Rattling vibrations and occupied antibonding states yield intrinsically low thermal conductivity of the Zintl-phase compound KSrBi

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Zintl-phase compounds garner attention as promising thermoelectric materials due to observations of phononglass electron-crystal (PGEC) behavior, in combination with tunability that allows optimization of properties and doping. However, this is very much dependent on the specific materials, and understanding the factors that lead to PGEC behavior in some Zintl compounds but not others is an important challenge. Here, we investigate KSrBi and SrLiBi. KSrBi exhibits a significantly lower lattice thermal conductivity than SrLiBi, with the 300 K thermal conductivity of KSrBi (0.7 W/mK) being only one third of that in SrLiBi (2.2 W/mK). We find that pronounced rattling behavior of the K atoms in KSrBi leads to strong anharmonicity. The behavior of the two compounds is distinct due to the presence of Sr atoms within the cagelike structure formed by Li and Bi atoms in SrLiBi. The resulting enhanced bonding interactions between Li and Bi weaken the rattling vibrations of Li atoms in SrLiBi, hence influencing its thermal conductivity. Conversely, in KSrBi, K atoms reside within a framework formed by Sr and Bi atoms, exhibiting significant rattling vibrational behavior within this framework. This behavior results in strong scattering of heat-carrying phonons, and in particular large anharmonic scattering rates. Additionally, we find an antibonding electronic state involving the Bi 6p orbital and Sr 4p orbitals around the valence band edge in KSrBi but not SrLiBi. These antibonding states significantly weaken the bonding, resulting in a softer lattice and reduced sound velocity. Consequently, the combined effects of the strong rattling vibrations of K atoms and the presence of occupied antibonding states near the valence band maximum contribute to a lower lattice thermal conductivity in KSrBi relative to SrLiBi.

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I. INTRODUCTION

Energy conversion and energy harvesting technologies are of increasing interest due to a renewed focus on global warming and reduction of fossil fuel use. Thermoelectric (TE) devices in particular have attracted attention because scalable solid-state direct thermal to electrical energy conversion has wide potential application, for example, in solar thermal generation and waste heat recovery [1]. The conversion efficiency of TE devices is limited by the performance of the underlying semiconductor TE materials from which they are made. This is quantified by the dimensionless figure of merit, $ZT = S^2 \sigma T / \kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and κ is the thermal conductivity [2]. The thermal conductivity consists of two components: a lattice thermal conductivity κ_l governed by phonon transport and an electrical thermal conductivity κ_e governed by charge carriers [3], i.e., $\kappa = \kappa_l + \kappa_e$. Identifying materials with higher ZT values is crucial for

The of merit, ent, σ is the erature, and conductivity ductivity κ_l hermal con- $\kappa = \kappa_l + \kappa_e$. crucial for materials with strong phonon scattering and, at the same time, high carrier mobility (i.e., weak electron scattering). In fact, considerable effort has been devoted to increasing *ZT*. This has led to significant advances through both the optimization of known TE materials and discovery of new TE materials. Approaches include band engineering to increase the valley and orbital degeneracies of the bands near the Fermi level [8–10], increasing the PF, as reported in SnSe [11] and CoSb₃ [12]. Another approach is the suppression

> of lattice thermal conductivity scattering phonons through the control of various structural defects, including alloying [13] and grain boundaries [14], especially at the nanoscale [15,16]. Generally, lattice thermal conductivity is influenced

> improving the energy conversion efficiency of TE devices and is a key challenge for enabling widespread applications for

> energy conservation. In principle, this can be achieved by

enhancement of electronic transport, specifically the power

factor $PF = \sigma S^2$, and by suppressing the thermal conductivity,

in particular the lattice thermal conductivity. S, σ , and κ_e

 $(\kappa_e = L\sigma T, \text{ where } L \text{ is Lorentz number } [4,5])$ are interrelated

through the electronic band structure, carrier scattering, and

carrier concentration. However, κ_l can be a relatively inde-

pendent parameter. This is the basis for the phonon-glass

electron-crystal (PGEC) concept [6,7], in which one seeks

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by specific heat, phonon relaxation time, and phonon group velocities. Mechanisms for minimizing lattice thermal conductivity include reducing phonon mean free paths through strong anharmonicity, liquidlike behavior [17], chemistry-based approaches, including lone pair electrons [18,19] and resonant bonds [20,21], the use of rattling modes [22,23], and reduced phonon group velocities through structural complexity. In the end, it is necessary to achieve improvements in both electrical properties and thermal conductivity to realize the high-performance materials that will be needed for practical TE energy technologies with broad impact.

Zintl phases offer a well-recognized route to realizing PGEC behavior, and many of these compounds have been found to be good TE materials when optimized. However, this is an extremely large and diverse class of materials, of which relatively few have been studied as thermoelectrics. As mentioned, some of these materials are excellent PGEC TE materials. However, many others are not. Understanding the reasons is therefore an important direction in thermoelectrics research. Here, we explore two closely related compounds, KSrBi and SrLiBi, which differ in the replacement of the large and very electropositive K by smaller and less electropositive Li (here the International Union of Pure and Applied Chemistry convention based on Pauling electronegativity is used for the order of elements in the chemical formulas; the electronegativity of Li, 0.98, is slightly higher than that of K, 0.82). We find rather distinct behavior in these two materials and identify the underlying reasons, providing insights into the distinct behaviors observed in Zintl phases.

Zintl phases are compounds in which electropositive ions donate charge to anionic units [24,25]. These electropositive ions stabilize the structure through closed-shell repulsion between these cations and the neighboring atoms and through the long-range Coulomb interaction but typically do not contribute significantly to the electronic structure near the Fermi level (note that the effective sizes of cations, controlled by closed-shell repulsion and characterized, for example, by the Shannon ionic radii [26], play key roles in selecting stable structures and preventing structures from collapsing, particularly when the frameworks lack rigidity, while attractive Coulomb interactions between anions and cations provide cohesion). The polyanionic units, if connected, provide conducting pathways near the Fermi level and then are central to the charge transport. Thus, there are two distinct parts of the structure, the electropositive ions and the anionic framework. In addition, two types of bonding are involved, specifically ionic and closed-shell interactions between the electropositive cations and the polyanions and the more covalent bonding internal to the polyanions. These characteristics provide the opportunity to tune both lattice thermal conductivity, often using the electropositive cations, for example, as rattlers, and the electrical transport, which is controlled by the properties of the anionic framework [27,28].

This separation provides a conceptual framework for realizing PGEC behavior and TE performance. The presence of electropositive ions suggests the possibility of these being weakly bonded, leading to rattling behavior, and the complex structures of many Zintl compounds may also favor low thermal conductivity [29]. Notably, many materials exhibiting rattling modes have been experimentally shown to have remarkably low lattice thermal conductivity [30]. Rattling behavior refers to the occurrence of large-amplitude vibrations in weakly bound atoms or atom clusters, resulting in softening of the acoustic phonon branches due to the avoided crossing effect. Such rattling behavior has been observed in partially filled skutterudites [31] and clathrates [32,33]. Clathrates, including Ba₈Ga₁₆Ge₃₀, provide excellent examples of Zintl thermoelectrics with rattling behavior. In Ba₈Ga₁₆Ge₃₀ largeamplitude anisotropic motion of the Ba ions and a tendency to off center at low temperature, presumably due to the small size of Ba²⁺ relative to the rigid clathrate cage, have been observed using diffraction [33]. However, in other important Zintl thermoelectrics, such as Mg₃Sb₂, the connection between rattling and low thermal conductivity is less evident, although soft anharmonic phonons have been observed [34]. The rattling concept can also be generalized to account for thermal conductivity reduction due to weakly bound atoms, even when these atoms lead to dispersive as opposed to flat phonon branches, as is often the case in half-Heusler thermoelectrics [35]. However, in practice the electropositive ions and the anionic framework do interact, often in complex ways that can complicate the search for new TE materials.

Examples of Zintl TE materials include Ca₅Al₂Sb₆ (ZT > 0.6 at 1000 K) [36], Yb₁₄AlSb₁₁ (ZT = 1.3 at 1223 K) [37], and Sr_3AlSb_3 (*ZT* = 0.3 at 600 K) [38]. More recently, calcium-based Zintl-phase materials CaLiPn (Pn = As, Sb, Bi) have exhibited exceptionally low thermal conductivity (0.4-1.0 W/mK) combined with favorable electrical transport properties [39]. Strontium-based pnictogen compounds, such as SrLiAs [40] and SrLiSb [41], have characteristics of promising TE materials. Materials containing heavier constituent elements tend to have lower sound velocity and lower intrinsic lattice thermal conductivity. Thus, one may anticipate that SrLiBi, being heavier than SrLiAs and SrLiSb and having the same crystal structure, may also have promising thermoelectric properties. In addition, one may note that monovalent cations tend to have weaker ionic interactions and thus are often good rattlers in the context of thermal conductivity, with some examples being CsAg₅Te₃ [42], Cu_{1.6}Bi_{4.8}S₈ [43], and $AgBi_3S_5$ [30]. It is also noteworthy that although it is a light atom, Li can yield rattling behavior due to weak bonding in a large cage.

In the present work, we investigate the known compound SrLiBi [44] and compare it with KSrBi. For this purpose, we determined the ground state structure of KSrBi using a first-principles structure search via the CALYPSO code [45]. We found that SrLiBi and KSrBi have the same space group, Pnma (No. 62), and basic structure. However, they differ significantly in the cation positions. The positions of the monovalent cation (K^+) and the divalent cation (Sr^{2+}) are exchanged relative to SrLiBi. This results in a considerable difference in the calculated lattice thermal conductivities of KSrBi (0.7 W/mK) and SrLiBi (2.2 W/mK). This is connected to the different cage structures for the cations and different rattling behaviors. We performed a comprehensive analysis of the thermoelectric properties and electronic structure as related to bonding. In addition to the different behaviors of the rattling ions, we find an antibonding state near the band edges and a softer lattice structure in KSrBi.

II. COMPUTATIONAL DETAILS

A. Density functional theory calculations

We used two density functional codes in this work. The present density functional theory calculations for the total energies, phonons, dynamics, and structure determinations were performed with the projector augmented wave (PAW) method, as implemented in the Vienna Ab initio Simulation Package (VASP) [46]. This package has efficient structure relaxations and dynamics, and it is well suited to calculations for large unit cells as needed for phonon and dynamics calculations. We used the generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE-GGA) [47]. We used an energy cutoff for the plane wave expansion of 400 eV for total energy calculations along with a $7 \times 12 \times 7$ Monkhorst-Pack k-point mesh. We tested the energy convergence for the two compounds by doing total energy calculations with different cutoff energies. The geometry was relaxed until the total energy was below 10^{-8} eV and the Hellmann-Feynman forces were less than 10^{-4} eV/Å .

The electronic structures were calculated using the augmented plane wave (APW) plus local orbital method [48], as implemented in the WIEN2K code [49]. For this purpose, we included spin-orbit coupling (SOC) and utilized the modified Becke-Johnson potential of Tran and Blaha (TB-mBJ), known for providing accurate electronic band structures and band gaps in simple insulators and semiconductors [50,51]. This is important for the electronic aspects of TE performance. The WIEN2K code provides very high accuracy for the electronic structures, including for calculations with the TB-mBJ potential and SOC. A basis set cutoff parameter of $R_{mt}K_{max} = 9$ was employed, where R_{mt} is the smallest APW sphere radius and K_{max} is the plane wave cutoff parameter. The resulting electronic structures were used to obtain electrical transport properties [50]. This was done using semiclassical Boltzmann theory [52] and the BOLTZTRAP code [53] with first-principles electronic structures evaluated on approximately 30 000 k points in the irreducible Brillouin zone (BZ). The transport calculations were done with the constant scattering time approximation.

B. Lattice thermal conductivity

The lattice thermal conductivity depends on phonon dispersions and anharmonic couplings. We used the temperaturedependent effective potential (TDEP) method to extract the anharmonic force constants. This method can provide stable and well-constrained interatomic force constants (IFCs) for complex crystal structures such as those of KSrBi and SrLiBi [54]. The TDEP calculation was based on Born-Oppenheimer molecular dynamics with the PAW method, utilizing a Nosé thermostat at 300 K [55]. In these calculations, the electronic degrees of freedom are fully relaxed for each time step, i.e., for each set of nuclear positions, and the nuclear dynamics is then governed by the resulting energy and its gradients from the electronic structure calculation. For this purpose, we used 96-atom supercells of KSrBi and SrLiBi with a simulation time of 10 ps, a time step of 1 fs, and a plane wave cutoff of 320 eV. The phonon dispersion relations of KSrBi and SrLiBi were obtained from second-order IFCs using the PHONOPY package [56]. A $4 \times 6 \times 4$ Monkhorst-Pack **k**-point grid and $2 \times 2 \times 2$ supercells with 96 atoms were employed. We used these anharmonic IFCs from the TDEP calculation as input to the thermal conductivity calculation. The thermal conductivity was determined from the second-order and thirdorder IFCs using the SHENGBTE package [57]. We employed a well-converged phonon momentum **q** mesh of $11 \times 19 \times 10$ for KSrBi and $9 \times 12 \times 9$ for SrLiBi in this calculation (see Fig. S1 in the Supplemental Material [58] for convergence tests establishing accuracy and convergence). It should be noted that we consider anharmonicity at only third order. In general, higher-order terms can open additional scattering channels, leading to further reductions in thermal conductivity. This was noted, for example, in the (Sc,Y)AgSe₂ system [59], and the effects of these new scattering channels can, for example, allow scattering that is forbidden at third order by phonon band gaps [60,61].

C. Electrical transport properties

The electrical transport parameters (*S* and σ/τ) were obtained within Boltzmann theory using the BOLTZTRAP code [53]. Within this approach a relaxation time τ is needed to calculate σ . For this purpose, we used values of τ obtained with deformation potential theory in the form from Bardeen and Shockley [62],

$$\tau = \frac{2\sqrt{2\pi}\hbar^4 \rho v_l^2}{3E_d^2 (m^* k_B T)^{3/2}},$$
(1)

where \hbar is the reduced Planck constant, ρ is the mass density, υ_l is the longitudinal sound velocity, E_d is the deformation potential constant, m^* is transport effective mass, and k_B is the Boltzmann constant. υ_l are obtained from $\upsilon_l = \sqrt{\frac{B+4/3G}{\rho}}$, where *B* and *G* are the bulk modulus and shear modulus (see Table II), respectively [63]. The transport effective mass can be determined from $(m^*)^{-1} = \sigma/ne^2\tau$, where *n* is the carrier density [64]. The deformation potential E_d is defined as $E_d = \Delta E/(\frac{\Delta V}{V})$. E_d for holes and electrons is calculated from the energy changes in the valence band maximum (VBM) and conduction band minimum (CBM) with volume change $\Delta V/V$. The electronic thermal conductivity was calculated using the Lorenz formula $\kappa_e = L_0 \sigma T$, where L_0 is the single parabolic band Lorenz number,

$$L_{0} = \left(\frac{k_{B}}{e}\right)^{2} \left\{ \frac{\left(r + \frac{7}{2}\right)F_{r + \frac{5}{2}}}{\left(r + \frac{3}{2}\right)F_{r + \frac{1}{2}}} - \left[\frac{\left(r + \frac{5}{2}\right)F_{r + \frac{3}{2}}}{\left(r + \frac{3}{2}\right)F_{r + \frac{1}{2}}}\right]^{2} \right\}, \quad (2)$$

where r = -1/2 and F_x are the Fermi integrals $F_x(E^*)$. Specifically, $F_x(E^*)$ is expressed as

$$F_x(E^*) = \int_0^\infty \frac{E^x}{1 + exp(E - E^*)} dE,$$
 (3)

where E^* (= E_F/k_BT) is the reduced chemical potential. We tested this formula against transport calculations done using BOLTZTRAP at 300 K, with the correction for open-circuit boundary conditions [5] and found good agreement except for *p*-type KSrBi, which has very flat valence bands and is not predicted to be a reasonable thermoelectric compared to



FIG. 1. Energies of structures in different generations as obtained in the global optimization search for the ground state of KSrBi. The red point indicates the ground state energy. The blue points indicate the space groups P4/nmm (11 meV/atom above the ground state), *Pbca* (12 meV/atom above the ground state), and C2/m (17 meV/atom above the ground state).

n-type KSrBi. Detailed calculated values are provided in the Supplemental Material.

III. RESULTS AND DISCUSSION

A. Crystal structures and thermodynamic stability

SrLiBi forms within the orthorhombic TiNiSi structure with space group *Pnma* (No. 62) and a primitive unit cell containing 12 atoms. The calculated PBE-GGA lattice constants, a = 8.20 Å, b = 4.93 Å, and c = 8.67 Å, are in reasonable agreement with reported experimental values, a = 8.29 Å, b = 4.93 Å, and c = 8.76 Å [44] and a = 8.113 Å, b = 4.8852 Å, and c = 8.571 Å [65].

KSrBi is not a known compound. We investigated its structure and stability, starting with the structure of SrLiBi with Li replaced by K and also the same structure with K and Sr interchanged. We then used first-principles structure determination to search for a ground state. For this, we used the unbiased particle swarm structure search method as implemented in the CALYPSO code [45]. In this search, we considered unit cells up to 4 f.u. in size. The evolutionary search was done for 50 generations, with each generation comprising 50 structures. The lowest-energy structure was found to be the *Pnma* space group with inverted structure, i.e., the SrLiBi structure with the monovalent and divalent cations interchanged.

Figure 1 shows the progress of the evolutionary search. The lowest-energy state was found quickly and appeared in the third generation of the search. No new ground state was generated in subsequent generations. These results confirm that the ground state structure of KSrBi is orthorhombic, with optimized lattice parameters of a = 9.22 Å, b = 5.56 Å, and c = 10.03 Å. We found that when relaxed, this interchanged structure is lower in energy compared to the SrLiBi structure by approximately 0.07 eV/atom.

We additionally calculated the formation energies ΔE of KSrBi and SrLiBi,

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$$\Delta E = E_{(\text{SrXBi})} - E_{(\text{Sr})} - E_{(X)} - E_{(\text{Bi})}, \qquad (4)$$



FIG. 2. AIMD evolution for the energy of KSrBi and SrLiBi at 300 and 800 K.

where $E_{(SrXBi)}$ is the total energy of SrXBi; $E_{(K)}$, $E_{(Li)}$, $E_{(Sr)}$, and $E_{(Bi)}$ are energies of the elements per atom. The calculated formation energies for KSrBi and SrLiBi are -2.1 and -2.5 eV, respectively. Furthermore, to investigate the thermal stability of KSrBi and SrLiBi, we performed *ab initio* molecular dynamics (AIMD) simulations at 300 K and 800 K, as depicted in Fig. 2. The total energy and temperature exhibited only slight fluctuations during 40 ps AIMD simulations done at both 300 and 800 K using 96-atom supercells. There was no evidence of bond breakage or structural changes during the simulations. These results imply that both compounds are at least metastable, which is in accord with the experiment for SrLiBi, whose melting temperature is likely in excess of 1200 K based on the reported synthesis conditions between 1250 and 1350 K [44].

The crystal structures are depicted in Fig. 3. The Sr in KSrBi is fourfold coordinated in an irregular tetrahedral arrangement by Bi, with Sr-Bi distances ranging from 3.388 to 3.422 Å. The Bi-Sr-Bi angles range from 103° to 116° [Fig. 3(c)]. The Bi atoms form cagelike structures around K. The structure of SrLiBi is related but differs in that Sr now occupies the cages. In addition, presumably due to the small ionic radius of Li, there is considerable variation in the Li-Bi distances, which range from 2.918 to 3.133 Å [Fig. 3(f)].

We performed a crystal orbital Hamilton population (COHP) analysis in order to gain insight into the bonding, as shown in Fig. 4. This method allows for the identification of different chemical bonds by dividing the electronic energy based on the band structure into pairs of orbital interactions. Additionally, the integral COHP (ICOHP) provides an assessment of the overall bond strength by examining the contribution of chemical bonds to the single-particle band energies [66]. Positive and negative COHP represent antibonding and bonding interactions, respectively. The results show that the stronger interactions in the two compounds are those involving Sr-Bi (ICOHP = -0.47 eV) in KSrBi and Li-Bi (ICOHP = -0.64 eV) in SrLiBi. This is consistent with the inverted sites between the two structures.

Interestingly, the Bi-Sr interaction displays an antibonding behavior near the valence band edge in KSrBi due to p - p coupling between Bi 6p and Sr 4p orbitals. The presence of



FIG. 3. (a) and (d) Crystal structures of KSrBi and SrLiBi in a $2 \times 2 \times 2$ supercell, with Li, Bi, Sr, and K atoms shown as yellow, blue, green, and pink spheres, respectively. (b) and (e) Primitive cells of KSrBi and SrLiBi, respectively. (c) SrBi₄ tetrahedra and (f) LiBi₄ tetrahedra.

occupied antibonding states destabilizes the Bi-Sr bond, resulting in weaker interatomic interactions in KSrBi compared to SrLiBi. As shown in Fig. S2, in KSrBi, the Bi-Sr antibonding state is derived mainly from Bi 6p and Sr 4p orbitals. Li, which takes the place of Sr in the structure of SrLiBi, does not exhibit this chemistry, and antibonding states are confined to the conduction band. The occupied antibonding states in KSrBi near the valence band maximum give rise to a softer lattice, which favors anharmonicity and reduced lattice thermal conductivity. This is supported by the calculated Grüneisen parameters γ for KSrBi and SrLiBi, as shown in Fig. S3. It is apparent that KSrBi exhibits significantly larger values of γ , which is a distinct characteristic associated with its low thermal conductivity. It should also be noted that the very large positive γ for some acoustic branches, especially near the zone center, suggests that there will be a structural phase transition under lattice expansion. We tested this by doing phonon calculations with a 0.5% volume expansion of the lattice and indeed found phonon instabilities in that case.

B. Lattice dynamics and phonons

The calculated phonon dispersion curves and projected phonon densities of states (PHDOSs) for KSrBi and SrLiBi



FIG. 4. Crystal orbital Hamilton population (COHP) of the nearest-neighbor atomic pairs for (a) KSrBi and (b) SrLiBi. The dashed line denotes the position of the valence band maximum.

are shown in Fig. 5. The compounds are dynamically stable, and in particular there are no unstable modes in the dispersions. Analysis of the PHDOS shows that the different atoms contribute in different frequency ranges. The low-frequency region in both compounds is dominated by Bi contributions, as might be expected based on the high atomic mass of Bi (208.98 amu) compared to the other atoms. In KSrBi, the



FIG. 5. Projected phonon dispersions and partial density of states for KSrBi (top) and SrLiBi (bottom). The symbol size denotes the contributions of Bi (blue), K/Li (green), and Sr (red).

TABLE I. The phonon velocity $v_{TA,TA',LA}$ (m/s) along the x, y, and z directions in KSrBi and SrLiBi.

Compound	$v_{\mathrm{TA}x}$	v_{TAy}	$v_{\mathrm{TA}z}$	$v_{\mathrm{TA}'x}$	$v_{\mathrm{TA}'y}$	$v_{\mathrm{TA}'z}$	$v_{\mathrm{LA}x}$	$v_{ m LAy}$	v_{LAz}
KSrBi	1244.8	1464.2	1395.7	1416.7	1564.4	1480.5	1693.5	2564.9	2550.9
SrLiBi	1750.9	2023.4	1820.5	2140.0	2134.4	2260.3	3145.5	3336.4	2569.2

K and Sr contributions are in the mid- and high-frequency phonon modes with a continuous distribution of modes from the acoustic branches up to maximum phonon frequency near 4 THz. In SrLiBi, the phonon spectrum is gapped between a lower frequency range with primary Bi and Sr contributions up to approximately 4 THz and then two sets of higherfrequency optical branches of Li character.

The K modes in KSrBi exhibit relatively dispersionless behavior around 2 to 3 THz. This is one of the characteristics associated with rattling in thermoelectric materials [31,67]. Avoided crossings between the acoustic and optical modes are also an indicator of rattling. In KSrBi there is folding of the acoustic modes due to the presence of 4 f.u. in the cell. This complicates the analysis. We present the phonon dispersion and corresponding displacement vectors along different paths (Fig. S4). For KSrBi there are avoided crossings between the acoustic and optical modes along $S - Y (\Gamma - X)$ and $\Gamma - Z$ $(Y - \Gamma)$, spanning the frequency range from 0 to 1.5 THz. Similar behavior is found in SrLiBi in the frequency range from 0 to 2 THz. As illustrated in Fig. S4, for instance, points A and B along the S - Y path exhibit distinct atomic displacement vectors, while points A(B) and D(C) share similar displacement vectors. The same behavior is found in other paths with avoiding crossings. Notably, the avoided crossing results in a reduction of the group velocities and therefore the heat propagation and thermal conductivity.

It is noteworthy that the maximum phonon frequency in KSrBi is approximately 4 THz. This value is comparable to those of Bi₂Te₃ (4.6 THz) [68], Sb₂Te₃ (5.2 THz) [69], and SnSe (5.6 THz) [70]. On the other hand, SrLiBi exhibits a higher cutoff frequency due to the high-frequency Li phonons. Importantly, the acoustic frequencies in KSrBi are lower than those in SrLiBi, indicating lower acoustic phonon velocities in KSrBi. The phonon group velocity is given by the slope of the acoustic phonon dispersion around the Γ point $(v_i = \frac{\partial \omega_i(k)}{\partial k})$ [71]. We calculated the phonon group velocities along the Γ -x, Γ -y, and Γ -z directions. For KSrBi (SrLiBi), the first transverse phonon velocities along the x, y, and z directions are 1244.8 (1750.9), 1464.2 (2023.4), and 1395.7 (1820.5) m/s. The group velocities of other acoustic branches as presented in Table I. The group velocities of KSrBi along the x, y, and z directions are significantly lower than those of SrLiBi. Consequently, it can be anticipated that KSrBi may exhibit lower thermal conductivity than SrLiBi. Also, it may be noted that the lowest average acoustic phonon velocities and the lowest longitudinal acoustic velocity (normally the most important branch for heat conduction) for SrLiBi are along the z direction, which is the lowest thermal conductivity direction.

As mentioned, the analysis of the phonon dispersions is complicated by the size of the unit cell, which leads to folded branches. We calculated the atomic displacement parameters (ADPs) and potential energies of KSrBi and SrLiBi in order to better address the issue of rattling. ADP values reflect the magnitude of the mean-square displacement of atoms around their equilibrium positions, serving as an indicator of chemical bond strength within a crystal [72]. Generally, a large ADP value implies a shallow energy surface, i.e., lower force constants and a weakly bonded atom [73]. Hence, significant rattling behavior can be identified by the large ADP or shallow potential energy well. As illustrated in Fig. 6, the K atoms in KSrBi clearly demonstrate pronounced rattling behavior, characterized by their substantial ADPs and correspondingly shallow potential wells. Conversely, the Li in SrLiBi exhibits a lower ADP, reflecting a deeper potential energy well (it may be noted that the Li ADP is largest in the x direction, which has a shallower potential well than for the other Cartesian directions and is the direction of the longest Li-Bi distance). Consequently, since large ADP correlates with low thermal conductivity, this indicates that KSrBi may exhibit lower thermal conductivity compared with SrLiBi.

Rattler atoms are characterized by weak bonding with neighboring atoms [74]. To further analyze the forces between K or Li atoms and the neighboring atoms, we calculated effective spring constants k for the different atoms based on analysis of the phonon spectra. The effective spring constant $(k = \varpi^2 m)$ is obtained from moments of the PHDOS and serves as a measure of the effective binding of atoms, while the ratio of k_{\min} to k_{\max} is useful for identifying the presence of



FIG. 6. Calculated atomic displacement parameters (ADPs) for (a) KSrBi and (b) SrLiBi. The calculated potential energy curves for all the atoms as a function of displacement around the equilibrium positions along the x, y, and z directions for (c) KSrBi and (d) SrLiBi.

Compound	$k_1(Sr)$	<i>k</i> ₂ (Bi)	<i>k</i> ₃ (K/Li)	$k_{\rm min}/k_{\rm max}$	B (GPa)	G (GPa)	ρ (kg/m ³)
KSrBi	46.49	38.23	15.97	0.34	18.32	9.34	4334.6
SrLiBi	45.15	52.73	29.78	0.56	31.17	23.73	5752.4

TABLE II. The spring constant k (N/m) for each atom and the ratio between the minimum and maximum spring constants, the bulk modulus B and shear modulus G, and density ρ for KSrBi and SrLiBi.

underbonded rattling atoms in a crystal structure [35]. A small k_{\min}/k_{\max} indicates weak bonding involving at least one atom. The calculated effective spring constant k (N/m) for each atom and the ratio between of the minimum and maximum spring constants in KSrBi and SrLiBi are provided in Table II. Our calculations demonstrate that both K and Li atoms exhibit rattling vibrational behavior. Notably, SrLiBi exhibits a small k_{\min}/k_{\max} ratio, indicating weak bonding involving at least one atom. Comparing the k values, the small k value (29.78) of Li relative to Sr (45.15) and Bi (52.73) suggests that the Li atom is weakly bonded with Sr and Bi atoms. This weak bonding is a characteristic feature of classical rattling. However, because the Li optical branches are, nonetheless, at high frequency far from the heat-carrying acoustic branches, this rattling may be relatively ineffective in suppressing heat transport. An even smaller ratio k_{\min}/k_{\max} is found for KSrBi, indicating stronger underbonding of K in that compound relative to Li in SrLiBi. However, K is a better rattler from the point of view of both the ADP and the effective spring constant. This is further evidenced by the larger ADP and shallower potential energy well observed for the K atom. Furthermore, the K modes are at lower frequency closer to the acoustic branches and, from this point of view, are more likely to interact with the heat-carrying phonons. The more pronounced rattling vibrations of K atoms in KSrBi suggest a lower thermal conductivity compared to SrLiBi. This expectation is confirmed by detailed thermal conductivity calculations, described below.

The calculated temperature-dependent lattice thermal conductivity of KSrBi and SrLiBi using the TDEP package [54] is shown in Fig. 7. Our calculations show that KSrBi indeed



FIG. 7. The lattice thermal conductivity as a function of temperature for KSrBi and SrLiBi.

has a much lower lattice thermal conductivity than SrLiBi, 0.7 compared to 2.2 W/mK at 300 K. To better demonstrate the role of phonon modes in the heat conduction process, we calculated the cumulative lattice thermal conductivity at room temperature, as shown in Fig. 8. This increases rapidly in the low-frequency acoustic modes of 0 to 1 THz (0 to 1.7 THz) for KSrBi (SrLiBi), and this phonon frequency range contributes 78% (76%) of the lattice thermal conductivity. For KSrBi, in the frequency range of 1 to 4 THz, κ_l also has an increasing trend, which is mainly due to the influence of optical phonons. In SrLiBi, the frequency range of 1.7 to 2 THz makes a significant contribution to κ_l , which involves low-frequency optical branches. As expected, the high-frequency Li modes in the frequency range of 4 to 10 THz make no significant contribution to the thermal conductivity. There is also significant direction dependence in these orthorhombic compounds. KSrBi has the smallest κ_l along the x direction, while SrLiBi has the smallest κ_l along the z direction. This can be mainly ascribed to the lower acoustic group velocities of KSrBi along the x direction ($v_{LAx} = 1693.5 \text{ m/s}$) and SrLiBi along the z direction ($v_{LAx} = 2569.2 \text{ m/s}$; as shown in Table I).

We conducted an analysis of the anharmonic phononphonon scattering in order to better understand the thermal conductivity. Figure 9(a) presents the calculated anharmonic scattering rates at 300 K for KSrBi and SrLiBi. It is evident that the anharmonic scattering rates generally exhibit an increasing trend throughout the frequency range. In the low-frequency regions (below 2 THz) important for thermal conductivity, KSrBi exhibits larger scattering rates compared to SrLiBi. It is worth mentioning that both KSrBi and SrLiBi show more pronounced peaks in their anharmonic scattering rates at approximately ~ 1.3 THz. This can be attributed to the coupling between the low-frequency optical and acoustic branches. Furthermore, the anharmonic scattering rates of KSrBi are significantly enhanced within the frequency range of 2-3 THz. This reflects anharmonic coupling between the rattling K ions and the other phonon branches. Higher



FIG. 8. The cumulative lattice thermal conductivity in (a) KSrBi and (b) SrLiBi at 300 K as a function of frequency.



FIG. 9. (a) Anharmonic scattering rates as a function of frequency for KSrBi and SrLiBi. (b) Calculated three-phonon anharmonic scattering phase space W^{\pm} of KSrBi and SrLiBi. The + (-) sign represents three-phonon absorption (emission) phase space.

anharmonic scattering rates are associated with shorter phonon lifetimes, resulting in reduced contributions of these phonons to the lattice thermal conductivity. Thus, the presence of rattling K atoms plays a crucial role in reducing the lattice thermal conductivity of KSrBi.

The three-phonon anharmonic scattering phase space W^{\pm} is depicted in Fig. 9(b). This provides information regarding the contribution of phonon modes to the anharmonic scattering rate. As observed, the scattering phase space for KSrBi is larger than that of SrLiBi, explaining the significantly lower thermal conductivity of KSrBi compared to SrLiBi. In particular, the relatively weak bonding K in KSrBi, as evidenced by larger ADPs, shallower potential wells, and lower effective spring constant in comparison to Li atoms in SrLiBi, leads to a more substantial anharmonic scattering rate and scattering phase space, ultimately resulting in the lower thermal conductivity of KSrBi relative to SrLiBi. These findings highlight the importance of the rattling concept in reducing thermal conductivity in Zintl-phase compounds.

C. Electronic properties and electrical transport

While the focus of the current work is on the thermal conductivity, it is, nonetheless, of interest to estimate the thermoelectric properties, including the electronic transport, since thermoelectricity is a main source of interest in low lattice thermal conductivity semiconductors. For this purpose we use the first-principles electronic structure and an estimation of the scattering time for Boltzmann transport based on deformation potential theory. This has the advantage of being computationally tractable and including material and temperature dependence [52,75]. It should be noted, however, that while used extensively in identifying potential thermoelectrics, it has a number of severe approximations, for example, treating all electron-phonon scattering as nonpolar acoustic scattering [76]. As such, while it may be a reasonable approach for identifying potential thermoelectrics [77], the values for thermoelectric performance obtained here should be regarded as semiquantitative estimates.

Figures 10(a) and 10(b) show the band structures of KSrBi and SrLiBi, respectively. Both materials are direct gap semiconductors with the CBM and VBM located at the Γ point in the BZ. The band gaps E_g are 1.63 and 1.07 eV for KSrBi and



FIG. 10. Calculated band structure of (a) KSrBi and (b) SrLiBi. The black dashed line represents the valence band maximum.

SrLiBi, respectively. In Fig. 10(a), it is evident that the CBM in KSrBi displays dispersive states, while the bands around the VBM exhibit considerably less dispersion. Consequently, it is expected that flat and heavy valence band edges will lead to a high *p*-type Seebeck coefficient. However, this characteristic also is expected to lead to a significant suppression of hole mobility, resulting in low *p*-type electrical conductivity. This is consistent with our calculated transport results, given in Fig. 11. Turning to SrLiBi, it is worth noting that there is a secondary conduction band energy valley at point *T*, which is only 0.12 eV away from the Γ -point CBM. It is also noteworthy that this compound shows more similarity between electrons and holes, and in particular, the valence bands near the band edge are much more dispersive than in KSrBi.

As mentioned, the Seebeck coefficient and electrical conductivity are countercorrelated, so heavy mass leads to a higher Seebeck coefficient and lower conductivity. Nonetheless, it is possible to use special band structures and band engineering to find materials that have both good conductivity and a high Seebeck coefficient. Examples include high valley degeneracies, band anisotropy, and band convergence, as



FIG. 11. Calculated electrical transport properties as a function of doping level (*p* or *n*) for KSrBi and SrLiBi at 300 K: (a) electrical conductivity σ , (b) transport effective mass m^* , and (c) Seebeck coefficient *S*.



FIG. 12. The calculated ZT values of (a) KSrBi and (b) SrLiBi as a function of carrier concentration at 300, 600, and 800 K.

discussed above. As shown in Fig. S5(a), the isoenergy surface for SrLiBi above the CBM (shown as +0.18 eV above) reveals four one quarter pockets at the *T* point, with a symmetry degeneracy of 1. Additionally, there is one pocket at the Γ point. Thus, N_v of the conduction band is effectively 2, provided that the doping and temperature are such that both pockets are active in transport. Furthermore, there is a secondary valence band maximum located at the Γ point, 0.11 eV lower than the VBM. Additionally, a hole light band at Γ is only 0.04 eV below the secondary valence maximum. Due to the small energy difference between these bands, these bands may become active in transport. The effective degeneracy of the valence band can reach 3, as observed in Fig. S5(b).

Figure 11 presents the calculated effective transport mass m^* , electrical conductivity σ , and *S* at 300 K for KSrBi and SrLiBi. The transport effective mass of *p*-type KSrBi is larger than that of *n*-type KSrBi, and this higher effective mass suppresses the electron mobility ($\mu \propto 1/m^{*2/3}$), resulting in low conductivity of *p*-type KSrBi [Fig. 12(a)]. The overall electrical transport properties are generally better for *n*-type KSrBi, primarily influenced by the electrical conductivity. For SrLiBi, the high effective mass of electrons leads to a higher Seebeck coefficient for the *n* type compared to the *p* type ($S \propto N_v^{2/3}m^*$). As observed, the electrical conductivity of *n*-type SrLiBi is similar to that of *p*-type SrLiBi. Considering these factors, it is evident that the thermoelectric performance of *n*-type SrLiBi surpasses that of *p* type.

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The resulting ZT values of KSrBi and SrLiBi, based on their electrical and thermal transport properties, are presented in Fig. 12. The ZT values of both n-type KSrBi and SrLiBi are higher than their corresponding *p*-type counterparts. At 300 and 800 K, the peak ZT values of n-type KSrBi are approximately 0.90 and 2.80, with the corresponding optimum carrier concentrations being 2.01×10^{18} and 3.63×10^{18} cm⁻³, respectively. For *n*-type SrLiBi, the peak ZT are approximately 0.92 and 3.42, with the corresponding optimum carrier concentrations being 1.84×10^{19} and 4.03×10^{19} cm⁻³, respectively. Despite KSrBi having a lower thermal conductivity than SrLiBi, the ZT values for both n- and p-type SrLiBi are higher than those of KSrBi. This can be primarily attributed to the more favorable electronic structure of SrLiBi. In any case, both of these compounds are predicted to be reasonable thermoelectric materials when optimally doped.

IV. SUMMARY AND CONCLUSIONS

We investigated thermal and electronic properties of two closely related Zintl-phase compounds, KSrBi and SrLiBi. We found that these compounds exhibit remarkably different thermal conductivities. The underlying cause for this difference was found to be rattling of K ions in KSrBi and a softer lattice associated with occupied antibonding states. Consequently, a synergistic effect emerges, wherein the combination of the strong rattling scattering of K atoms and the presence of antibonding states below the VBM in KSrBi leads to a significantly lower thermal conductivity compared to SrLiBi. Overall, our findings shed light on the potential role played by antibonding states in Zintl compounds as well as the analysis of rattling in complex materials using ADP and effective spring constants.

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