pi}{6} \right)^{1/3} k_B \frac{h^{2/3}}{T} \sum_a u_{p,a} \\
    &\times \left( \frac{T}{T_{D,a}} \right)^2 \int_0^{T_{D,a}/T} \frac{x^3e^x}{(e^x - 1)^2} dx,
\end{align*}
\]

where \( \alpha \) is the phonon branch, \( u_{p,a} \) is phonon velocity, and \( T_{D,a} \) is Debye temperature for each branch as

\[ T_{D,a} = u_{p,a} k_B (6\pi^2 n) \frac{1}{T_{D,a}}. \]

The acoustic phonon velocities are \( u_{p,a} = 1300, 1581, \) and 2988 m/s for two transverse and one longitudinal phonons in the vicinity of Brillouin zone center (no dispersion) [48]. The minimum \( k_p \) is almost flat in a wide range of temperature (Fig. 13) after reaching a plateau at \( T_{D,\alpha} \) [1] (average of \( T_{D,\alpha} = 191 \) K). The calculated \( k_{p,min} \) is 0.35 W/m K, the same
FIG. 12. The $D_e$ of (a) solid Sb (unit cell), (b) liquid Sb (2 × 2 × 2 supercell at 950 K; $T_{sl} = 904$ K), and (c) liquid Cd (3 × 3 × 2 supercell at 700 K; $T_{sl} = 594$ K). The Fermi energy is set to be zero. The solid Sb is semimetal, considering the deep valley at 0 eV. After melting, the liquid Sb becomes a metal and the valley almost disappears. It shows that the overlap of charge density distribution between Sb atoms in liquid CdSb does not imply that Sb atoms are forming covalent bonds. The 4d orbital of the liquid Cd mainly contributes to the deep electron energy states, whereas both the 5s and the 5p orbitals of Cd contribute to the states near the Fermi level.

as the reported result [48]. The $k_p$ calculated from Eq. (8) is nearly $k_{p,\text{min}}$ at $T_{sl}$. This low $k_p$ is caused by the deficiency of valence electrons (3.5 electrons per atom) which results in the complicated structure (Fig. 6). The weak three-center bonding leads to a small force constant and modulus, which lower phonon velocities and $\Delta T_D$, and strong anharmonic branches, which induce a large Grüneisen parameter [48,94]. Also, the strong coupling between soft optical phonon and acoustic phonon enhances scattering and contributes to the low $k_p$ [48,94].

A theoretical model is used for $k_{e+h}$ prediction, i.e. [141,142],

$$k_{e+h} = \frac{\sigma_e \sigma_h}{\sigma_e + \sigma_h} (\alpha_h - \alpha_e)^2 T,$$

where $\sigma_i = n_i \epsilon_i \mu_i$ is the electrical conductivity of charge carrier $i$ (carrier charge $e_i$) and $\alpha_i$ is the Seebeck coefficient. The Seebeck coefficient for a single parabolic band is expressed as [143,144]

$$\alpha_i = \pm \frac{k_B}{e} \left[ \eta_i - \frac{(\lambda_i + 5/2) F_{\eta_i + 3/2}(\eta_i)}{(\lambda_i + 3/2) F_{\eta_i + 1/2}(\eta_i)} \right],$$

where $\lambda_i$ is the carrier scattering parameter ($\lambda_i = -1/2$, assuming acoustic phonon scattering), $\eta_i$ is reduced Fermi energy, and $F_\beta$ is the Fermi integral of the order of $\beta$. The $\eta_i$ and $F_\beta$ can be written as [143,145–147]

$$\eta_e = (E_F - E_e)/k_B T,$$

$$\eta_e + \eta_h = -\Delta E_{e,g}/k_B T,$$

$$F_\beta(\eta_i) = \int_0^\infty \frac{x^\beta}{1 + e^{x-\eta_i}} dx,$$

where $E_F$ is the Fermi energy and $E_e$ is conduction band energy. With the assumptions that $(E_e - \mu) \gg k_B T$ (electron energy $E_e$ and chemical potential $\mu$) and $\mu$ is analogous to $E_F$, then $n_i$ can be derived theoretically as [2]

$$n_i = 2 \left( \frac{m_i \epsilon_k T}{2 \pi \hbar^2} \right)^{3/2} \exp(\eta_i).$$

The $m_{i,e}$ for electrons at conduction band minimum and for holes at valence band maximum toward each direction [148] were averaged by the geometric mean (density of state effective mass [149]) with degeneracy factors of 2 for valence band and 6 for conduction band from band structure [Fig. 13(a)] [94,149,150]. The temperature-dependent band-gap energy ($-6 \times 10^{-4}$ eV/K and 0.45 eV at room temperature) [79] was used with constant Fermi level position (0.032 eV/0.46 eV) [151], and $\mu_i$ was extrapolated from the measured data (100 K–280 K) [152] and mobilities of hole and electron are the same [153]. The extrapolated $\mu_i$ has the temperature
dependence of $T^{-1.4}$ consistent to previous claims ($T^{-1.5}$) [154], and is about 350 cm$^2$/Vs at 300 K similar to the measured mobility (300 cm$^2$/Vs at 300 K) [155]. The estimated $k(s)$ is similar to the reported result [48] at the low temperatures (<450 K) and near $T_{sl}$, but the difference is observed in intermediate temperatures. The reason is because of the steep increase in $k_{s+t}$ estimated; actual $k_{s+t}$ will increase gradually from 400 K, and the discrepancy would occur due to the $h_{f}$ extrapolation in a wide range of temperature (300–$T_{sl}$, lack of data). We believe that the result can be improved with precise mobility data, and $k_{s+t}$ prediction is meaningful for distinguishing and assessing each contribution to $k(s)$.

The solid $\sigma_e$ starts increasing near 400 K (thermal excitation of electrons) and is about 180 (Ω cm)$^{-1}$ at $T_{sl}$ (Fig. 14), equivalent to 0.2 W/m K. The liquid $\sigma_e$ is about 5.2 $\times$ 10$^3$ (Ω cm)$^{-1}$ at $T_{sl}$ [47,60] in the metallic regime [80] and equivalent to 9.4 W/m K. Although its electronic properties like Hall coefficient and thermoelectric power are metallic [131], the semiconductor behavior of liquid $\sigma_e$ (increasing with temperature) is observed due to the short-range order interactions in low-temperature liquid CdSb [60]. The liquid $\sigma_e$ increases as a logarithmic function (Fig. 14); semiconductor behavior becomes weak and the short-range interactions reduce as temperature increases [156]. Thus, liquid $\sigma_e$ will start decreasing eventually when the clusters of short-range order totally disappear and metallic behavior begins. The previous reports [128,157] indicate that it occurs at 773 K, so there is a contradiction with the experiment [47]. We believe that the disappearance point is higher than 890 K because of the evidence for the presence of clusters in liquid $D_e$ at 800 K [Fig. 11(b)]. Also, the data [156] shows that liquid specific heat is higher than predictions by the Neumann-Kopp law (the weighted average with fractions of constituents) over 890 K, the same as $\sigma_e$ due to the short-range order. Therefore, the disappearance point is expected to be above 890 K.

The liquid $\sigma_e$ is obtained at several temperatures (750 K–900 K) using the K-G formula with snapshots of AIMD calculations (Fig. 14). The $ab$ initio prediction, however, shows metallic behavior (decreasing with temperature) and higher values than the experiment. This is due to the assumption of the K-G formula, derived from the Kubo formula with the approximation of noninteracting Fermi system for the current operator [158]. It suggests that the K-G formula is suitable only for perfect crystal without inelastic processes, but the scattering between the electrons and the phonons always occurs in the semiconductor [158,159]. Also, the formula cannot directly describe zero $\sigma_e$ for localized states [159]. Therefore, the result shows that the predicted $\sigma_e$ is for ideal metallic behavior (NFE metal) without any consideration of remaining short-range interactions. Although there is a large discrepancy, the result can be used to assess the liquid $\sigma_e$ for the Ag-added CdSb not reported so far (see next section).

The estimated $k(s)$ and $k(l)$ at $T_{sl}$ are 2.0 and 9.9 W/m K, respectively, and lead to $Z_{TCS}$ = 4.0. The high thermal conductivity jump is achieved by the transition from solid semiconductor to liquid metal (metallic melting). Also, the electron-poor characteristic yields high $Z_{TCS}$ by lowering the $k_p$ contribution. Therefore, CdSb is one of the notable TCS materials. Furthermore, the $Z_{TCS}$ can be enhanced by suppressing $k_{s+t}$ by adding Ag. We will discuss the transport characteristics of Ag-added CdSb in the next section.
D. Effect of Ag addition on CdSb

The point-defect (impurity) scattering is considered to predict \( k_p \) for Ag-added CdSb. The impurity in the base material, called static imperfection \([1]\), hinders phonon transport, thus lowers \( k_p \). The effect of point-defect scattering is found using the relation \( 1/k_p(x) = 1/k_p(0) + 1/k_{p,d} \) \([160]\), and \( k_{p,d} \) is found from \([161,162]\)

\[
k_{p,d} = \frac{k_B}{4\pi a_{1}(C T)^{1/2}},
\]

where \( u_{p,g,A} \) is the acoustic phonon group velocity, \( a_{1} \) is coefficient for the Rayleigh point-defect scattering, and \( C T \) is relaxation time for interphonon scattering. These parameters can be written as \([1,160–162]\)

\[
\frac{1}{u_{p,g,A}} = \frac{1}{3} \left( \frac{1}{u_{p,g,\text{LA}}} + \frac{1}{u_{p,g,\text{TA1}}} + \frac{1}{u_{p,g,\text{TA2}}} \right),
\]

\[
a_{1} = \frac{4\pi}{3} \frac{V_{c}}{u_{p,g,A}},
\]

\[
\Gamma = \sum x(1-x) \left[ \frac{M(X)}{M_t} \right]^{2},
\]

\[
C T = \frac{(6n)^{1/2}k_B}{2\pi^{2/3}k_g(0)},
\]

where \( \text{LA} \) and \( \text{TA} \) denote for the longitudinal and transverse acoustic, \( V_{c} \) is unit cell volume, \( \Gamma \) is mass fluctuation scattering parameter, \( x \) and \( M(X) \) are fraction and mass of added atom \( X \), and \( M_t \) is mass of an average cluster. It can be assumed that the average unit cell volume and phonon group velocities of materials with small content of impurity (small \( x \)) are almost the same as pure base material (negligible effect). For unit cell \( \text{CdSb}_{8-} \text{SbAg}_{x} \), \( M_t = (8-x)M(\text{Cd}) + xM(\text{Ag}) + 8M(\text{Sb}) \), where \( M(\text{Cd}) = 112.411, \ M(\text{Ag}) = 107.868, \) and \( M(\text{Sb}) = 121.760 \text{ g/mol} \). Using \( x = 0.008 \text{ (0.1\%)} \), \( u_{p,g,A} = 1450 \text{ m/s (for entire Brillouin zone)} \) \([94]\), and the Slack relation for pure CdSb to the \( k_{p}(0) \), \( k_{p} \) for 0.1% Ag-added CdSb, is predicted in the Fig. 15. The calculated \( k_{p} \) is slightly lower than \( k_{p} \) for pure CdSb, 0.06 and 0.02 W/m K at 300 K and \( \Gamma_{1} \) (about 5\%), respectively. This shows that addition of Ag does not change \( k_{p} \) significantly. It is expected that the \( k_{f} \) is also lowered because the speed of sound will decrease, but the effect is minor. We assume \( k_{f} \) is the same as \( k_{p} \) at \( \Gamma_{1} \), which makes it lower than pure CdSb; this way \( Z_{\text{TCS}} \) is slightly underestimated.

The solid \( k_{s} \) (Fig. 15) of Ag-added CdSb is 0.8 W/m K at \( \Gamma_{1} \) much higher than pure CdSb (0.2 W/m K); thus, the addition of an Ag atom exerts an effect to the solid-state electronic structure. The estimated \( k(s) = k_{p} + k_{e} \) is almost the same to the experimental result \([48]\) and suggests that \( k_{e} \) is significantly decreased. This is because of an increase in hole concentration, which leads to a decrease in Seebeck coefficient \([48,73]\) and unbalanced \( \sigma_{e} \) between majority (hole) and minority (electron) carriers. So, although \( k_{e} \) increases, \( k(s) \) decreases highly about 0.8 W/m K, due to the considerable decrease in the \( k_{e} \). Therefore, \( Z_{\text{TCS}} \) can enhance noticeably, provided that the liquid \( \sigma_{e} \) is still as high as that of pure CdSb.

The liquid \( \sigma_{e} \) of Ag-added CdSb at 800 K is calculated by the K-G formula, with the same method used for pure CdSb. Two Cd atoms in the CdSb supercell are replaced with Ag atoms (3.1%) positioned as far as possible between them. Note that such a small addition is hard to be realized by \textit{ab initio} calculations due to large system size. The result shows that the predicted \( \sigma_{e} \) at 800 K is 8074 (\( \Omega \text{ cm}^{-1} \)), almost the same as pure CdSb (8164 (\( \Omega \text{ cm}^{-1} \)), and should be the same for 0.1% Ag addition. Because the short-range order will not change with small content of Ag atom, the \textit{ab initio} calculations suggest that the addition of Ag atom does not affect to the electron transport properties of liquid CdSb and \( k_{e} \) is the same as pure CdSb (9.4 W/m K at \( \Gamma_{1} \)).

The estimated \( k(s) \) and \( k(l) \) at \( \Gamma_{1} \) are 1.2 and 9.9 W/m K, respectively, and lead to \( Z_{\text{TCS}} = 7.3 \) for the 0.1% Ag-added CdSb, significantly higher than that of pure CdSb (4.0) due to the \( k_{e} \) suppression. Therefore, the TCS performance of CdSb can be enhanced by the addition of an Ag atom.

VII. HIGH \( Z_{\text{TCS}} \) \( \text{ZnSb}_{2} \)

A. Lattice and transport properties of \( \text{ZnSb}_{2} \)

\( \text{ZnSb} \) compounds (\( \text{ZnSb}, \text{ZnSb}_{3}, \) and \( \text{ZnSb}_{2} \)) are known as semiconductors \([163]\) undergoing metallic melting \([52]\), and the first two are thermoelectric (TE) materials for their low thermal conductivity \([95,96,164–167]\). Their liquid \( \sigma_{e} \) at \( \Gamma_{1} \) is higher than Cd-Sb \([52]\), so large \( Z_{\text{TCS}} \) is expected when \( k(s) \) is low near \( \Gamma_{1} \). While \( \text{ZnSb} \) undergoes incongruent
melting, Zn$_3$Sb$_2$ data is rare [92], but its $Z_{TC}$S is expected not to be smaller than the better-known Zn$_4$Sb$_3$. So we examine structure and transport characteristics of Zn$_4$Sb$_3$ comparing with Zn$_3$Sb$_2$. Zn$_4$Sb$_3$ has several solid phases (transitions between $\alpha/\beta$ and $\beta/\gamma$ occur at 253 K and 763 K) and melts at 857 K [168]. We analyze yet better-known TE $\beta$-Zn$_4$Sb$_3$ with rather low thermal conductivity 0.75 W/m K over a wide temperature range (Fig. 16), unlike CdSb; i.e., $k_e$ is negligibly due to the large band gap (1.0 eV [88]).

The low $k_e$ of $\beta$-Zn$_4$Sb$_3$ is due to its complicated structure, which has uncertainty due to partial occupancy of Zn atoms, and the stoichiometry is not 4:3 rather 3.95:3 [95]. The main structure is rhombohedral as Zn$_3$Sb$_2$ with the electron deficiency [91], and Sb atoms have full occupancy at each site but Zn1 atoms have 90% occupancy. There are three additional interstitial sites for Zn atoms (Zn2, Zn3, and Zn4) with partial occupancy of about 5% (36 available positions for each site). These interstitial Zn atoms make up for the electron-poor nature of main structure so that the charge balance is achieved [91]. Therefore, the partially occupied interstitial sites lead to significant point-defect scatterings [96]. Because of its soft and anharmonic bonding (loosely bound Zn atoms), the ionic conductivity is high and Zn atoms will move to vacancies easily (leading to less-ordered structure), and the Sb dumbbells (vertical Sb-Sb bonds) [169] cannot rattle independently [96,166]. Also, there are nanovoids or nanoparticles of Zn or ZnSb within the structure [96], causing significant phonon scattering.

FIG. 16. Temperature dependence of the thermal conductivities of $\beta$-Zn$_4$Sb$_3$ for the solid and liquid phase, assuming that the transport characteristic of $\beta$-Zn$_4$Sb$_3$ is the same as $\gamma$-Zn$_3$Sb$_2$. The $k_e$ is very small, due to the interstitial Zn atoms which cause considerable phonon scattering. Also, the dependence of solid $k_e$ on temperature make it small, resulting from solid $\sigma_e$ decreasing with temperature increase (Fig. 17). However, the liquid $k_e$ is larger than that of CdSb.

Its solid $k_e$ is also small over a wide range of temperature, since its $\sigma_e$ decreases with temperature $[93,96,170–172]$ (Fig. 17) due to the decay in electron mobility $[96]$ compensating for increase in charge density. The acoustic phonon scattering is the source for the reduced mobility $[96]$. This can be associated with the partially occupied Zn atoms moving to vacancies more frequently as temperature increases and the atomic structure becomes much less ordered; thus, much active phonon-electron scattering as well as phonon-phonon scattering is expected as temperature increases. In addition, its smaller solid Lorenz number than metals or heavily doped semiconductors $\langle 1.86 \times 10^{-8} \text{ W/K}^2 \rangle$ at 300 K $[172]$ leads to small $k_e$. Its liquid $\sigma_e$ is about 5500 $(\Omega \text{cm})^{-1}$ [52] and $k_e$ is 11.5 W/m K (higher than CdSb due to the higher $\sigma_e$ and $T_{sl}$). The $\sigma_e$ data (Fig. 17) and the previous reports $[104,173]$ show that clusters of short-range order remain (same as CdSb), so liquid $k_e$ increases with temperature (Fig. 16). Using the Bridgman model and data $[104]$ on speed of sound and molar volume give $k_f = 0.26 \text{ W/m K}$ at $T_{sl}$, slightly lower than $k_p$ at $T_{sl}$ (0.34 W/m K).

These transport properties of $\beta$-Zn$_4$Sb$_3$ give high $Z_{TC}$S = 14.7, the highest identified yet for bulk, passive TCS, if the transport characteristics of $\gamma$ phase are the same $\beta$ phase and the structure is stable at $T_{sl}$. There is controversy about its congruent melting $[88,168]$ and it can be due to its instability. The Zn atoms may sublime decomposing into ZnSb and Zn before melting $[165,168]$. However, its high temperature was claimed recently $[167]$, some Zn-Sb bonds break over 425 K and $\beta$ phase becomes mixture of Zn and ZnSb, but it will become stable again over 565 K by reactions between ZnSb with Zn, when the structure of $\beta$ phase is not decomposed too much between 425 K and 565 K.

We perform ab initio studies of the stability of $\beta$ phase at high temperature to shed light. The structure has the space group of $R3c$ and the lattice constants are $a = b =$
of the highest $Z_{\text{TCS}}$ from the Zn-Sb system, especially for the high-temperature stable Zn$_3$Sb$_2$ compound with congruent melting [91,104] at 853 K [62]. A recent report [97] regarding the structure of Zn$_3$Sb$_2$ suggests its TCS suitability. The structure is orthorhombic and has 6 atomic sites for Sb atoms and 18 for Zn atoms in the interstices made by Sb atoms (eight available positions for each site). The atomic sites for Sb atom have full occupancy, but the only one site for Zn has the full occupancy. Considering the partial occupancies for other Zn atoms, the actual composition of Zn$_3$Sb$_2$ is Zn$_{3.66}$Sb$_3$ = Zn$_4$Sb$_3$, almost the same as Zn$_4$Sb$_3$ (Zn$_{3.95}$Sb$_1$) but with slightly larger Zn content. There are 48 Sb in the unit cell of Zn$_3$Sb$_2$ and only 8 Zn are fully occupied, so there are additional 56 Zn (on average) at 136 possible positions in the unit cell. Thus, Zn$_3$Sb$_2$ has a significantly lower-ordered structure, more complicated and with a larger unit cell than Zn$_4$Sb$_3$. So, stronger anharmonicity, softer bonding, and higher ionic conductivity compared to Zn$_4$Sb$_3$ is expected with vigorous phonon-phonon and phonon-electron scatterings. Therefore, the $k_p$ and solid $\sigma_e$ would not be higher than those of Zn$_4$Sb$_3$. Also, considering the actual composition, it is evident that the liquid Zn$_3$Sb$_2$ and Zn$_4$Sb$_3$ have similar transport properties; i.e., Zn$_4$Sb$_3$ should have some $k(l)$ as Zn$_4$Sb$_3$. The previous report [52] identified Zn$_3$Sb$_2$ for liquid properties at 40% atomic fraction of Sb, but we believe that this is due to the lack of information for the structure and actual composition of Zn$_3$Sb$_2$ at that time. Therefore, it is expected that the $Z_{\text{TCS}}$ of Zn$_3$Sb$_2$ is not smaller than Zn$_4$Sb$_3$ ($Z_{\text{TCS}} = 14.7$), and because of its stability it is anticipated that Zn$_3$Sb$_2$ is a promising TCS material.

VIII. CONCLUSIONS

After a review of TCS materials, focusing on s/l phase change, we note that transition with nonelectronic transport ($k_p$ and $k_f$) offers near-room-temperature $T_{sl}$, but not high $Z_{\text{TCS}}$; i.e., electronic transitions are preferred. Between M/M and S/M transitions, although M/M presents the highest $\Delta k$, S/M has the best potential for highest $Z_{\text{TCS}}$. The low $k_p$, absence of $k_{z+h}$, and large jump in $k_e$ (i.e., $\sigma_e$) during the s/l, S/M transition are required to obtain high $Z_{\text{TCS}}$. While examining potential semiconductor compounds, we found that combinations of metal and semimetal/semiconductor elements are promising, especially with the semimetal elements (Sb and As) as the base elements. The binary antimonide and arsenide compounds with metal elements in group 12–15 are promising, especially with the semimetal elements (Sb and As) as the base elements. The binary antimonide and arsenide compounds with metal elements in group 12–15 are then investigated. The Sb is superior due to the higher $\sigma_e$ of antimonides compared to arsenides (with the same metal element), and the Ag-added CdSb and possibly Zn$_3$Sb$_2$ have the highest $Z_{\text{TCS}}$ (7.2 and 14.7, respectively).

Due to the electron-poor nature, the CdSb structure has nonuniform bond lengths and angles, and its three-center interaction (Cd-Sb-Cd) induces low phonon velocities and the strong anharmonicity, so the $k_p$ of CdSb is low and its $Z_{\text{TCS}}$ can be high. Using the charge density distribution and ELF, the electron local-/delocalization characteristics of the solid and liquid phases were demonstrated. In solid CdSb, the valence electrons are localized in the Cd-Sb and Sb-Sb covalent bonds, and one electron pair is shared in the three-center interaction, but the pair is more likely to be located on one side with

![Image](image-url)
a shorter bond length. It is expected that the Cd atoms act as a metal in the liquid CdSb and contribute to its metallic properties, as in elemental liquid Cd. The ELF confirms that CdSb undergoes metallic melting and the retained short-range order interactions are for Cd, Sb, and clusters (the Sb-Sb cluster does not exist). Also, the $D_c$ reveals that the main contribution to the band gap in the solid and in the metallic liquid is the $5p$ orbital of the Sb atoms.

The thermal conductivities in solid and liquid CdSb are obtained from existing experimental results and from theoretical and $ab$ initio calculations. The $\Delta k_p$ is the main contribution to the high thermal conductivity jump, and the $k_{+h}$ is estimated and distinguished from the $k_p$. It has been reported that the addition of Ag (0.1%) can significantly reduce the high thermal conductivity jump, and the $\Delta k_{+h}$.

Specifically, $\beta$-Zn$_4$Sb$_3$ has a significantly low $k(x)$ of about 0.75 W/m K, due to the partial occupancy of the main and interstitial Zn atoms (which induce a very large unit cell, soft and anharmonic bonding, and active phonon scattering). However, Zn$_3$Sb$_2$ cannot be a TCS due to its structural instability at high temperatures and its incongruent melting. Although there are almost no data for the stable Zn$_3$Sb$_2$, it is expected that it has lower $k(s)$ compared to $\beta$-Zn$_4$Sb$_3$. The structure of Zn$_3$Sb$_2$ is more disordered than $\beta$-Zn$_4$Sb$_3$ since it has 17 Zn atom sites with partial occupancies and larger unit cell, so much more pronounced anharmonicity, softer bonds, and higher ionic conductivity are expected, so we expect its $k(s)$ will not be larger than that of $\beta$-Zn$_4$Sb$_3$ and should have $Z_{TCS}$ higher than 14.7. We hope there will, in the future, be a detailed transport characterization of Zn$_3$Sb$_2$ as a distinct TCS material (and also as a high-temperature, high-$Z_{TE}$ material).

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