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Exploiting Chemical Bonding Principles to Design High-Performance Thermoelectric Materials

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Abstract

Thermoelectric materials offer unique opportunities to convert otherwise wasted thermal energy into useful electrical energy. Many of the traditional thermoelectric materials, such as bismuth telluride and lead telluride contain scarce and toxic elements. This has motivated the search for new high-performance materials containing readily-available and environmentally-less-damaging elements. Numerous advances in the development of high-performance thermoelectric materials exploit fundamental chemical-bonding principles. Much of the thermoelectric literature lies at the interface of chemistry, physics, and materials science. In this Review, progress in the design of high-performance materials is discussed in terms of ideas that are familiar in chemistry. This includes the influence of concepts such as bonding heterogeneity, covalency, polarizability, lone pairs, and different bonding models, including multi-center, metallic, and ionic-covalent archetypes. In this way, we seek to present aspects of this diverse field of research in terms that are accessible to the chemistry community.

[H1] Introduction

Thermoelectric devices, comprising an array of n- and p-type semiconductors (Fig. 1a,b), afford the unique capability of converting waste heat directly into useful electrical energy or when operated in reverse, to provide an all solid-state cooling device. Such devices have potential applications¹ in the consumer, industrial, medical, aerospace, and military sectors that span a wide range of temperatures, while there is increasing interest in applications associated with the online activity as well as with wearable devices.^{2,3} Thermoelectric performance is determined by the transport properties of the semiconductors, embodied in a dimensionless figure-of-merit (ZT),

$$ZT = \frac{S^2 \sigma T}{\kappa}$$

where S , σ , and κ are, respectively, the Seebeck coefficient, the electrical conductivity and thermal conductivity, which has contributions from charge carriers (κ_e) and from lattice vibrations (κ_L).

The electrical (S , σ) and thermal (κ_e) transport properties show differing dependencies (Fig. 1c) on the charge-carrier concentration (n). This imposes considerable constraints on the development of high- ZT materials. Although the figure-of-merit affects device efficiency, a high average value (\overline{ZT}) for each of the n- and p-type components at temperatures between the

hot and cold sides has a greater impact on optimising device performance than simply maximising the figure-of-merit.

Design strategies (Fig. 1d) that seek to maximize the numerator ($S^2\sigma$, termed the power factor) or minimize the thermal conductivity (κ) have emerged.^{4,5,6} Specific approaches include phonon-glass electron-crystal⁷ and phonon-liquid electron-crystal⁸ behaviours, nanostructuring,⁹ nanocompositing,¹⁰ manipulation of band structures through the introduction of resonant levels,¹¹ low-dimensionality¹² and the interaction of magnetic ions with the charge carriers.¹³ These strategies have been increasingly applied to new high-performance materials containing more abundant and less toxic elements in an effort to obviate concerns associated with tellurium. Investigations have encompassed chalcogenides,¹⁴ oxychalcogenides,¹⁵ oxides,¹⁶ skutterudites,¹⁷ half-Heusler phases,¹⁸ Zintl phases,¹⁹ pnictides,²⁰ clathrates,^{21,22} silicon-germanium alloys²³, and silicides.²³ Spectacular advances in thermoelectric performance have been achieved. Figures of merit routinely exceed unity, with higher values in what have been termed second and third generation materials.²⁴

Fundamental chemical-bonding principles underpin many of the high-performance materials. Here, progress in thermoelectric materials is discussed in terms of concepts familiar to the wider chemical community. The intention to focus on fundamental chemical concepts means that the coverage of individual classes of materials is necessarily selective. However, several reviews^{23,25,26,27,28,29,30} provide comprehensive coverage of thermoelectric materials, while an extensive compilation of thermoelectric data is also available.³¹

[H1] Requirements for High Thermoelectric Performance

Electrical conductivity (σ) is related to the charge-carrier concentration (n), carrier mobility (μ), and electronic charge (e) by:

$$\sigma = n\mu e$$

It is inversely dependent on the inertial effective mass along the conduction direction (m_ℓ^*). For an isotropic band this is equal to the band effective mass, m_b^* — the effective mass of a carrier within a given band. The mobility of the charge carrier is a function of m_b^* and the average time between electron-scattering events (τ):

$$\mu = \frac{e\tau}{m_b^*}$$

For a single-valley band, the inertial effective mass, (and hence m_b^*) and density of states (DOS) effective mass (m_{DOS}^*) are related by the valley degeneracy (N_v) through

$$m_{DOS}^* = N_v^{2/3} m_b^*$$

leading to:

$$\sigma = \frac{ne^2\tau N_v^{2/3}}{m_{DOS}^*}$$

High electrical conductivity is therefore favoured by high carrier concentrations, a high valley degeneracy, a long relaxation time for scattering of electrons, and a low DOS effective mass, which itself implies broad bands (Box 1).

Orbital overlap and hence bandwidth is affected by the differences in base orbitals ($\Delta\chi_{A-x}$ ⁷), leading to the use of anion substitution to tailor the electron-transport properties of a

thermoelectric material, through changes to bandwidth, mobility, and — due to a different value of α for A and X — the band gap (Box 1). For example, partial replacement of selenium by sulfur, leads to band narrowing, reflected in an increase in effective mass in $\text{PbSe}_{1-x}\text{S}_x$,³² decreased mobility in $\text{Cu}_2\text{ZnGeSe}_{4-x}\text{S}_x$ ³³ and loss of its metallic character in $\text{TiSe}_{2-x}\text{S}_x$.³⁴ Conversely, Cu_5FeS_4 , becomes increasingly metallic as sulfur is replaced with selenium.³⁵

According to the Mott relationship, the Seebeck coefficient is related to the derivative of the DOS at the Fermi level, E_F .

$$S = \frac{\pi^2 k^2 T}{3e} \left\{ \frac{d[\ln\sigma(E)]}{dE} \right\}_{E=E_F}$$

Where $\sigma(E)$, the electrical conductivity as a function of band filling, is proportional to the DOS, providing charge-carrier scattering is independent of energy. Reduced dimensionality introduces structure into the DOS (Figures 1(d) and 2(a)^{36, 37}), and tuning E_F to a discontinuity may increase the Seebeck coefficient¹² and enhance performance. For a degenerate semiconductor, the Seebeck coefficient is proportional to m_{DOS}^* :

$$S = \frac{8\pi^2 k_B^2}{3e\hbar^2} m_{DOS}^* T \left[\frac{\pi}{3n} \right]^{2/3}$$

Although large values of m_{DOS}^* enhance the Seebeck coefficient, the corresponding reduction in carrier mobility arising from increased effective mass can be detrimental to the overall performance. This is illustrated by considering the quality factor³⁸ (denoted Q here to avoid confusion with the overlap integral) introduced to guide the search for high ZT materials.

$$Q \propto \frac{N_v}{m_l^* \kappa_L}$$

Large values of m_b^* , or a large valley degeneracy (N_v) each increase m_{DOS}^* (and hence S), but the former also necessitates a large m_l^* , which degrades Q and performance. Pei et al³⁹ demonstrated that while the Seebeck coefficient of $\text{La}_x\text{Pb}_{1-x}\text{Te}$ ($x < 0.01$) is higher than that of $\text{PbTe}_{1-x}\text{I}_x$ ($x < 0.01$), the power factor of the latter is 20% greater due to a lower effective mass.

The impact of N_v has led to the use of band engineering to enhance properties⁴⁰ where there are sub-bands of different degeneracy in the vicinity of E_F . Chemical substitution adjusts the position of E_F . This leads to band convergence, increasing the overall degeneracy and hence m_{DOS}^* ($\propto N_v^{2/3}$), thereby enhancing the Seebeck coefficient. In PbTe , convergence of a light upper valence band ($N_v = 4$) and a second heavy valence band ($N_v = 12$) about 0.2 eV below it, increases the effective valley degeneracy to $N_v = 16$ (Fig. 2b).⁴¹ Convergence may be induced by increasing temperature⁴¹ or partial substitution of Pb^{2+} by the closed-shell cation, Mg^{2+} .⁴² A similar approach has been applied to $\text{Mg}_2\text{X}_{1-x}\text{Sn}_x$ ($\text{X} = \text{Si, Ge}$), where progressive substitution by tin, leads to the convergence of light and heavy bands, raising the figure-of-merit to $ZT = 1.3$ in $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$, at $x \approx 0.7$.⁴³ Similar results are obtained in the corresponding germanium-containing series and the pseudo ternary system $\text{Mg}_2\text{Si}_{1-x-y}\text{Ge}_x\text{Sn}_y$ ($0 \leq y \leq 0.15$).⁴⁴ In the filled skutterudite, Yb_xCoSb_3 ⁴⁵ band convergence has been related⁴⁶ to dopant-induced changes in electronic structure and structural changes in the Sb_4 rings, narrowing the energy gap between the primary and secondary conduction bands (Fig. 2c–f). In the tetragonal semiconductors chalcopyrite, kesterite, and stannite, band convergence (Fig. 2g) can be induced by a change in the distortion parameter,⁴⁷ η ($=c/2a$). At $\eta = 1.0$, two of the valence bands converge,⁴⁸ increasing N_v and thus m_{DOS}^* .

Heat transport in thermoelectric materials is dominated by the phonon contribution (κ_L). The phonon group velocity (v_g , Box 2), which determines κ_L , is proportional to $(k/m)^{1/2}$ where k is a force constant and m the atomic mass — low lattice thermal conductivities are therefore found in materials containing heavy elements that are weakly-bonded. Empirical approaches^{49,50} suggest that increasing ionicity in the metal-anion bond decreases κ_L . By considering average bond lengths, which relate directly to bond strength and hence k and v_g , Zeier *et al* have shown that shorter bonds correspond to higher thermal conductivities.⁵¹ As a consequence of Pauling's second rule, a large coordination number generally results in longer and weaker bonds. Therefore, increasing the coordination number of ions is associated with decreasing κ_L .⁵⁰ For example, compounds adopting the zinc blende structure — in which zinc cations are tetrahedrally coordinated — tend to exhibit higher thermal conductivities than those adopting the rock salt structure, where ions exhibit octahedral coordination.

Many solid-state materials deviate from ideal harmonic behaviour. Anharmonicity may be quantified by the Grüneisen parameter (γ , Box 2). In cases where heat transport is dominated by acoustic phonons and Umklapp phonon-phonon scattering, in which there is a change in phonon momentum, then:⁵²

$$\kappa_L = \frac{A\bar{M}\delta\theta_D^3}{Tn^{2/3}\gamma^2}$$

where A is a constant, \bar{M} , the average atomic mass; δ^3 , the average volume per atom, n , the number of atoms in the primitive unit cell, and θ_D , the Debye temperature. Strongly anharmonic systems, (large γ) exhibit low thermal conductivity. Anharmonicity is characteristic of materials containing elements of high atomic number,⁵³ those with complex crystal structures and considerable bonding heterogeneity,^{54,55,56} and materials with stereochemically active lone pairs,^{57,58,59,60} and local structural distortions.⁶¹

[H1] Embedding chemical bonding concepts into the design of thermoelectric materials
 In the following sections, we explore how advances in the development of high-performance thermoelectric materials can be related to key chemical concepts. This includes how differences in the bonding interactions, including the simultaneous presence of different types of bond in a chemical compound, resonant bonding and multiple cation-anion interactions, can affect the transport properties that determine thermoelectric performance. The impact on both crystal structure and electronic structure of fundamental properties such as polarizability and electronegativity is discussed. The key role played by stereochemically-active lone pairs of electrons in inducing local structural distortions and modifying the electronic band structure is highlighted, together with their capacity to introduce anharmonicity, which has a critical impact on lattice thermal conductivity.

[H2] Bonding heterogeneity

The co-existence of bonding interactions that are predominantly covalent, ionic, or metal-metal in nature, often described as bonding heterogeneity, occurs in many high-performance thermoelectric materials. For instance, in Zintl phases (Fig. 3a), ionic and covalent bonding contributions coexist,⁶² with distinct components providing different properties. The covalently-bonded network of complex anions leads to high-mobility semiconduction, while

the ionically-bonded electropositive cations provide regions that can be doped to control electron concentrations and disrupt phonon transport through alloy scattering.

Among the Zintl phases, the large family of layered AM_2X_2 (A = Group 2 or divalent rare earth element; M = transition metal or main-group element, X = Group 14 or 15) compounds adopting the $CaAl_2Si_2$ structure (Fig. 3a) are attracting considerable interest as thermoelectric materials.⁶³ Within this family, the binary Mg_3Pn_2 (Pn = Sb and Bi) phases have emerged as potential n-type replacements for Bi_2Te_3 due to their high ZT values near room temperature.^{64, 65, 66, 67} Band structure calculations for AM_2X_2 phases show multi-valley degeneracy with anisotropic carrier pockets at and near the conduction band minimum, features which are beneficial for enhancing the thermoelectric power factor.⁶⁸ According to the Zintl concept, AM_2X_2 phases can be understood as consisting of covalently-bonded $[M_2X_2]^{8-}$ slabs, separated by octahedrally-coordinated A^{δ+} cations. However, when the electronegativity of X is large in comparison to that of M, M should not be considered to be an anion forming two-centre-two-electron (2c-2e) bonds with X. In these cases, M is better described as a cation with a close-shell configuration, as previously shown for $YbCd_2Sb_2$, which is better formulated as $[Yb^{2+}][Cd^{2+}]_2[Sb^{3-}]_2$.⁶⁹ Moreover, while the crystal structure of Mg_3Pn_2 is usually described as covalently-bonded $[Mg_2Pn_2]^{2-}$ layers and Mg²⁺ cations, work by Zhang *et al.*^{70, 71} challenges this interpretation, showing that there is a nearly uniform 3D bonding network, with a very similar degree of ionicity for intralayer and interlayer bonds. The abnormally low lattice thermal conductivity of Mg_3Pn_2 has been attributed to soft and unstable A-X intralayer bonding, which flattens the anharmonic transverse acoustic phonon modes.⁷² When A = Mg²⁺, the cation-to-anion radius is below the stability limit of 0.414 given by Pauling's rule for octahedral coordination, leading to soft and unstable A-X intralayer bonding.⁷² Indeed, Mg_3Bi_2 becomes superionic at high temperatures.⁷³

In general, the nature of the bonding can be assessed by considering the electronegativity differences between constituent elements, the analysis of computationally-determined Bader charges, which are derived by partitioning the charge density in regions associated with each atom, as well as by comparing the bonding distances within the solid to the sums of tabulated ionic or covalent radii. Analysis of the computationally-determined electron localisation function (ELF) can be used to determine if the bonding interactions involve shared or unshared electrons.⁷⁴ Alternatively, the quantum theory of atoms in molecules (QTAIM),⁷⁵ which defines chemical bonds using a topological analysis of the electron density distribution, has been exploited, although its use in thermoelectrics research is more limited.^{76, 77} The hierarchical nature of bonding interactions within a material can lead to phenomena such as phonon glass electron crystals (PGECs)⁷⁸ and phonon-liquid electron-crystals (PLECs),⁷⁹ described below.

[H3] Bonding in Phonon Glass Electron Crystal materials

A PGEC⁷ simultaneously possesses the periodic structure of a crystalline material that governs charge transport and a disordered atomic arrangement, akin to a glass, that increases phonon scattering. The concept was initially realised in cage-like compounds, such as filled skutterudites,^{17, 80} and intermetallic clathrates,^{81, 82} which exhibit enhanced thermoelectric performance due to weakly-bound filler species within an open framework structure. The fillers

exhibit localised low-energy optical vibrational modes (known as rattling modes). These are often described as Einstein oscillators, as their contribution to the heat capacity is consistent with the Einstein model of a solid consisting of independent harmonic oscillators. The rattling modes scatter the acoustic phonons, responsible for carrying most of the heat, while leaving the electron transport relatively unaffected.⁷⁸ The presence of rattlers within a crystal structure is characterised by large atomic displacement parameters (ADPs) for the rattling species. In phonon dispersion curves, rattlers appear as flat (dispersionless) low-energy optical modes, where crossings between the rattler modes and the acoustic-phonon branches are avoided (Fig. 3b),⁸³ and with a corresponding sharp peak in the phonon density of states at low energies (Fig. 3c). The frequency of the rattling modes is often determined from heat capacity measurements⁸⁴ or the temperature dependence of the ADPs.⁵⁵ While it is accepted that rattler modes within the acoustic range would reduce κ_L , the mechanism by which this happens is a matter of debate as both resonant scattering and a reduction in group velocity have been proposed.⁸⁵

CoSb₃-based skutterudites possess a framework of tilted [CoSb₆] octahedra (Fig. 3d). Typical fillers include rare-earth, alkaline, and alkaline-earth cations, which strongly scatter phonons.^{86,87,88,89,90} This is most effective for phonons with frequencies comparable with the resonance frequency of the filler, leading to the use of multiple fillers to facilitate scattering across a broader range of the phonon spectrum.⁹¹ Hybridization between the vibrational modes of the rattler and Sb, enabling coupling between the rattling modes and the collective vibrations of the skutterudite framework,^{92,93} may also play a role in determining heat transport.⁹⁴ The filler has minimal impact on the band structure near the conduction band minimum.³¹ n- and p-type behaviour can be induced through substitution of cobalt by elements with more or fewer electrons, respectively.⁹⁵ This enables optimization of the charge-carrier concentration. When coupled with nanostructuring or deformation processes, this produces filled skutterudites with high figures of merit⁹⁶ — $ZT \approx 2$ in n-type materials^{97,98} and $ZT \approx 1.2\text{--}1.4$ in p-type counterparts.^{99,100}

Intermetallic clathrates^{101,102} in which weakly-bonded guest atoms are contained within cavities created by a framework of tetrahedrally-coordinated atoms¹⁰³ show similar behaviour. Electron-precise compositions exhibit semiconducting behaviour ($E_g < 2$ eV), but the chemical flexibility affords the capacity to adjust E_g , giving rise to both *n*- and *p*-type metallic behaviour.^{101,104} Type I clathrates (Fig. 3e) of general formula G₈A_xB_{46-x}, where G, is an electropositive group 1 or 2 element and framework elements A and B are drawn from groups 13 and 14,⁸¹ are among the most investigated for thermoelectric applications. The large number of atoms in the unit cell, produces a dense continuum of optical branches, restricting the phase space accessible to acoustic phonons, effectively reducing the efficiency of heat conduction.¹⁰⁵ DFT calculations for the Ge-based clathrates¹⁰⁶ suggest the optimized composition of type I Sr₈Ga₁₆Ge₃₀ could exhibit $ZT = 0.5$ at room temperature, rising to 1.7 at 800 K, while $ZT = 1.35$ has been achieved experimentally for the barium analogue, Ba₈Ga₁₆Ge₃₀.¹⁰⁷ Roy et al.¹⁰⁵ identified the presence of Ga-Ge site disorder, which reduces phonon group velocities, contributing to a marked reduction in thermal conductivity despite similar masses of Ga and Ge. Sn-based clathrates exhibit lower thermal conductivities due to the increased average atomic mass of the framework.^{108,109}

However, non-cage-like materials can also contain rattlers. For example, in mixed-valent InTe, which consists of covalently-bonded $[\text{InTe}_2]^-$ chains separated by ionically-bonded In^+ cations, the rattling vibrations of the In^+ cations lead to an ultralow lattice thermal conductivity of about $0.4 \text{ W m}^{-1} \text{ K}^{-1}$.¹¹⁰ Similarly, the low thermal conductivity of In_3Se_4 has been attributed to the rattling vibrations of the In^+ cations located between covalently-bound $[(\text{In}_3)^{5+}(\text{Se}^{2-})_3]^-$ layers.¹¹¹ Evidence of Einstein-like rattling modes has been reported for a wide variety of materials, including layered oxides, such as $\text{Na}_{0.8}\text{CoO}_2$ ¹¹² as well as many copper and silver chalcogenides.^{28, 113} In the latter, the weak bonding of the copper and silver cations, which leads to rattling, originates from the presence of p - d^* antibonding states at the top of the valence band.¹¹⁴ These antibonding states are formed by hybridisation of Cu^+ and Ag^+ - d orbitals and anion- p orbitals.¹¹⁵

[H3] Bonding in Phonon Liquid Electron Crystal materials

Above a critical temperature, a PLEC enters a superionic state as its cations become mobile, while the anion sub-lattice remains rigid. This confers liquid-like characteristics and κ_L approaches that of a glass, while the electronic properties of a crystalline phase are retained. The ultralow thermal conductivity of PLEC materials was initially attributed to the disappearance of the transverse acoustic phonon modes.⁸ Voneshen et al. have shown that, in Cu_2Se , the hopping timescales of the mobile ions are considerably longer than the phonon relaxation times for the transverse phonon branches, and therefore the transverse phonon modes persist into the superionic state.¹¹⁶ Moreover, this work demonstrates that the ultralow thermal conductivity of Cu_2Se arises from anharmonicity.¹¹⁶ Studies on other superionic materials, including CuCrSe_2 and Ag_8SnSe_6 , likewise suggest that the ultralow thermal conductivity of PLEC materials is also a consequence of strong anharmonicity, not the suppression of the transverse phonon modes.^{117, 118}

PLEC behaviour is favoured by: large anions that form the framework, within which cations migrate; small cations, which experience a low potential barrier for movement; and, a crystallographic structure containing vacancies of similar energy.⁷⁹ These criteria are frequently satisfied in materials containing polarizable anions, including $\text{Cu}_{2-\delta}\text{Q}$ ($\text{Q} = \text{S, Se, Te}$),^{8, 119, 120} Ag_2Q ($\text{Q} = \text{S, Se, Te}$),^{121, 122} Cu and Ag-argyrodites^{123, 124}, Cu tetrahedrites¹²⁵ and diamond-like $\text{Cu}_{1-x}\text{Ag}_x\text{GaTe}_2$ phases.¹²⁶ All exhibit an ultralow low thermal conductivity (~ 0.2 – $0.5 \text{ W m}^{-1} \text{ K}^{-1}$) due to diffusion of Ag and Cu cations. The onset of liquid-like behavior¹²⁷ is characterized by an almost temperature-independent thermal conductivity, contrasting with the approximate T^{-1} dependence of Umklapp scattering. Large Grüneisen parameters, which as noted in Box 2 are associated with the volume dependence of the phonon frequency, also signify a high level of anharmonicity.

In copper chalcogenides, the increase in the energy of anion valence orbitals with decreasing electronegativity decreases E_g , which falls from 0.30 eV in Cu_2S to 0.13 eV in the analogous selenide, while the corresponding telluride is metallic.¹²⁸ The increasing covalency of the Cu-Q interaction on progressing from S to Te, also increases orbital overlap, leading to broader bands and decreased carrier effective mass, thereby enhancing mobility and electrical conductivity.²⁸ p-type Cu_{2-x}Se exhibits $ZT > 2$ at temperatures around $1,000 \text{ K}$ (Fig. 3f), while

the value for that of Cu_{2-x}S is close to 2.^{120,129,130} The majority of the Ag analogues are n-type, with a performance ($ZT = 1.2$ for Ag_2Se at 390 K¹³¹) that lags behind p-type phases.

Ionic mobility in thermoelectric materials is not restricted to chalcogenides containing Cu^+ and Ag^+ cations. Although intermetallic $\beta\text{-Zn}_4\text{Sb}_3$ was initially described as a PGEC material, after the discovery of glass-like interstitial partially occupied Zn sites,¹³² work has shown that this material is a mixed ionic–electronic conductor, containing mobile Zn^{2+} cations above 425 K.¹³³ In contrast to the Zintl formalism, which suggests the presence of six Sb^{3-} anions, two Sb_2^{4-} dumbbells, and thirteen Zn^{2+} cations, the electronic structure of $\beta\text{-Zn}_4\text{Sb}_3$ actually shows a more complex picture with delocalized multi-center bonding.¹³⁴ Similarly, MgAgSb — which adopts a cubic half-Heusler structure above 633 K — can reach $ZT = 1.4$ at 450 K,¹³⁵ where migration of both Ag^+ and Mg^{2+} ions plays an important role in the thermoelectric transport properties.¹³⁶

The high ionic mobility found in PLECs leads to degradation under operating conditions, due to ion migration and metal deposition at the cathode, hindering their practical application. It was shown that tetrahedrite, ¹³⁷ $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$, is an incipient ionic conductor (Fig. 3g), in which the copper ions, although mobile above 200 K, are predominantly confined to cages within the crystal structure. The discovery of incipient ionic conductivity, found in materials on the verge of ionic conduction, containing ions with appreciable mobility, but in which long-range ionic diffusion is suppressed due to the trapping effect of the underlying crystal structure, may provide a route to overcome the degradation issues of PLECs.

[H2] Polarizability and Covalency

The elements of groups 15–17 present in the majority of thermoelectric materials, exhibit considerable differences in polarizability (Fig. 4a,b) and electronegativity (Fig. 4c). In addition to its effect on bandwidth, the anion has a marked effect on structure. Highly polarizable anions favour anisotropic bonding. This introduces low-dimensional character, which is also favoured by the lower formal charges when the covalency of the metal-chalcogen interaction increases.

Low-dimensionality promotes high thermoelectric performance through both the more structured DOS and scattering of phonons at interfaces between structural sub-units.¹³⁸ Low-dimensionality implies bonding heterogeneity, reflected in Grüneisen parameters that are higher than those for isotropic structures. For example, the Grüneisen parameters of TiO_2 and MgAl_2O_4 are $\gamma = 1.28$ and $\gamma = 1.13$, respectively,¹³⁹ while those of layered SnSe and BiOCuSe discussed below are much larger ($\gamma = 3.13$ and $\gamma = 2.5$, respectively). Furthermore, the weak inter-layer bonding results in soft optical phonons, which can couple with the heat-carrying acoustic phonons.

Transition-metal dichalcogenides constructed from metal-centered polyhedra are archetypal two-dimensional structures (Fig. 4d). The modest figure-of-merit of stoichiometric TiS_2 ($ZT = 0.33$),¹⁴⁰ is slightly enhanced by selenium substitution ($ZT = 0.41$ for $\text{TiS}_{1.5}\text{Se}_{0.5}$ at 700 K).³⁴ Insertion of electropositive species into the van der Waals' gap, facilitated by weak inter-slab bonding, is accompanied by charge transfer, altering the carrier concentration with minimal structural perturbation. Insertion may involve self-intercalation, $\text{Ti}_{1+8}\text{S}_2$, ($(ZT)_{\text{max}} = 0.48$ at 700 K¹⁴¹) or that of a second type of cation, M_xTiS_2 ($\text{M} = \text{Co}$,¹⁴² Cu ,¹⁴³ or Ag ¹⁴⁴). Optimum properties occur at low levels of insertion, reflecting the balance between

unfavourable reductions in Seebeck coefficient due to increased carrier concentration, and favourable reductions in κ_L arising from disorder (Fig. 4e,f). Figures of merit of about 0.5 are commonly observed in the temperature range $700 \text{ K} \leq T \leq 825 \text{ K}$.¹⁴⁵

In SnSe, distortion of the rocksalt structure produces strongly bonded, two-atom thick slabs (Fig. 4g), linked through weaker inter-slab interactions along the [001] direction. SnSe, metallic at 525 K, undergoes a metal-semiconductor transition at 525 K. A phase transition from the *Pnma* to *Cmcm* space group occurs at about 800 K, above which the electrical conductivity is temperature independent.¹⁴⁶ The electrical conductivity is strongly anisotropic⁵⁶ and the highest power factor in a single crystal is observed along [010]. Together with an ultra-low thermal conductivity, this leads to the exceptional figure-of-merit, $ZT = 2.6$ along [010] at 923 K (Fig. 4g).⁵⁶ Both n- and p-type variants of SnSe may be prepared by doping with iodine¹⁴⁷ and silver¹⁴⁸, respectively. Remarkably, the exceptional performance observed in single crystals has been translated into polycrystalline materials,^{149,150} and a figure-of-merit ($ZT \approx 3.1$ at 783 K) in excess of that of single crystalline materials has been reported for a sodium-doped polycrystalline material.¹⁵¹

The isostructural sulphide, SnS, shows a similar anisotropy¹⁵² and silver-doped phases exhibit $ZT = 0.6$ at 873 K.¹⁵² The solid solution $\text{SnS}_{1-x}\text{Se}_x$ enables tuning of E_g ,¹⁵³ which above $x = 0.2$, increases the electrical conductivity and produces in $\text{SnS}_{0.2}\text{Se}_{0.8}$, a four-fold increase in the figure-of-merit over that of the binary sulphide ($ZT = 0.82$ at 823 K).

The presence of low-dimensional structural motifs in otherwise three-dimensional structures can also introduce structure into the DOS. Materials such as $\text{A}_3\text{M}_2\text{S}_2$, ($\text{A} = \text{Ni, Co, Rh, Pd}$; $\text{M} = \text{Pb, In, Sn, Tl}$) related to the mineral shandite, contain two-dimensional kagome-like A_3M layers, which results in narrow bands of predominantly Co-*d* character in the region of E_F . Cation substitution in $\text{Co}_3\text{Sn}_2\text{S}_2$ to effect electron and hole doping^{154,155,156,157} has been used to tune E_F within this highly structured region of the DOS, leading to figures of merit $ZT = 0.2\text{--}0.32$ at relatively modest temperatures (525–673 K). Similarly, in n-type pavonite-related phases ABi_4S_7 ($\text{A} = \text{Fe, Mn}$),¹⁵⁸ linkage of A- and Bi-centered polyhedra confers layer-like character. The bonding heterogeneity results in anharmonicity ($\gamma = 1.16$), which contributes to $\kappa < 1 \text{ W m}^{-1} \text{ K}^{-1}$. There are both heavy and light bands near the conduction band minimum. The former contributes to a relatively high Seebeck coefficient, despite the metal-like $\rho(T)$ behaviour, resulting in moderately high power factors, which when coupled with the low thermal conductivity, result in $(ZT)_{\text{max}} = 0.21$ at 700 K in MnBi_4S_7 .¹⁵⁸

When two anions are simultaneously present, the coordination environment around a given cation may be heteroleptic or homoleptic, where in the latter, different bonding preferences of the cations lead to segregation and the formation of distinct structural units. This is exemplified by the oxychalcogenides, ROCuQ ($\text{R} = \text{Ln, Bi}$; $\text{Q} = \text{S, Se, Te}$), in which the harder less-polarisable R^{3+} cations preferentially coordinate to smaller, harder oxide anions to form $[\text{R}_2\text{O}_2]^{2+}$ layers, and the softer more polarizable Cu^+ cations form $[\text{Cu}_2\text{Q}_2]^{2-}$ slabs with the softer chalcogenide anion (Fig. 4h). The covalent interactions favour broad bands through strong overlap, promoting high mobility, while more ionic interactions favour low thermal conductivity. Bismuth containing materials, with smaller band gaps due to the presence of Bi 6p states in the region of the conduction band minimum,¹⁵⁹ exhibit the highest performance. Anion substitution has been used to tune E_g and $[\text{BiO}][\text{CuSe}_{1-x}\text{Te}_x]$ exhibits improved electrical

transport properties,¹⁶⁰ whereas sulfur substitution increases the resistivity, degrading performance.¹⁶¹ Aliovalent substitution at the Bi³⁺ site^{162,163,164} improves electrical properties¹⁵ of the *p*-type materials. Similar enhancements in performance arise from copper-site vacancies ($ZT = 0.81$ at 923 K for [BiO][Cu_{0.975}Se]¹⁶⁵), and from vacancies at both cation sites ($ZT = 0.84$ at 750 K for [Bi_{0.975}O][Cu_{0.975}Se],¹⁶⁶ while double doping leads to further increases in the figure-of-merit to $(ZT)_{\max} \approx 1.5$.¹⁶⁷ Efforts to create *n*-type analogues through doping at the copper site have been unsuccessful,¹⁶⁸ which may stem from carrier compensation through the preferential formation of Cu⁺ vacancies.

[H2] Lone pairs

Heavy elements in groups 13–16 of the periodic table can exhibit an ($N-2$) oxidation state where N is the group oxidation state, due to the presence of an ns^2 lone pair.¹⁶⁹ The stability of the lower oxidation state increases down a group and with increasing group number. Hence, while Tl⁺, Pb²⁺, and Bi³⁺ are the predominant oxidation states in period 6, Ga⁺, Ge²⁺, and As³⁺ (period 4) are less common. The presence of a lone pair is often evidenced by an eccentric charge density around the cation (Fig. 5a). This creates a local dipole, affects the cation coordination geometry, and can lead to distorted low-symmetry cation coordination environments. Classically,¹⁷⁰ a stereochemically-active lone pair has been attributed to *s-p* mixing of cation orbitals, although Walsh *et al.*¹⁷¹ have identified the strength of the cation-anion *s-p* interaction as an important factor in determining stereochemical activity of a cation lone pair. Waghmare *et al.* found¹⁷² that the cation ns^2 electrons interact strongly with the anion *p* states in the valence band, forming bonding and antibonding states (Fig. 5b). Distortion of the cation coordination environment leads to mixing of the antibonding state, at the top of the valence band, with cation *p* states, resulting in the stabilisation of occupied cation *p* states. The distortion and the resulting contribution of cation *s* states to the antibonding state, required for stereochemically-active lone pairs is critically dependent on the relative energies of the cation *s* and anion *p* states.^{171,172} This is evidenced by the adoption by SnS and SnSe of the highly-distorted rocksalt structure,¹⁷³ in contrast to the cubic rocksalt structure of SnTe (Fig. 5c and d).

The local polyhedral distortions associated with stereochemically active lone pairs, may be correlated over long length scales, and the average crystal structure can be determined using conventional crystallographic techniques. However, the lone-pair-induced distortions can also be uncorrelated, and standard crystallographic methods yield inaccurate high-symmetry structural models.¹⁶⁹ In such instances, whereby the distortion around each cation depends on the local orientation of the corresponding lone pair, unusually large atomic displacement parameters or split sites with partial occupancies may occur. Disorder may be static or dynamic, where the lone-pair charge density (and hence the local dipole) fluctuates in magnitude or direction.^{174,175} The high-symmetry crystal structure determined at low temperatures may distort locally to lower symmetry upon warming, in a controversial phenomenon known as emphanisis.¹⁷⁶ While the pair distribution function (PDF) analysis of neutron scattering data that resulted in the discovery of emphanisis, revealed local off-centering of Pb²⁺ by ~0.2 Å in PbTe and PbS,¹⁷⁶ the anomalous temperature dependence of the unit-cell parameters and the non Debye-like atomic displacement parameters have been questioned,¹⁷⁷ while an EXAFS study found no evidence of Pb²⁺ off-centering.¹⁷⁸ In subsequent studies, emphanisis has been

primarily identified through the appearance of asymmetric peaks, at short length scales, in the neutron or X-ray PDF (Fig. 5e). Emphantitic behaviour has been proposed for several cubic rocksalt phases, including PbQ ($\text{Q} = \text{S, Se, and Te}$),^{176,179} SnTe ¹⁸⁰ and $(\text{SnSe})_{0.5}(\text{AgSbSe}_2)_{0.5}$.¹⁸¹ The local off-centering of lone-pair cations induces local aperiodicity and strong anharmonicity, hence substantially reducing the lattice thermal conductivity. Dynamic crystallography, demonstrated on GeTe ,¹⁸² is a technique that involves the collection of snapshots of structural data over varying time scales applicable to atomic motions. The capacity to bridge the time-averaged and instantaneous structures may help resolve the disagreement between methods that probe the local structure and spectroscopic or average crystallographic methods.

The presence of lone pairs has a marked effect on electron transport properties, as ns^2 lone pairs change the character of the bands near the Fermi level — which become antibonding¹⁷² — and can shift the band gap from the low-degeneracy Γ point to lower symmetry positions.¹⁸³ This increases the band degeneracy (N_v) and produces highly-desirable multi-valley Fermi surfaces in which there are multiple band extrema. These may increase N_v through degeneracy, or when additional bands separated by a small energy from the primary band edge are created, afford opportunities for band tuning, or can increase, m_{DOS}^* . For instance, due to the presence of the lone pair, in PbTe and SnTe , the top of the valence band is found at L ($N_v = 4$) rather than at Γ . As discussed above, the presence of multiple band extrema within a small energy range can also be exploited through band convergence to increase the band degeneracy further, and hence increase the power factor. Moreover, as a consequence of the orbital hybridisation (Fig. 5b), which raises the valence band maximum, materials containing cations with ns^2 lone pairs exhibit lower band gaps than those found for isostructural compounds lacking a lone pair.^{184,185}

Lone pairs also have a substantial effect on the lattice thermal conductivity. Skoug and Morelli⁵⁹ have shown that Cu_3SbSe_3 (containing Sb^{3+}), has a markedly lower lattice thermal conductivity (Fig. 5f) than the analogous Sb^{5+} -containing phase, Cu_3SbSe_4 . Nielsen *et al.* demonstrated the reduction in κ_L was due to the lone pairs in ABQ_2 chalcogenides ($\text{B} = \text{Sb}^{3+}$ and Bi^{3+}).⁵⁸ Calculations for NaSbSe_2 suggest the lone-pair charge density is highly deformable. In particular, the $\text{Sb}^{3+} 5s^2$ lone pairs are strongly polarizable along the $[1\bar{1}0]$ direction and, as a consequence, the stiffness of the Sb-Se bonds changes when Se is displaced along $[1\bar{1}0]$. The presence of stereochemically active lone pairs therefore results in strong anharmonicity, reflected in large values of the Grüneisen parameter.⁵⁸ Dynamic lone pairs may also cause reductions in κ_L as observed in the mixed-valent compound, InTe , in which In^+ ions are located in channels along the $[001]$ direction. Displacement of In^+ ions along $[001]$, arising from an unstable electronic structure driven by the $5s^2$ lone pairs, is responsible for dynamically unstable phonon modes.¹⁷⁴ The low-energy phonon modes corresponding to the displacement of In^+ along $[001]$ show very large values of the mode-resolved Grüneisen parameter (up to $\gamma \approx 5$), indicating enormous anharmonicity. The lone-pair may also play a role in the low thermal conductivity of TI^+ -containing phases.^{186,187}

In aikinite, CuPbBiS_3 , with $\kappa \approx 0.5 \text{ W m}^{-1} \text{ K}^{-1}$ at 298 K, ab initio molecular dynamics simulations, coupled with inelastic neutron scattering data (Fig. 5g), show that the Pb^{2+} lone pairs are rotating.¹⁷⁵ The ultralow thermal conductivity arises from the coupling of rotating

Pb^{2+} lone pairs with the vibrational motion of the Cu^+ cations (Fig. 5h). Although anharmonicity is widely considered as the root cause for the reduction in lattice thermal conductivity in compounds containing lone pairs, it has been argued that the strong antibonding character of the top of the valence band leads to weakened chemical bonds.¹⁸⁸ As discussed above, materials with weak chemical bonding interactions, should have low lattice thermal conductivities.

[H2] Resonant or multi-center metavalent bonding

The nature of the bonding in binary group 14 chalcogenides, which include many of the best thermoelectric materials, has been a matter of considerable debate. These materials crystallize either in the rocksalt structure, or in distorted variants, in which the cation is octahedrally coordinated. While the narrow band gaps and reasonably high electrical conductivities of these materials are not consistent with ionic bonding, the number of available valence electrons is insufficient for conventional covalent bonding. In octahedral coordination, the chemical bonds around the cation violate the 8- N rule and are clearly electron deficient. It has been proposed that σ resonant bonding (Fig. 6a), analogous to π resonant bonding in benzene, explains the unusual physical properties of these materials.¹⁸⁹ The ns^2 electrons were considered non-bonding, with each atom having on average three valence p -electrons resonating over six available bonds. It was proposed that this leads to a highly delocalised electron density, accounting for the anomalously large Born effective charges, and the large electronic polarizabilities of these materials. A half-filled p -band induces a weak Peierls distortion, involving off-centering of the cations, stabilising the structure. Wuttig *et al* have proposed an alternative type of bonding, termed metavalent bonding, that is fundamentally different from ionic, covalent, or metallic bonding.^{190,191} Different types of bonding, which are determined using chemical-bonding descriptors derived by QTAIM,⁷⁵ can be classified by considering a plot of the number of electrons shared between adjacent atoms versus the electrons transferred (normalised to the oxidation state) (Fig. 6b). Ionic solids are characterized by an electron transfer greater than 0.5 — but modest electron sharing — while covalent solids have a small electron transfer but share up to two electrons. In the region of metavalent behaviour, the electron share is approximately one. Wuttig describes metavalent bonding as a two-centre-one-electron bond, corresponding to a bond order of 0.5.¹⁹² Metavalent bonding has also been identified in binary group 15 chalcogenides and in ternary AgBQ_2 phases (B = Sb, Bi; Q = Se, Te).^{192,193}

The ‘fingerprints’ of materials with metavalent bonding, sometimes described as incipient metals, are: moderate electrical conductivities; large effective coordination numbers which violate the 8- N rule; high optical dielectric constants; high Born effective charges (and therefore high chemical bond polarizability); and high Grüneisen parameters for transverse optical modes.¹⁹⁰ Jones *et al.* have questioned whether metavalent bonding is a new bonding mechanism or simply multi-center bonding.¹⁹⁴ In molecular chemistry, multi-center bonding is a well established concept.¹⁹⁵ For example, in diborane, B_2H_6 , (Fig. 6c) bonding is described in terms of three-centre-two-electron (3c-2e) bonds, in which the central B_2H_2 ring contains two 3c-2e bonds, and thus four electrons in total.¹⁹⁶ Multi-center 3c-2e bonds would be consistent with one shared electron, as shown in Fig. 6b for metavalent bonding. Analysis of Wannier functions for the valence bands of PbTe (Fig. 6d) indicate multi-center character, and

reveals that bonding involves long-range charge transfer along [100], induced by the off-centering of ns^2 cations, along linear chains of at least five atoms.¹⁹³ The low bond order of chemical bonds in these materials in comparison to conventional 2c-2e bonds is consistent with low lattice thermal conductivities. The long-range interaction along [100] results in optical phonon softening and strong anharmonic phonon scattering.¹⁹⁷ The concept of metavalent bonding has been exploited to design materials with high values of ZT .^{198,199,200,201} For example, rhombohedral $(\text{GeSe})_{0.9}(\text{AgBiTe}_2)_{0.1}$, resulting from alloying GeSe, which exhibits covalent bonding (coordination number 3) and a low intrinsic charge carrier concentration, with AgBiTe_2 ,¹⁹⁹ (coordination number 6), exhibits metavalent bonding. The multivalley electronic band structure and band convergence boosts the power factor, which when coupled with a low κ_L , increases ZT from about 0.2 in GeSe to about 1.35 in $(\text{GeSe})_{0.9}(\text{AgBiTe}_2)_{0.1}$.

[H2] Heteroleptic polyhedra

As noted above, oxychalcogenides such as BiOCuSe , containing homoleptic polyhedra, have attracted interest as thermoelectric materials due to their relatively low thermal conductivities.^{202,203} Although mixed-anion solids containing heteroleptic polyhedra, in which a cation is coordinated to more than one type of anion, have been less studied,²⁰⁴ a small number of reports highlight their exceptionally low thermal conductivities.^{205,206,207} Sato and coworkers²⁰⁷ compared the thermal conductivity of single-anion CuTaS_3 with the structurally-similar mixed-anion phase MnBiS_2Cl (Fig. 6e). The former contains homoleptic polyhedra, while the latter contains heteroleptic $[\text{MnS}_4\text{Cl}_2]$ and $[\text{BiS}_5\text{Cl}_2]$ polyhedra. Remarkably, the experimentally-determined thermal conductivity of MnBiS_2Cl ($\kappa \approx 0.5 \text{ W m}^{-1} \text{ K}^{-1}$ at 298 K) is seven times lower than that of CuTaS_3 ($\kappa \approx 3.5 \text{ W m}^{-1} \text{ K}^{-1}$). While calculations indicate that the anharmonicity and Grüneisen parameters of both materials are similar, the presence of multiple anions in MnBiS_2Cl results in interatomic cation-anion force constants that are widely different (that is, bond heterogeneity). The phonon DOS of CuTaS_3 shows a gap between acoustic and optical phonons. This disappears in MnBiS_2Cl , due to a split in the phonon DOS peaks, arising from different interatomic force constants. Consequently, the number of phonon scattering processes in the low-to-medium phonon energy range increases considerably in MnBiS_2Cl compared to CuTaS_3 , leading to a substantial reduction in κ_L . The ultralow thermal conductivity of $\text{Sn}_2\text{SbS}_2\text{I}_3$ ($\kappa \approx 0.3 \text{ W m}^{-1} \text{ K}^{-1}$), which is lower than that of the heavier analogue $\text{Pb}_2\text{SbS}_2\text{I}_3$ ($\kappa \approx 0.7 \text{ W m}^{-1} \text{ K}^{-1}$), has been attributed to strong anharmonicity, arising from the presence of the lone pair of the Sn^{2+} cations at the top of the valence band.²⁰⁶ In $\text{CsAg}_5\text{TeS}_2$, containing heteroleptic $[\text{AgTe}_2\text{S}_2]$ tetrahedra, the Ag^+ cations are locally off-centered — the local disorder induces low-frequency optical phonons — which increase phonon scattering leading to $\kappa_L \approx 0.4 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K.²⁰⁸

[H1] Conclusions and Future Perspectives

Advances in the understanding of the complex relationships between chemical compositions, structure across a range of length scales, and transport properties has driven a renaissance in thermoelectric research. The emergence of a series of design strategies that target enhanced electrical performance or reductions in thermal conductivity has resulted in new materials with promising thermoelectric performance, while simultaneously addressing environmental and

sustainability issues. Remarkable advances in materials performance have produced figures of merit that exceed $ZT = 2$ in several systems. The presence of relatively heavy atoms is common to many of the state-of-the-art materials, as this favours low thermal conductivity. However, factors such as entry of the cation sub-lattice into a liquid state or the presence of low-dimensional structural units can lead to high-performance even when lighter anions such as oxygen or sulfur are present. Understanding the role of chemical bonding will underpin future advances, particularly when coupled with strategies such as the control of the micro- and nano-structure, through composition, precipitation, and texturing. There is considerable scope to exploit cation lone pairs to introduce local structural distortions, with an impact on both the electronic band structure and on phonon transport, to achieve high performance. Mixed-anion systems are relatively under-explored and may assume greater prominence in the discovery of thermoelectric materials, as they offer scope to fine-tune structural features, through judicious choice of cation and anion combinations.

A further factor in determining thermoelectric performance that applies to the crystalline solids discussed here, is that of disorder. In addition to that arising from thermal displacement of atoms about their equilibrium positions, exhibited by all crystalline materials at finite temperatures, disorder can also be associated with departures from periodicity of composition, ionic charge, atomic displacements, chemical bonding, or orbital occupancies.²⁰⁹ Local atomic ordering, distinct from the long-range order of the average structure, as occurs in the defective half-Heusler, $\text{Nb}_{1-x}\text{CoSb}$ ²¹⁰ can considerably reduce thermal conductivity. A similar feature has been observed in the Zintl phase, Eu_2ZnSb_2 in which vacancy order on a local scale co-exists with long-range Zn-site disorder,²¹¹ resulting in an exceptionally low thermal conductivity ($\kappa_L \approx 0.4 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K). The disordered feature may also show a degree of correlation. The impact on physical properties of correlated disorder,^{212, 213} has led to the development of sophisticated techniques to probe the characteristic deviations from periodicity,^{214, 215} and to investigate the relationship between disorder and thermoelectric performance. For example, 3D-PDF analysis has established²¹⁶ that the PLEC material, Cu_{2-x}Se , adopts a structure at low temperature in which 2D ordered layers are stacked in a disordered sequence.

Hidden locally-asymmetric atomic motifs²¹⁴ within an average crystal structure, have a marked impact on thermal conduction by phonons. Disorder can take the form of off-centring,²¹⁷ in which an atom is displaced from its parent site. This reduces the crystal symmetry leading to lattice strain which impacts the propagation of heat-carrying phonons. Even when the displacement is sufficiently small to not impact on the overall symmetry, the local coordination may become asymmetric. The stereochemically-active lone pairs discussed above can lead to off-centring. In the case of the rocksalt-structured AgSbSe_2 , in which cation sites are occupied by a statistical mixture of Ag^+ and Sb^{3+} , PDF analysis of X-ray scattering data²¹⁸ reveal a local distortion of the ideal octahedral symmetry at the cation sites. The $5s^2$ lone pair associated with Sb^{3+} induces displacement of cations along the $\langle 100 \rangle$ direction, resulting in one short, four medium, and one long M-Se bond in the MSe_6 octahedron. The resulting lattice strain enhances phonon scattering, thereby reducing the thermal conductivity. Similar lone-pair-induced displacements that result in local symmetry breaking, have been observed in a variety of binary^{176,179,180,219} and ternary chalcogenides^{217,220,221,222} containing elements from groups 13 and 14. Local off-centring can also arise from the incorporation of

atoms whose bonding preferences are incompatible with the site symmetry (termed ‘discordant atoms’),^{223,224} the presence of small atoms in a large void²²⁵ or weak hybridization²²⁶.

Ranking the effectiveness of the available strategies for improving thermoelectric performance is problematic as each approach generally applies to a different family of materials. For example, anharmonicity driven by the presence of an s^2 lone pair, requires the heavier cations drawn from groups 13–15 of the periodic table. However, more generally, strong anharmonicity resulting from a range of factors, including lone pairs, bonding heterogeneity, weak chemical bonding, anisotropy or disorder, appears to be a particularly effective means of reducing thermal conductivity and increasing thermoelectric performance. We compare the performance of materials that exploit the chemical bonding principles outlined in this review in Table 1.

A considerable barrier to the implementation of thermoelectric technology is the difficulty in translating materials advances into device performance, due to technical, engineering and economic challenges.²²⁷ Poor electrical and thermal contact is the principal factor in the loss of performance. Improved solders and electrode materials are required to reduce the contact resistance at the interface between the thermoelement and electrode. Elemental diffusion under operating conditions also limits the efficiency and lifespan of a device, necessitating the development of appropriate diffusion barrier layers, with thermal expansion coefficients compatible with the other components, in order to prevent thermomechanical stress and failure. Cost, elemental abundance, and environmental considerations are also factors. The toxic element tellurium which is at the heart of commercial devices constructed from PbTe and Bi₂Te₃ is scarce (1 ppb) and classified as a critical mineral by the US government.²²⁸ As outlined in the preceding sections this has motivated the search for alternative materials, the high performance of which can be rationalised in terms of their chemical bonding properties. New materials present their own challenges in device construction, arising from volatilization, surface oxidation, or increased reactivity with other device components at elevated temperatures. Coating with a chemically-inert protective layer can help mitigate some of these issues.^{229,230} In PLEC materials, the ion mobility that promotes high performance can lead to degradation under operational conditions.^{231,232,233} Ion-blocking interfaces, through the introduction of secondary phases or modifying the stoichiometry of the leg,²³⁴ doping,^{233,235,236,237} nanoinclusions,^{238,239,240,241} grain boundary engineering²⁴² and tailored geometries of thermoelements²⁴³, have all been used in an effort to alleviate these problems. It has been demonstrated²⁴⁴ that co-doping of Cu₂Se can increase the barrier for ionic conduction and lead to the stabilization of the PLEC phase under operating conditions. Moreover, a maximum figure of merit, $ZT \approx 3$ was achieved at 1050 K.

While many new materials will derive from application of one or more established design strategies, the rapid and widespread development of artificial intelligence (AI) offers exciting opportunities for discovery of new thermoelectric materials.²⁴⁵ Efficient computer-based methods are a cost-effective alternative to expensive and time-consuming first-principle calculations for materials design and discovery. The advantages and limitations of each of the common AI-based methods including machine learning (ML), deep learning, and artificial neural networks have been discussed by Maleki *et al.*²⁴⁶

ML methods are used to model and predict candidate materials with diverse functionalities, including thermoelectric materials.^{247,248,249} Such algorithms typically use

existing experimental and/or theoretical data to train a statistical model, which is then used to predict new materials and compositions with targeted physical properties. Training requires a database containing information on crystal structure, composition, and physical properties for a range of compounds. From this information a set of descriptors that uniquely characterizes the physical properties may be formulated — those most directly related to chemical bonding principles include bond strength, bond length, electronic band structure, Pauling electronegativity, and anharmonicity. Regression methods^{250, 251, 252} are most commonly used in the search for thermoelectric materials. ML-based methods have enabled the prediction and validation of new thermoelectric compounds that include half-Heuslers,²⁵³ oxides,²⁵⁴ chalcogenides²⁵⁰, and others.²⁵⁵ The application of ML and AI approaches is likely to assume increasing importance in the future discovery of new high-performance thermoelectric materials, although Cheetham and Seshadri²⁵⁶ have suggested that the results of ML approaches need to be treated with caution. However, when coupled with experimental validation of the predictions, and the appropriate expertise in synthesis and crystallography, ML offers exciting opportunities for the future of thermoelectrics research.

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Competing interests

The authors declare that there are no competing interests

Short Summary

Many of the advances in high-performance thermoelectric materials can be related to fundamental chemical-bonding principles. Application of concepts including bonding models, lone pairs, bonding heterogeneity, multi-centre bonding, and polarizability to the development of advanced thermoelectric materials are discussed here.

Table 1 | Chemical bonding strategies found in selected high-performance thermoelectric materials

Material	Chemical bonding strategy	ZT_{\max}	T_{\max} / K	Ref.
(Bi,Sb) ₂ Te ₃ (Nanostructured)	Bonding heterogeneity (polarizability) Lone pairs	1.4	373	263
PbTe	Metavalent, resonant bonding Lone pairs Band convergence	1.8	850	41
GeTe	Lone pairs Band convergence	2.4	600	264
SnSe	Bonding heterogeneity Lone pairs	3.1	783	151
Cu ₂ Se	Bonding heterogeneity (PLEC)	~3	1,050	244
Ag ₉ GaSe ₆	Bonding heterogeneity (PLEC)	1.5	850	124
CuAgTe	Bonding heterogeneity (PLEC)	1.6	670	122
MgAgSb	Bonding heterogeneity (PLEC)	1.4	450	135
BiOCuSe	Bonding heterogeneity (homoleptic polyhedra)	1.5	873	167
Mg ₂ (Sb,Bi) ₃	Soft bonding	1.85	723	67
Filled skutterudite Sr _{0.12} Ba _{0.18} DD _{0.39} Fe ₃ CoSb ₁₂	Bonding heterogeneity (PGEC)	1.2	800	96
Clathrate Ba ₈ Ga ₁₆ Ge ₃₀	Bonding heterogeneity (PGEC)	1.35	900	107

* Note: PLEC: phonon-liquid electron-crystal. PGEC: phonon glass electron crystal.

Figures:

Fig. 1 | From thermoelectric devices to chemical design strategies. (a) Schematic view of a thermoelectric couple, composed of an n-type and a p-type semiconductor. They are joined at the bottom by a metal (grey bar), to make a junction. When the junction is heated, both types of carriers conduct heat towards the top and power is generated. (b) A commercial thermoelectric module, which consist of several thermoelectric couples connected electrically in series and thermally in parallel. (c) Dependence of the Seebeck coefficient (S), electrical conductivity (σ) and the electronic (κ_e) and lattice (κ_L) contributions to the thermal conductivity on the charge carrier concentration n , for a bulk material (d) Selected chemical bonding approaches to consider when designing thermoelectric materials.

Fig. 2 | Electronic structures of thermoelectric materials. (a) An illustration of the more structured density of states (DOS) that results from a low-dimensional structure (BiOCuSe)³⁶ compared with a three-dimensional solid such as PbSe ³⁷. (b) Band convergence induced in PbTe by increasing temperature, in which an upper valence (L) band of degeneracy, $N_v = 4$ in blue, falls in energy, until at a critical temperature, it converges with a lower Σ band ($N_v = 12$, in green), resulting in an effective degeneracy of $N_v = 16$. CB denotes the conduction band (c) Band structure of the unfilled skutterudite, CoSb_3 , and the filled analogue, $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12}$ showing how the energy gap (ΔE_{CB}) between an upper (CB_2) and lower (CB_1) is reduced on electron doping.⁴⁶ (d) The temperature dependence of ΔE_{CB} illustrating that effective band convergence (defined as $\Delta E_{\text{CB}} \leq 2kT$) occurs at a lower temperature in the filled skutterudite. (e) Sb_4^{4-} rings present in the skutterudite structure, with long and short Sb-Sb distances indicated. (f) Temperature-induced structural changes in the Sb_4^{4-} rings, characterized by the changes in Sb-Sb distances in the unfilled and filled skutterudite as measured with temperature, demonstrating the different sensitivities to electron doping of the long and short Sb-Sb distances. (g) Schematic representation of band convergence in quaternary diamond-like semiconductors, kesterite (left) and stannite (right), as a function of the distortion parameter, η .⁴⁷

Fig. 3 | Bonding heterogeneity in thermoelectric materials. (a) A Zintl phase, CaZn_2Sb_2 , consisting of covalently-bonded $[\text{Zn}_2\text{Sb}_2]^{2-}$ layers, separated by Ca^{2+} cations. (b) Illustration of the avoided crossing between the acoustic phonon mode (top/bottom band) of the clathrate framework and the flat optical mode (top/bottom band) of the guest atom.⁸³ (c) Comparison of the experimental phonon density of states of the skutterudite $\text{Yb}_{0.2}\text{Co}_4\text{Sb}_{12}$, determined by inelastic neutron scattering measurements, with calculated partial densities of states, illustrating the low-energy rattling mode of the filler.⁹³ (d) The filled skutterudite $\text{Yb}_{0.2}\text{Co}_4\text{Sb}_{12}$, showing the framework of cobalt-centred octahedra (blue), with the Yb filler atoms in orange. (e) The type I clathrate $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$, with the framework of Ga and Ge atoms (blue) holding Ba guest atoms (green) inside two types of cages, dodecahedral (orange) and tetradecahedral (blue). (f) The thermoelectric figure-of-merit of liquid-like $\text{Cu}_{2-x}\text{Se}_{0.5}\text{S}_{0.5}$ as a function of temperature.¹³⁰ (g) Left, the sodalite framework found in $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$, showing the $\text{SCu}(2)_6$ octahedra (yellow) located inside the sodalite cages. Each node in the sodalite framework represents a $\text{Cu}(1)\text{S}_4$ tetrahedron. Middle, a $\text{SCu}(2)_6$ octahedron inside a

sodalite cage, with the jumps of the copper cations highlighted by blue arrows. Right, two views of the trajectory of a copper ion around a $\text{SCu}(2)_6$ octahedron, determined by molecular dynamics simulations.¹³⁷

Fig. 4 | Low dimensionality arising from bond polarization. (a) The effect of polarizability on a bond. Top, ideal cation-anion pair with no polarization; middle, mutually polarized cation-anion pair; bottom, a polarized covalent bond. The dashed lines represent the unpolarized ions. (b) Polarizability of elements in groups 15-17. (c) Electronegativity of elements in groups 15-17. (d) Layered TiS_2 , with the TiS_6 octahedra shown in blue. (e) Temperature dependence of the electrical resistivity (ρ) and Seebeck coefficient (S) of TiS_2 and cobalt-intercalated $\text{Co}_{0.06}\text{TiS}_2$, illustrating the marked difference between measurements made along the in-plane direction (full symbols), and cross-plane measurements (empty symbols).¹⁴² (f) Temperature dependence of the thermal conductivity (top) and ZT (bottom) of TiS_2 and cobalt-intercalated $\text{Co}_{0.06}\text{TiS}_2$.¹⁴² (g) Temperature dependence of ZT for a single crystal of SnSe .⁵⁶ Inset shows the crystal structure of SnSe along [010]. (h) The homoleptic oxide $[\text{Bi}_2\text{O}_2]^{2+}$ and chalcogenide $[\text{Cu}_2\text{Q}_2]^{2-}$ layers found in BiCuSeO .

Fig. 5 | Lone pair effects in thermoelectric materials. (a) Calculated electron density contour map of SnS . Contour levels shown are between 0 (blue) and 0.4 $\text{e}/\text{\AA}^3$ (red).¹⁷³ (b) Schematic illustration of the cation and anion orbital interactions in Pb^{2+} chalcogenides. (c) Undistorted rocksalt structure with octahedral coordination of cations and anions; and (d) the highly distorted octahedral coordination of Sn^{2+} in SnS . Short bonds ($< 3\text{\AA}$) are shown in blue and long bonds ($> 3\text{\AA}$) in red. Key: Sn^{2+} , grey sphere; S^{2-} , yellow sphere. (e) X-ray pair distribution function refinements at short range ($r = 2.0\text{--}4.66\text{\AA}$) for emphanitic $(\text{SnSe})_{0.5}(\text{AgSbSe}_2)_{0.5}$ at 100 K; left, undistorted structure, right, Se displaced along [111].¹⁸¹ (f) Temperature dependence of the lattice thermal conductivity of Cu_3SbSe_3 and Cu_3SbSe_4 .⁵⁹ The coordination environment of antimony in each compound is shown. (g) Inelastic neutron scattering intensities for aikinite, CuPbBiS_3 , as a function of temperature, together with Gaussian fits.¹⁷⁵ The temperature evolution of the peaks corresponding to the Pb^{2+} -based vibration (black fit) and that for the Cu^+ rattling vibration (blue fit) are consistent with a thermally activated interaction between Cu^+ and Pb^{2+} cations. (h) View along [100] of a Cu^+ (blue)- Pb^{2+} (black) layer in aikinite, and illustration of the cooperative interaction between the rotating lone pair on the Pb^{2+} cations and the Cu^+ cations.

Fig. 6 | Chemical bonding effects in thermoelectric materials. (a) Illustration of the concept of σ resonant bonding in group 14 chalcogenides, showing two possible resonance forms. (b) Plot classifying the types of chemical bonding. Regions for resonant, metallic, van-der-Waals', covalent, ionic and metavalent bonding are shaded in different colours.¹⁹¹ (c) Diborane molecule, B_2H_6 , with the 3c-2e bonds highlighted in red. (d) Wannier function (left) and its schematic representation (right) for the valence band of PbTe , corresponding to a p_x orbital centered on a Te^{2-} anion, revealing $p-p$ σ -bonding interactions with neighbouring Pb^{2+} cations, weak π -bonding interaction with neighbouring Pb^{2+} cations, and antibonding σ^* and π^* interactions between cations and anions in the next shell, illustrating the multi-center

character of the bonding.¹⁹³ (e) Crystal structures of CuTaS₃ and MnBiS₂Cl and their lattice thermal conductivities.²⁰⁷ Key: Cu/Mn, blue; Ta/Bi, grey; S, yellow; Cl, green.

Boxes:

BOX 1 | Electronic structure of solids

A chemically-intuitive approach to bonding in a solid^{257,258} extends the concepts of the linear combination of atomic orbitals (LCAO) familiar in molecular systems. The key features can be illustrated through the consideration of a regularly-spaced one-dimensional chain of atoms, separated by a repeat distance, a . The wave function (ψ_k) of an orbital combination is related to that of the basis orbitals (χ) by:

$$\Psi_k = \sum_0^n e^{ikna} \chi_n$$

where the summation is taken over the n atoms in the chain and k is a wave number lying in the first Brillouin zone, $-\pi/a \leq k \leq \pi/a$. The energy $E(k)$ of an orbital combination is given by:

$$E(k) = \alpha + 2\beta \cos(ka)$$

where α and β are the energy of an electron in one of the constituent atomic orbitals and the overlap integral between neighbouring orbitals, respectively. This expression corresponds to a parabolic band, symmetrical about $k = 0$. For an s -orbital basis, β is negative. As shown below the combination at $k = 0$ is therefore bonding and lower in energy ($\alpha + 2\beta$), than the antibonding combination ($\alpha - 2\beta$) at $k = \pi/a$. In the case of a p_σ -basis, the relative energies at the extremes of the first Brillouin zone are reversed. The bandwidth, $4|\beta|$, is governed by the strength of the interaction between neighbouring orbitals — greater overlap producing broader bands.

For small values of k in the LCAO treatment, the expression above reduces to:

$$E(k) = (\alpha + 2\beta) - \frac{(ka)^2}{\beta}$$

which when compared with the results from the free electron theory of solids ($E(k) = V_0 + (\hbar k)^2/(2m)$), leads to the introduction of an adjustable parameter, the effective mass, m^* . This can be considered a measure of the curvature of $E(k)$. m^* is inversely proportional to the overlap integral, β , according to:

$$m^* = \frac{\hbar^2}{2a^2\beta}$$

where \hbar is the reduced Planck constant ($h/2\pi$). An electron therefore has a small effective mass when overlap results in broad bands, while m^* is large if bands are narrow.

Extension to two- and three dimensions, introduces additional coefficients (k_x, k_y, k_z), which are components of the wave vector (\mathbf{k}), that defines the orbital combination ψ_k . The band structure is represented by a plot of the energy of an orbital combination along specific directions (k -values) in the first Brillouin zone, while the Density of States (DOS) below, represents the number of energy levels between an energy E and $(E + dE)$ on progressing through the band.

Band filling follows the same principles as in molecules: each level accommodating two electrons. At absolute zero, the Fermi level (E_F) defines the boundary between occupied and

unoccupied energy levels analogous to the HOMO and LUMO, respectively, of molecular orbital theory. At finite temperatures, the electron distribution follows Fermi-Dirac statistics, smearing the distinction between filled and empty states, although E_F remains a useful concept for solids at real temperatures.

For a compound, AX, orbitals of the more electronegative element X, are lower in energy than those of the less electronegative A. A large difference in electronegativity $\Delta\chi_{A-X}$ results in weak orbital overlap as illustrated below. The resulting bands are narrow (m^* large) and comprise a lower lying valence band (VB), of mainly X-type (anionic) character separated from a higher lying conduction band (CB) of A-type (cationic) character. Decreasing $\Delta\chi_{A-X}$, increases the covalency of the interaction, and raises the energy of the (formally) anion-based valence orbitals of X. This decreases the energy gap (E_g) between the VB and CB, broadening the bands through more effective overlap. DFT²⁵⁹ is generally used for the calculation of electronic band structures, generating the parameters identified above. Further information can be found in the book by Parr and Yang.²⁶⁰

Box 2 | Fundamentals of vibrations in solids

Heat in a poorly electrically-conducting solid is transported primarily via the thermal vibrations of the atoms about their equilibrium positions. The quantized modes of vibrations are termed phonons and determine the lattice thermal conductivity of a material. Consider the one-dimensional (1D) chain shown in the figure, containing two atoms (masses M_1 and M_2) per repeat unit (unit cell), vibrating with frequency ω with a wavevector k . For each wavevector, there are as shown, two possible polarisations: transverse, where the vibration vector is perpendicular to the wavevector; and longitudinal, where the vibration vector is parallel to the wavevector. Solving the equations of motion gives the $\omega(k)$ -dependence which is important in understanding the behaviour of the lattice thermal conductivity of a material. For each mode of polarisation in the propagation direction, the phonon dispersion ($\omega(k)$) relation contains two branches — acoustic and optical — leading to longitudinal-transverse acoustic (LA-TA) modes and longitudinal-transverse optical (LO-TO) modes. In the case of two atoms per unit cell with different masses, an acoustic mode corresponds to the two atoms vibrating (in-phase) together, with their centre of mass moving, whereas in an optical mode, the atoms vibrate against each other (out-of-phase), and the centre of mass remains fixed. In the three-dimensional (3D) case, if there are q atoms per primitive cell and N primitive cells, the total number of atoms is qN , each with three degrees of freedom, giving $3qN$ degrees of freedom overall. The acoustic branches constitute a total of $3N$ modes, corresponding to $3N$ degrees of freedom, while the remaining $(3q-3)N$ degrees of freedom are associated with the optical branches. The group velocities (v_g) of the different modes represent the gradient $d\omega/dk$ of the $\omega(k)$ phonon dispersion relation. The lattice thermal conductivity depends on v_g through:

$$\kappa_L = 1/3 C_v v_g^2 \tau_{ph}$$

where C_v , v_g and τ_{ph} are the specific heat, phonon group velocity and phonon relaxation time, respectively. Therefore, it is desirable for phonons in a thermoelectric material to exhibit low group velocities, corresponding to a weak k -dependence and low dispersion. In the majority of solids, the acoustic modes are highly dispersed (high v_g) whereas the optical modes are

nearly dispersionless (low v_g). Hence, heat in solids is primarily transported by the acoustic modes.

In some materials, the vibration of the atoms may be asymmetric about the equilibrium position, resulting in anharmonicity, whereby the restoring force is no longer proportional to the atomic displacement. The vibrational energy of an anharmonic oscillation cannot be approximated by a quadratic function and higher-order anharmonic terms need to be considered in the potential. The extent and nature of such asymmetric or anharmonic vibrations is dependent on the coordination environment, site symmetry, local potential, and/or local distortions. The degree of anharmonicity in a material may be quantified by the Grüneisen parameter (γ),²⁶¹ defined as the change in the phonon frequency with specific volume (V), which is a function of the thermal expansion coefficient (α_T), heat capacity (C_V) and bulk modulus (G):

$$\gamma = \frac{\alpha_T G V}{C_V}$$

A variety of *ab-initio* methods to calculate phonon dispersion curves have been described.^{259,262}

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