Intrinsic nanostructure induced ultralow thermal conductivity yields enhanced thermoelectric performance in Zintl phase Eu$_2$ZnSb$_2$

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The Zintl thermoelectric phase Eu$_2$ZnSb$_2$ has a remarkable combination of high mobility and low thermal conductivity that leads to good thermoelectric performance. The key feature of this compound is a crystal structure that has a Zn-site with a 50% occupancy. Here we use comparison of experimental thermal conductivity measurements and first principles thermal conductivity calculations to characterize the thermal conductivity reduction. We find that partial ordering, characterized by local order, but Zn-site disorder on longer scales, leads to an intrinsic nanostructuring induced reduction in thermal conductivity, while retaining electron mobility. This provides a direction for identifying Zintl compounds with ultralow lattice thermal conductivity and good electrical conductivity.
Understanding heat conduction in solids is an ongoing challenge in condensed matter physics with important practical implications. This is particularly so in low thermal conductivity materials of importance for thermoelectrics and in thermal barrier materials, where for example perturbative pictures based on phonons and phonon scattering may breakdown due to strong scattering from disorder and/or strong anharmonicity. Moreover, identifying mechanisms that allow reduction of thermal conductivity without commensurate reductions in electrical conductivity remains a central problem in thermoelectrics research. It has been addressed by the introduction of rattling modes associated with weakly bound atoms, alloy scattering, disorder, nanostructuring, anharmonic bonds associated with lone pairs, and the selection of materials with complex Zintl structures or soft anharmonic phonons, for example near structural phase transitions. High thermoelectric performance has been achieved in materials with intrinsic low thermal conductivity including Cu$_2$Se$_2$, SnSe$_2$, MgAgSb$_2$, Yb$_{14}$MnSb$_{11}$, and Ag$_9$GaSe$_6$. These results illustrate the importance of searching for materials with low thermal conductivity to find thermoelectric compositions.

However, all approaches for achieving low thermal conductivity have limitations. In particular, phonon-based approaches generally yield very low thermal conductivities only at high temperatures, where the effects of anharmonic phonon scattering are strongest, while disorder-based approaches typically lower the thermal conductivity, but also in general strongly affect electronic conductivity so that only certain amounts and types of disorder can be used. Thus, understanding mechanisms for obtaining low thermal conductivity without degraded electrical properties remains an important challenge.

Here we demonstrate a direction, where a partially filled site behaves as if ordered for electrons but disordered for heat conduction. This can be understood in terms of the Zintl concept as providing electronic charge balance. As shown in Fig. 1, Zintl structures (space group: P6$_3$/mmc) in Eu$_2$ZnSb$_2$ there are 50% vacancies on the Zn site. This is understood in terms of the Zintl concept as providing electronic charge balance as monovalent Ag$^+$ is replaced by divalent Zn$^{2+}$. Thus the vacancies are needed for obtaining a semiconducting gap. Such a semiconducting gap is observed and is essential for thermoelectric performance. In addition, the stoichiometry is supported by X-ray diffraction Rietveld refinement. In contrast, the site is fully occupied by Ag atoms in EuAgSb$_2$. However, as noted, electronic structure calculations show that the details of the electronic structure near the band edges are dependent on the specific ordering of the Zn vacancies. In other words, there is an important interplay between Zn vacancy order and the electronic structure near the band edge. This implies strong electron scattering, and resulting low mobility, if the Zn atoms are strongly disordered on length scales comparable to electron mean free paths. Thus, although the exact structure is as yet unknown, two things are known, specifically that the Zn site in the average structure is at 50% occupancy and that there must be a high degree of Zn order at least locally. This is supported by imaging data shown in Supplementary materials, Fig. S1.

**Thermoelectric properties.** Thermoelectric samples of EuAgSb have both higher carrier concentration and carrier mobility, as compared with Eu$_2$ZnSb$_2$ (see Fig. 2). The high carrier mobility of EuAgSb is understood as mainly a consequence of the Ag–Sb framework, which is fully occupied and beneficial to the carrier transport. Temperature-dependent thermoelectric properties are shown in Fig. 3. Compared with Eu$_2$ZnSb$_2$, the higher carrier concentration of EuAgSb leads to higher electrical conductivity and smaller Seebeck coefficient, as usual. The maximum power factor of Eu$_2$ZnSb$_2$ is only $3.5 \mu W cm^{-1} K^{-2}$. This compares with the higher maximum power factor of EuAgSb, which can be greater than $10 \mu W cm^{-1} K^{-2}$.

However, the thermal conductivity of EuAgSb is much higher than that of Eu$_2$ZnSb$_2$. This total thermal conductivity includes both the lattice and electronic contributions. In order to obtain the lattice thermal conductivity, $\kappa_\text{L}$, the electronic contribution, $\kappa_\text{c}$ was subtracted from the measured total thermal conductivity, $\kappa$. The value of $\kappa_\text{c}$ was estimated based on the Wiedemann–Franz relationship ($\kappa_\text{c} = L_\text{0} T$). Here $L_\text{0}$ is the single parabolic band (SPB) model Lorenz number. This SPB model captures the reduction in $L$ near band edges of thermoelectric materials, and is based on the Seebeck coefficient that can be obtained experimentally. The agreement of this model with full Boltzmann transport calculations is generally reasonable, and going beyond it requires the detailed band structure and scattering models, which would depend on the details of the presently unknown Zn vacancy order. The electronic contribution is particularly important at higher temperature, where the limitations of this model should be kept in mind.

Importantly, the lattice thermal conductivity of Eu$_2$ZnSb$_2$ is close to that of EuAgSb at high temperature, but the value at room temperature is much lower. This leads to a higher $ZT$ for Eu$_2$ZnSb$_2$, especially at lower temperature. Thermoelectric device efficiency is governed by a temperature average, the so-called engineering $ZT$. The lower temperature range, while not enhancing the peak $ZT$ is important for the engineering $ZT$ and the efficiency of devices that might be made from this material. Understanding this difference in thermal conductivity is therefore key to understanding the high $ZT$ of Eu$_2$ZnSb$_2$. The phonon dispersion relations of Eu$_2$ZnSb$_2$ and EuAgSb as obtained from density functional theory calculations are shown in Fig. 4. For Eu$_2$ZnSb$_2$ these were obtained using ordered structures, with zigzag ordering of Zn vacancies within the ZnSb$_2$ plane. As

**Results and discussion**

**Crystallographic structure properties.** As shown in Fig. 1, Zintl-phase Eu$_2$ZnSb$_2$ and EuAgSb are based on the same hexagonal crystal structure (space group: P6$_3$/mmc). In the case of Eu$_2$ZnSb$_2$, there are 50% vacancies on the Zn site. This is understood in terms of the Zintl concept as providing electronic charge balance as monovalent Ag$^+$ is replaced by divalent Zn$^{2+}$. Thus the vacancies are needed for obtaining a semiconducting gap. Such a semiconducting gap is observed and is essential for thermoelectric performance. In addition, the stoichiometry is supported by X-ray diffraction Rietveld refinement. In contrast, the site is fully occupied by Ag atoms in EuAgSb$_2$. However, as noted, electronic structure calculations show that the details of the electronic structure near the band edges are dependent on the specific ordering of the Zn vacancies. In other words, there is an important interplay between Zn vacancy order and the electronic structure near the band edge. This implies strong electron scattering, and resulting low mobility, if the Zn atoms are strongly disordered on length scales comparable to electron mean free paths. Thus, although the exact structure is as yet unknown, two things are known, specifically that the Zn site in the average structure is at 50% occupancy and that there must be a high degree of Zn order at least locally. This is supported by imaging data shown in Supplementary materials, Fig. S1.
mentioned, the electronic structure of Eu$_2$ZnSb$_2$ at the band edges depends on the details of the Zn ordering, and in fact there are interesting topological aspects to this dependence. However, the bonding and chemistry is expected to be less sensitive to the particular ordering. Importantly, we find that this ordering yields dynamical stability as characterized both by stable phonons and stable ab initio molecular dynamics. This structure has a space group symmetry, Pmm2, which is lower than the global space group symmetry of Eu$_2$ZnSb$_2$. It should be noted that the dispersions show flat optic phonon branches in Eu$_2$ZnSb$_2$ at low energy starting below 1 THz. This leads to a strong peak in the phonon density of states, which has primary Zn character.

Physical properties of Eu$_2$ZnSb$_2$ and EuAgSb are listed in Table 1. Measured and calculated sound velocities, Debye temperatures, and bulk moduli are given. The measured values are in accord with the calculated properties. This supports the reasonableness of the structural model. There are not clear differences between the two compounds, and specifically none that would imply strong general softness of the lattice of Eu$_2$ZnSb$_2$ relative to that of EuAgSb, although Eu$_2$ZnSb$_2$ does have relatively soft acoustic phonons, as characterized by the low longitudinal sound velocity and the corresponding Debye temperature. These properties are comparable to those in EuAgSb, which as noted has a much higher thermal conductivity. Thus, while some of the differences in thermal conductivity could be ascribed to the softer lattice, the effect is not nearly large enough to explain the difference in thermal conductivity.

It is important to note that as temperature increases the experimental thermal conductivity approaches but is not lower than the minimum thermal conductivities allowed within a phonon model. The calculated minimum lattice thermal conductivities are 0.42 W/mK and 0.52 W/mK for Eu$_2$ZnSb$_2$ and EuAgSb, respectively. Thus, the temperature dependence where the thermal conductivity decreases toward a constant value as temperature is increased can be viewed as related to increased phonon scattering as temperature is increased, but the considerably weaker than 1/T temperature dependence for Eu$_2$ZnSb$_2$ suggests additional scattering beyond anharmonic phonon scattering. It is also noteworthy that in addition to the weak temperature dependence of the thermal conductivity in Eu$_2$ZnSb$_2$ there is a small but noticeable upturn at high temperature. Such upturns can be a consequence of increased thermal conductivity due to transport in localized vibrational modes, as in glassy materials, or bipolar electronic conduction. Such bipolar effects are possible in Eu$_2$ZnSb$_2$ due to the small ~0.17 eV band gap, and relatively low carrier concentration of ~4.5 × 10$^{18}$ cm$^{-3}$ at
ambient temperature. This is also consistent with the fact that, as shown in Fig. 3a, the Seebeck coefficient of Eu$_2$ZnSb$_2$ decreases with temperature at high temperature, while the conductivity is increasing.

Figure 4 shows the theoretical phonon dispersion curves and the (projected) phonon density of states (PDOS) of Eu$_2$ZnSb$_2$ and EuAgSb. Both compounds are dynamically stable, as expected. These dispersions show low frequency modes leading to peaks in the PDOS that come from the Zn and Ag. Specifically, there is a set of relatively flat phonon branches leading to a large peak in the PDOS near 1 THz in Eu$_2$ZnSb$_2$. This is reminiscent of a rattling ion peak, as in clathrates and filled skutterudites, where rattling has been associated with very low thermal conductivity. Importantly, this peak has Zn character. This shows that the Zn vibrations can be of particular importance in reducing the thermal conductivity. However, while rattling is expected to lower the thermal conductivity, it does not explain the temperature dependence of the thermal conductivity by itself as discussed below.

The calculated lattice thermal conductivities of Eu$_2$ZnSb$_2$ and EuAgSb are shown in Fig. 5, based on anharmonic phonon scattering. As seen, the calculated thermal conductivity of Eu$_2$ZnSb$_2$ is indeed lower than that of EuAgSb at all temperatures. However, it is higher than the experimental lattice thermal conductivity in the lower temperature region. The calculated lattice thermal conductivities of Eu$_2$ZnSb$_2$ are 0.55 W/mK and 0.21 W/mK at 300 K and 800 K, respectively. This may signal a breakdown of the phonon picture at high temperature, though not at ambient temperature. Specifically, at high temperatures or in highly disordered materials, strong scattering leads to localization and a breakdown of the phonon Boltzmann theory in certain materials. This type of breakdown is typically signaled by (1) a flat temperature dependence of the thermal conductivity and (2) a thermal conductivity that is higher than the phonon Boltzmann theory due to the contribution to heat conduction of localized incoherent vibrations. The present calculated result in comparison with experiment indicates that Eu$_2$ZnSb$_2$ is not in this strong scattering regime at least near ambient temperature though it apparently is at high temperature.

The very low lattice thermal conductivity of Eu$_2$ZnSb$_2$ compared to EuAgSb is due to a larger scattering phase space, as shown on a log scale in Fig. 6. This is the case over a wide frequency range starting below 1 THz. The enhancement in scattering phase space is particularly significant in the frequency

**Table 1 Physical properties of Eu$_2$ZnSb$_2$ and EuAgSb.**

| Property                        | Eu$_2$ZnSb$_2$ | EuAgSb  |
|---------------------------------|---------------|---------|
| Space group                     | P6$_3$/mmc    | P6$_3$/mmc |
| Lattice thermal conductivity at 300 K | 0.42 W m$^{-1}$K$^{-1}$ | 0.97 W m$^{-1}$K$^{-1}$ |
| Density (g cm$^{-3}$)           | Exp. data     | Exp. data |
| Longitudinal sound velocity, v$_l$ (m s$^{-1}$) | Calculated | Exp. data |
| v$_l$ (m s$^{-1}$)               | 3389 m s$^{-1}$ | 3501 m s$^{-1}$ |
| Young's modulus, E (GPa)        | Exp. data     | Exp. data |
| E (GPa)                         | 56.6 GPa      | 75.5 GPa |
| Poisson ratio, v$_p$             | Exp. data     | Exp. data |
| v$_p$                           | 0.23          | 0.24 |
| Bulk modulus                    | Exp. data     | Exp. data |
| Bulk modulus                    | Calculated    | Exp. data |
| Calculated                      | 42.39 GPa     | 53.6 GPa |
| Exp. data                       | 34.6 GPa      | 48.9 GPa |

The experimental data of Young’s modulus, shear modulus, Poisson ratio, Debye temperature, and bulk modulus are estimated using sound velocity.
range between approximately 0.8 THz and 3.5 THz. This reflects in part the Zn-related peak in the PDOS. There is also a significant difference in the anharmonic scattering rates. These are enhanced in Eu$_2$ZnSb$_2$ relative to EuAgSb, particularly below 2 THz, which is the range that is generally most important for thermal conductivity.

It is noteworthy that the Zn contribution to the PDOS has a two-peak structure in this frequency range, with a sharp peak and then a much broader peak at higher frequency, extending to approximately 3.5 THz. This can be understood as reflecting hybridization between soft Zn vibrations and the “host” lattice Eu–Sb modes. This is in analogy with filled skutterudites where a two-peak feature is also seen in neutron scattering experiments and is associated with thermal conductivity reduction. This provides a general explanation of why Eu$_2$ZnSb$_2$ has a lower thermal conductivity than EuAgSb, specifically anharmonic scattering involving relatively low-frequency Zn vibrations in analogy with rattling in filled skutterudites. It is interesting that in Eu$_2$ZnSb$_2$ the rattling atom is the lightest atom in the chemical formula, reflecting weak bonding of the Zn. This underlies the low thermal conductivity near 800 K. However, due to the
expected $1/T$ behavior at lower temperature, different from the experimental temperature dependence, the anharmonic phonon scattering picture does not fully explain the lower temperature data. The experimental data show behavior consistent with anharmonic phonon scattering for EuAgSb with a strong decrease in $\kappa_l$ as a function of temperature. In contrast, the nearly temperature-independent thermal conductivity in the lower temperature regime for Eu$_2$ZnSb$_2$ is instead consistent with a constant mean free path for the heat carrying phonons. At high temperature this mean free path is constrained by anharmonic phonon scattering, associated with the rattling behavior of the weakly bonded Zn atoms, constrained by the minimum thermal conductivity. This behavior and the difference from the behavior of EuAgSb point to disorder on the Zn site leading to a constrained mean free path as the key mechanism for thermal conductivity reduction at lower temperature. However, since Zn and its ordering play important roles in the band formation, random disorder would be expected to strongly depress the electronic mobility. This would be highly detrimental to the thermoelectric performance, in disagreement with the observed good performance of Eu$_2$ZnSb$_2$. Thus, there must be disorder on length scales that are of importance for the thermal conductivity and at the same time effective order on the shorter length scales needed for the favorable electronic behavior. This is similar to observations for artificially nanostructured thermoelectrics, where thermal conductivity has been found to be more sensitive to scattering at longer length scales compared to electronic transport. Due to shorter electron mean

**Fig. 6 Scattering phase space and scattering rates as a function of phonon frequency.** This is the phase space for different phonon modes of a zig-zag structure EuAgSb and b Eu$_2$ZnSb$_2$. The $+(-)$ sign represents three-phonon absorption (emission) phase space. The calculated anharmonic scattering rates for c EuAgSb and d Eu$_2$ZnSb$_2$. 
free paths electronic transport is affected by shorter length scales but can be relatively unaffected by scattering due to structure on longer length scales.\textsuperscript{16,47,48}

The Callaway model is useful for analyzing this. Considering the anharmonic phonon scattering due to the rattling like Zn vibrations, we focus on the low-frequency acoustic branches. We then apply the Callaway model to the longitudinal and two transverse acoustic modes, with velocities as in Table 1 and a fixed mean free path, l. Above room temperature, the model is \(\kappa = (C_l \nu_L + C_T \nu_T)/3\), where \(\nu_L\) and \(\nu_T\) are the longitudinal and transverse sound velocities, respectively, and the specific heats are taken as the classical harmonic values of \(R\) per branch (one longitudinal, two transverse), per mole and the factor of 1/3 is due to the direction averaging. This leads to an estimation of \(l = 0.15\ A\) needed for obtaining \(\kappa = 0.4\ W/\text{mK}\). This is much larger than the lattice parameter and the Zn–Zn spacing in the lattice. This Zn–Zn spacing is the scale that would be provided by random occupancy of the Zn sublattice, so the present result implies that the relevant length scale, \(l\) is much longer than that which would be provided by fully random Zn occupancy. The effect of the Zn disorder is then to provide a similar but very fine-grained nanostructure, with length scale of approximately 150 Å.

Thus, apparently the Zn atoms in Eu\(_2\)ZnSb\(_2\) are not fully long-range ordered. When considered at short length scales that are important for the electronic properties the material behaves as if it is ordered, but at length scales of \(l \sim 0.15\ A\) disorder is important and scatters phonons. This then allows a separation of length scales, where disorder is important at the longer lengths scales characteristic of mean free paths of heat-carrying phonons, but is less important at the shorter length scales important for electronic conduction. This is analogous to the effect of artificial nanostructuring where small grain sizes and associated interfaces on length scales important for heat-carrying phonons lower the thermal conductivity, without affecting the electronic transport as strongly.\textsuperscript{16,32,47} While the present results do not exclude other mechanisms for thermal conductivity reduction, they do illustrate a way of obtaining phonon–glass, electron–crystal behavior,\textsuperscript{8,12} specifically ultralow thermal conductivities over a wide temperature range accompanied by favorable electrical transport.

The intrinsic phonon–phonon interactions with rattling behavior, low bulk modulus, and scattering from disorder on the Zn sublattice lead to low lattice thermal conductivity of Eu\(_2\)ZnSb\(_2\). This leads to a semiconducting Zintl material with a lattice thermal conductivity close to the minimum thermal conductivity over a very broad temperature range starting at 300 K and extending to high temperature. At the same time, in contrast to the normal situation with a high degree of random disorder, Eu\(_2\)ZnSb\(_2\) maintains a good mobility leading to high thermoelectric performance. Weakly bonding Zn plays a key role in this. This points the way to a mechanism that can be applied to Zintl-phase materials, particularly the design of systems with disorder on one sublattice, but a local ordering tendency that produces different behavior on different length scales, effectively an intrinsic bulk nanostructured material.

Methods

Density functional calculations. Calculations are done using the generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE-GGA).\textsuperscript{49} Orthorhombic cells corresponding to the zig-zag structure of Eu\(_2\)ZnSb\(_2\) are used for this compound as well as EuAg\(_2\) although EuAg\(_2\) has a higher hexagonal symmetry. This is to facilitate comparison of the two compounds. The calculations are done using the projector augmented wave (PAW) method as implemented in the Vienna Ab-initio Simulation Package (VASP) code.\textsuperscript{50,51} Geometry optimization is done. A planewave energy cutoff of 500 eV is used along with a 10 \times 10 \times 10 uniform mesh for Brillouin zone sampling and an energy convergence criterion for self-consistency of 10\(^{-7}\) eV. The lattice constants are changed relative to the ideal (disordered) hexagonal structure following \(a_d = a_0 \times 2, b_d = b_0 \times \sqrt{3}, c_d = c_0\), where \(a_0, b_0\), and \(c_0\) are the unit cell parameters in the orthorhombic crystal system, and \(a_d, b_d, c_d\) are the unit cell parameters in the hexagonal structure. The optimized orthorhombic lattice parameters are 9.18, 15.94, and 8.20 Å for the zig-zag supercell Eu\(_2\)ZnSb\(_2\). The bulk modulus and related data in Table 1 are from zero K fitting of stress–strain curves. The temperature-dependent effective potential (TDEP) method is used to extract anharmonic force constants. This is done to provide a stable well constrained interatomic force constants (IFCs) for the complex crystal structure of these compounds. The TDEP calculation is based on Born–Oppenheimer molecular dynamics with the PAW method at 300 K with Nose thermostat temperature control.\textsuperscript{54} A simulation time of 140 ps, with a time step of 1 fs and planewave cutoff of 440 eV are used. An 80 atom zig-zag model supercell of Eu\(_2\)ZnSb\(_2\) is used for the TDEP calculation for that compound, and a 96 atom supercell is used for EuAg\(_2\). The phonon dispersions are obtained from the effect of second-order IFCs using the Phonopy package.\textsuperscript{55} The structure is dynamically stable. The thermal conductivities are obtained using the third-order anharmonic IFCs and the ShengBTE package.\textsuperscript{56} The convergence with respect to the reciprocal space grid was tested, as shown in Supplemental Material Figure S. The temperature dependence of the thermal conductivity is obtained using the temperature-dependent phonon occupations based on the 300 K IFCs.

Sample preparation and characterization. The samples were prepared by weighing out stoichiometric amounts of silver (Ag, 99.9%, shots), europium (Eu, 99.9%, chunks), zinc (Zn, 99.999%, chunks), and antimony (Sb, 99.999%, shots). These were for the EuAg\(_2\) and Eu\(_2\)ZnSb\(_2\) stoichiometries. These were then loaded into stainless steel jars. This was planewaves were ball-milled for 10 h using a high energy ball mill (SPEX 8000M) and subsequently sintered for 2 min using spark plasma sintering under an axial pressure of 60 MPa at 853 K, resulting in dense disks. The density of the resulting Eu\(_2\)ZnSb\(_2\) sample was 6.68 g/cm\(^3\), which is approximately 97% of the theoretical density of 6.66 g/cm\(^3\).

The experimental Young’s modulus, shear modulus, Poisson ratio, Debye temperature, and bulk modulus are approximated from the standard expressions in terms of sound velocities.\textsuperscript{57} The longitudinal (\(v_l\)) and transverse (\(v_t\)) components of the sound velocity were measured using an ultrasonic pulse receiver (Olympus) equipped with an oscilloscope (Tektronix). The Seebeck coefficient (S) and electrical conductivity (\(\sigma\)) were measured with a ZEM-3 apparatus. The Hall coefficient \(R_H\) as a function of temperature was measured using the van-der-Pauw technique with a reversible magnetic field of 1.5 T. The Hall mobility, \(\mu_H\), and Hall carrier concentration, \(n_H\), were calculated as \(\mu_H = eR_H\) and \(n_H = 1/(eR_H)\), respectively. The thermal conductivity \(\kappa\) was obtained from the thermal diffusivity, specifically \(\kappa = \alpha D_C\). Here, \(D_C\) is the volumetric density, which was determined by the Archimedes method, \(\alpha\) is the thermal diffusivity, which was measured using a laser flash apparatus (Netzsch LFA 457), and \(C_p\) is the specific heat, which was obtained using a differential scanning calorimetry thermal analyzer (Netzsch DSC 404 F3). We then calculated the lattice thermal conductivity by \(\kappa_l = \kappa - \alpha \cdot \rho \cdot T\), where the Lorenz number \((L)\) is from the SPB formula and the measured Seebeck coefficients.\textsuperscript{39}

Data availability

Data supporting the conclusions is included in the article. Additional data are available from the corresponding authors upon reasonable request.

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Competing interests
The authors declare no competing interests.

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