An Overview of Thermoelectric Concepts

Hadis Behjat Gharetape

Computational and Physical Chemistry Department, Shahid Beheshti University, Tehran, Iran
hadis.behjat@gmail.com

Abstract

Thermoelectric (TE) materials have emerged as promising candidates for addressing the global energy crisis by enabling waste heat recovery and sustainable cooling technologies. The performance of TE materials is governed by the dimensionless figure of merit $zT = \alpha^2\sigma T/\kappa$, which depends on three key interrelated parameters: the Seebeck coefficient (α), electrical conductivity (σ), and thermal conductivity (κ). Due to the conflicting nature of these interconnected variables, simultaneous optimization of all three parameters remains elusive. Two main strategies have been introduced to improve zT: phonon engineering and band engineering. The ultimate goal of these approaches is to develop phonon-glass and electron-crystal materials. Among the well-studied families of thermoelectric materials are chalcogenides (e.g., Bi_2Te_3, PbTe, and SnSe), skutterudites (e.g., $CoSb_3$), Zintl phases (e.g., $Yb_{14}MnSb_{11}$), and half-Heuslers (e.g., ZrNiSn), each offering distinct advantages across different temperature regimes. Despite considerable progress, a unified understanding of structure–property relationships remains elusive, motivating growing interest in computational methods. The design, prediction, and discovery of new and improved thermoelectric materials increasingly rely on density functional theory and machine learning, which complement experimental efforts by accelerating the identification of high-performance candidates. In this overview, we revisit the fundamental concepts and theories underlying these materials along with their key design strategies and applications.

Keywords: Thermoelectric Materials; Figure of Merit zT; Entropy Production; Nanostructuring; Phonon-Glass Electron-Crystal; Density Functional Theory; Machine Learning.

1 Introduction

Every year, more than two-thirds of global energy consumption is lost as waste heat [1]. This wasted energy is dissipated into the environment without being used. Thermoelectric materials offer a partial solution: they can capture a fraction of this waste heat and convert it into usable electricity, thereby improving overall energy efficiency.

Significant amounts of waste heat are produced by vehicles, industrial processes, power plants, and electronic devices such as computers and smartphones. Thermoelectric materials can act as thermoelectric generators, converting this waste heat into electrical energy, or they can alternatively function as Peltier coolers, actively lowering the temperature of electronic devices without moving parts [2]. However, their efficiency remains low, and significant research is ongoing to improve their performance [4].

The performance of a thermoelectric material is quantified by its figure of merit, $zT = \alpha^2\sigma T/\kappa$. A high zT requires high electrical conductivity (σ), a high Seebeck coefficient (α), and low thermal conductivity (κ). The main challenge is that these properties are correlated, making it difficult to satisfy all three conditions simultaneously [2, 4].

In this overview, we first explore the thermoelectric effects and the thermodynamic foundations that govern them, including entropy production and nonequilibrium transport [5]. We then introduce the figure of merit zT and explain why achieving high values remains difficult [2]. Next, we survey the engineering strategies used to improve thermoelectric efficiency (e.g., nanostructuring, phonon-glass electron-crystal concept, and band engineering) [4]. We then review classical and emerging thermoelectric materials, from Bi_2Te_3 to SnSe and half-Heuslers [2, 4]. Finally, we discuss how density functional theory and machine learning are used to compute thermoelectric properties and predict zT values for theoretically calculated materials not yet reported experimentally.

2 Fundamentals of Thermoelectricity

We begin by describing the governing principles of thermoelectric materials. Thermoelectric materials operate through the thermoelectric effects, which occur in the presence of a heat flow or an electric current. Since we are dealing with dynamic conditions, we need non-equilibrium thermodynamic equations to understand these phenomena. This can be well explained by applying Onsager's theorem [5]. In the following, we first introduce the thermoelectric effects, then discuss Onsager's principle and entropy generation.

2.1 Thermoelectric Effects

By thermoelectric effects, we mean the Seebeck effect discovered by T. J. Seebeck in 1821, the Peltier effect (J. Peltier in 1834), and the Thomson effect (Lord Kelvin in 1851). These

effects are related by the Thomson relations (Kelvin relations), which will be discussed briefly below. Although more than two centuries have passed since these effects were first discovered, thermoelectric materials are a relatively new topic of research. This is because efficient thermoelectric materials have been available since the discovery of Bi_2Te_3 in the 1950s, and continued advances in materials science have yielded better materials.

2.1.1 Seebeck Effect

The Seebeck effect implies that an electric potential is generated when a temperature difference exists between two junctions of a thermocouple, with no electrical current applied. The same principle applies to thermoelectric materials, which contain junctions of two semiconducting materials. The potential difference is related to the temperature difference by the Seebeck coefficient α_{AB}:

$$V = \alpha_{AB}\Delta T \tag{1}$$

2.1.2 Peltier Effect

In contrast to the Seebeck effect, the Peltier effect describes how applying an electric current between two junctions at the same temperature results in a heat flow. The direction of heat flow depends on the direction of the current:

$$\dot{Q}_{\text{Peltier}} = \pi_{AB} I \tag{2}$$

where π_{AB} is the Peltier coefficient and I is the electric current. The Peltier effect (see Figure 1) is reversible; the direction of heat flow depends on the direction of the current.

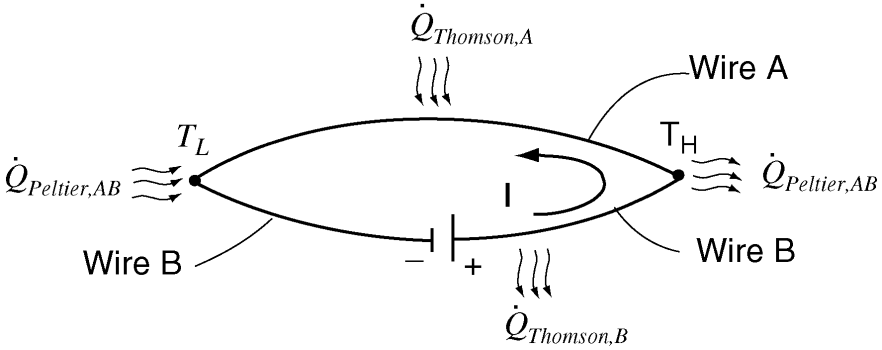

Figure 1: Schematic of the Peltier effect and Thomson effect. From Lee [3]. Reprinted with permission from John Wiley & Sons.

2.1.3 Thomson Effect

The Thomson effect (Figure 1), discovered by Lord Kelvin, occurs when both thermal flow and electric current exist simultaneously in a junction:

$$\dot{Q}_{\text{Thomson}} = -\tau_{AB} I \nabla T \tag{3}$$

where τ is the Thomson coefficient. It can be measured for a single material by connecting it to a superconductor as a reference at low temperature. Values at higher temperatures are then obtained by using the Kelvin relations [2].

2.2 Kelvin Relations

The thermoelectric phenomena described above are all reversible processes. However, irreversible Joule heating always exists in real systems.

Since both heat flow and electric current exist in the Thomson effect, the Thomson coefficient reveals how the thermoelectric effects are related. This was first derived by Lord Kelvin using the first and second laws of thermodynamics, assuming that reversible and irreversible processes in a thermoelectric device can be separated [3]. Joule heating is the irreversible process in a non-ideal thermoelectric device, caused by electrical resistance. The relations were later confirmed experimentally as a consequence of Onsager's reciprocity principle [8].

By separating reversible and irreversible processes, one can assume that the entropy change of the surroundings for reversible processes is zero in a closed circuit. This was the starting point for deriving the Kelvin relations [3]:

$$\pi_{AB} = \alpha_{AB} T \tag{4}$$

$$\tau_{AB} = T \frac{d\alpha_{AB}}{dT} = \tau_A - \tau_B \tag{5}$$

Equations (4) and (5) are known as the Kelvin relations. Since Thomson coefficients are measurable by experiments, the Seebeck coefficient can be calculated using these equations. These equations also imply that increasing the temperature results in an increase in the Seebeck coefficient.

We conclude this section with a brief review of the concepts discussed so far. Figure (2) shows a typical thermoelectric module containing many thermoelectric couples of p-type and n-type semiconductors connected both thermally and electrically (the materials will be discussed later). The schematic illustrates both generator and cooler operation. In generator mode, the top of the device is the hot reservoir and the bottom is the cold reservoir. In cooler mode, an external electric current drives charge carriers (electrons and holes) and heat is absorbed from the surroundings.

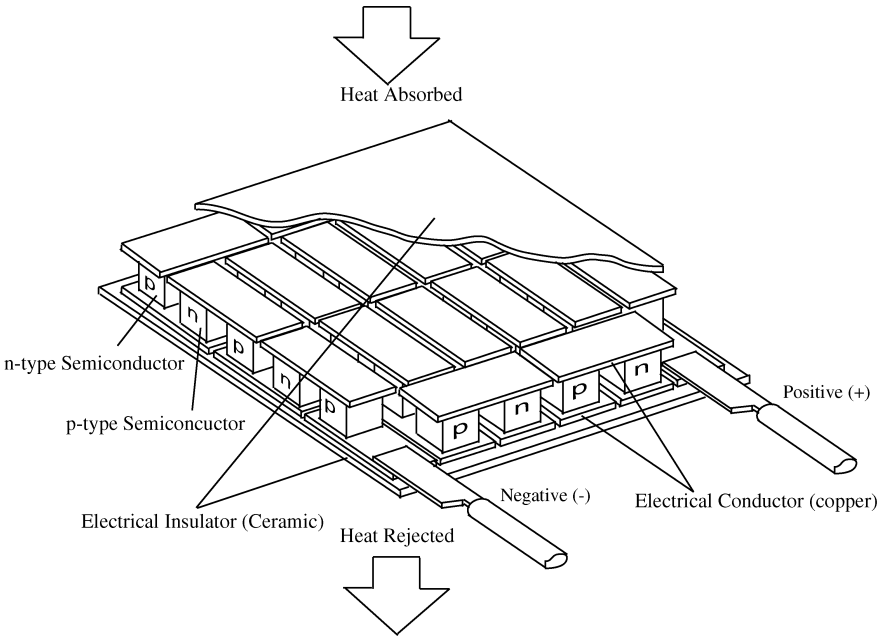

Figure 2: Cutaway of a typical thermoelectric module. From Lee [3]. Reprinted with permission from John Wiley & Sons.

2.3 Nonequilibrium Thermodynamics in Thermoelectric Systems

Having introduced the thermoelectric effects, we now turn to the thermodynamic framework that governs heat and charge transport, as this is essential for understanding the figure of merit zT. We follow Callen's explanation [5].

Callen introduces the local entropy density. This assumes that a nonequilibrium system can be divided into infinitesimal volumes, each part being in local equilibrium. It can be shown that entropy is produced in the presence of a temperature gradient or an electric current [5]. The following equation gives the change in local entropy density:

$$ds = \frac{1}{T}du - \sum_k \left(\frac{\mu_k}{T}\right) dn_k \tag{6}$$

where s is the local entropy density, u is the local energy density, μ_k is the electrochemical potential of component k, and n_k is the number density. This equation tells us that a change in energy (e.g., heat flow) and particle number leads to a change in local entropy [5].

The local entropy production rate per unit volume is:

$$\dot{s} = \nabla\left(\frac{1}{T}\right) \cdot \mathbf{J}_Q - \frac{1}{T}\nabla\mu \cdot \mathbf{J}_N \tag{7}$$

where $\mathbf{J}_Q$ is the heat current density and $\mathbf{J}_N$ is the particle current density. This equation shows how entropy is produced when heat flow and charge flow exist in the system. Entropy

can be generated independently by each of these factors. Since entropy production must be positive, each contribution is positive or zero [5].

3 Transport Properties

As Callen states, the electrical conductivity, the thermal conductivity, and the absolute thermoelectric power are the three physically significant dynamical properties of a medium [5].

There are different approaches to obtaining transport properties. The Onsager formalism relates fluxes to forces through phenomenological coefficients [5]. The Boltzmann Transport Equation, combined with the Fermi-Dirac distribution, provides a microscopic description of electron distribution [3]. Both yield the same results. We now define these three key properties.

3.1 Electrical Conductivity

Following Callen's formulation [5], for a system in which an electric field and heat current flow parallel to the x-axis with no magnetic field applied, the electrical conductivity is defined as:

$$\sigma \equiv -e\frac{J_N}{\frac{1}{e}\nabla\mu} \quad \text{for} \quad \nabla T = 0 \tag{8}$$

where eJ_N is the electric current density per unit potential gradient $\frac{1}{e}\nabla\mu$ in an isothermal system. In other words, a material with high electrical conductivity allows charge carriers to move freely with minimal resistance.

By writing the dynamic equations and applying Onsager's reciprocity, we obtain:

$$\sigma = \frac{e^2 L_{11}}{T} \tag{9}$$

where L_{11} is the direct coefficient for charge transport [5].

For a semiconductor, as Goldsmid derived from the Fermi-Dirac distribution, the electrical conductivity can also be expressed by:

$$\sigma = ne\mu \tag{10}$$

where n is the charge carrier concentration, e is the charge, and μ is the carrier mobility [2]. One should note that ionic compounds are not suited for thermoelectric materials since they have low mobility and ionic bonds, while a good thermoelectric material has covalent bonding.

3.2 Thermal Conductivity

Similarly, the thermal conductivity κ is defined as the heat current density per unit temperature gradient for zero electric current:

$$\kappa \equiv -\frac{J_Q}{\nabla T} \quad \text{for} \quad J_N = 0 \tag{11}$$

This equation implies that heat flows due to a temperature gradient when there is no electric current in the system.

This leads to:

$$\kappa = \frac{D}{T^2 L_{11}} \tag{12}$$

where D denotes the determinant of the kinetic coefficients [5]. The determinant is a positive number, so both thermal and electrical conductivities are positive.

From the kinetic theory of gases, the thermal conductivity is given by:

$$K = \frac{1}{3} C v l \tag{13}$$

where C is the heat capacity per unit volume, v is the average particle velocity, and l is the mean free path of a particle between two collisions [6]. Using this equation, Debye described the thermal conductivity of a dielectric solid with C as the heat capacity of the phonons, v the phonon velocity, and l the phonon mean free path.

The thermal conductivity of a solid consists of two parts: the electronic and the lattice thermal conductivity:

$$\kappa = \kappa_e + \kappa_{ph} \tag{14}$$

The electronic part κ_e follows the Wiedemann-Franz law:

$$\kappa_e = L \sigma T \tag{15}$$

where L is the Lorenz number. Using Sommerfeld's theory based on Fermi-Dirac statistics, the Lorenz number for free electrons is derived as:

$$L = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 \approx 2.44 \times 10^{-8} \ \mathrm{W} \cdot \Omega \cdot \mathrm{K}^{-2} \tag{16}$$

The Wiedemann-Franz law ($\kappa_e = L \sigma T$) states that electrical conductivity and electronic thermal conductivity increase together. This holds well for metals, where both are high. However, in semiconductors, lattice vibrations (phonons) are the primary contributors to thermal conductivity, not electrons [2]. This means the total thermal conductivity κ is dominated by κ_{ph}, which is not linked to σ. Therefore, reducing the lattice thermal conductivity κ_{ph} without affecting σ is the key strategy for improving thermoelectric efficiency.

3.3 Seebeck Coefficient

The relation between the three most important properties of a thermoelectric material is given by the entropy flow equation [5]:

$$J_s = \alpha e J_N + T\kappa\nabla\frac{1}{T} \tag{17}$$

where J_s is the entropy current density, α is the absolute thermoelectric power (Seebeck coefficient), κ is the thermal conductivity, and eJ_N is the electric current density.

The entropy production rate is the sum of the entropy currents contributed by each irreversible process. From this equation, we understand that entropy is produced and flows because charge carriers carry entropy (the first term), and also because heat flows, so entropy is produced along the way (the second term). With these fundamental equations, Lord Kelvin was able to derive the relations between the thermoelectric effects, which can also be derived from Onsager's reciprocity as shown in Callen's book [5].

3.4 Boltzmann Transport Equation and Transport Function

To complete the theoretical framework, we include a brief discussion of the Boltzmann Transport Equation (BTE). This equation accounts for all possible mechanisms that affect electrons in solids: the effect of applied fields, temperature gradients, and collisions (scattering) [3].

The Boltzmann Transport Equation is written as:

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \dot{k}\frac{\partial f}{\partial k} + \dot{r}\frac{\partial f}{\partial r} = \left(\frac{\partial f}{\partial t}\right)_{\text{coll}} \tag{18}$$

where f is the non-equilibrium electron distribution function. The three terms on the left represent the drift due to external fields, the drift due to spatial gradients, and the total time evolution, respectively, while the right-hand side represents the change in f due to scattering [3]. Solving this intractable equation demands simplifying assumptions.

With the introduction of the electron relaxation time τ (the average scattering time of electrons due to phonons, impurities, or defects), the Fermi-Dirac distribution in thermal equilibrium F_0, the Fermi energy E_F, the temperature gradient, and the electron group velocity v, we can obtain a simplified solution [3]:

$$f = \tau v\frac{\partial F_0}{\partial E}\left(\frac{\partial E_F}{\partial x} + \frac{E - E_F}{T}\frac{\partial T}{\partial x}\right) \tag{19}$$

From the above equation, the transport properties (σ, α, κ_e) can be derived by integrating over all energies.

These equations reveal how transport properties are connected to the electronic band

structure. The electrical conductivity depends on the density of states at the Fermi level $g(E_F)$ and the electron velocity $\langle v_x^2 \rangle$, which are determined by the band dispersion $E(\mathbf{k})$. The Seebeck coefficient, through the Mott formula

$$\alpha = \frac{\pi^2 k_B^2 T}{3e} \frac{d \ln \sigma(E)}{dE}\bigg|_{E=E_F},$$

depends on the energy derivative of the transport function, which is sensitive to changes in band structure near E_F. Thus, features such as band gap, effective mass, and band degeneracy directly influence σ and α [3].

In practice, these equations are solved numerically using DFT-calculated band structures. BoltzTraP, a widely used code, integrates the transport distribution function over the Brillouin zone to compute σ, α, and κ_e as functions of temperature and carrier concentration [9]. This approach enables high-throughput screening of thousands of candidate materials before experimental synthesis, as will be discussed in Section 7.

4 Figure of Merit zT

As Goldsmid discusses [2], the thermoelectric effects are reversible in origin and no energy losses occur during such phenomena. However, in real materials, irreversible effects like thermal conduction and electrical resistance exist, so the performance of a thermocouple—which was the original model of a thermoelectric material—depends on these properties as well. Goldsmid describes how the performance of a thermocouple was first evaluated by calculating the coefficient of performance for a refrigerator and cooler. From the cooling power equation and the electrical power input [2], Goldsmid obtained the quantity ZT, defined as:

$$Z = \frac{(\alpha_p - \alpha_n)^2}{(K_p + K_n)(R_p + R_n)} \tag{20}$$

where $(\alpha_p - \alpha_n)^2$ is the differential Seebeck coefficient, K_p and K_n are thermal conductances of the p-type and n-type branches respectively, and R_p and R_n are electrical resistances of the p-type and n-type branches respectively.

The quantity ZT is the figure of merit for a thermocouple and has dimensions of inverse temperature. Since ZT depends on temperature, experiments typically report the dimensionless quantity ZT, obtained by multiplying ZT by absolute temperature. This is done because it allows one to compare the performance of materials across various temperature ranges.

The figure of merit of a thermoelectric material describes its efficiency and is defined by:

$$zT = \frac{\alpha^2 \sigma}{\kappa} T \tag{21}$$

where the Seebeck coefficient, the electrical conductivity, and thermal conductivity have units of μV/K, Ω^{-1}cm^{-1}, and W m^{-1}K^{-1}, respectively. The product $\alpha^2\sigma$ is defined as the power factor of a thermoelectric material.

To be more specific, ZT is the figure of merit for a pair of materials used to calculate performance, and for a single material one uses zT, the figure of merit for a single material:

$$z = \frac{\alpha^2\sigma}{\kappa} \tag{22}$$

where α is the Seebeck coefficient, σ is the electrical conductivity, and κ is thermal conductivity. The quantity z cannot be used to calculate the performance of a thermocouple; for this purpose the figure of merit Z must be used, and since Z is close to the average of z_p and z_n, this is reasonable.

Therefore, an efficient thermoelectric material has a high zT, which means the material has high electrical conductivity, a high Seebeck coefficient, and low thermal conductivity. However, achieving this aim is challenging, since these parameters are related, and altering one changes the others, which limits the maximum zT we can achieve. The most efficient thermoelectric materials have zT on the order of unity at room temperature. Advanced materials such as SnSe have achieved zT values up to 2.6 at high temperatures [4], representing a significant milestone in the field.

Although we consider zT as the property that measures the efficiency of a thermoelectric material, the actual efficiency η is a function of zT as follows:

$$\eta = \frac{\Delta T}{T_h} \cdot \frac{\sqrt{1+zT}-1}{\sqrt{1+zT}+\frac{T_c}{T_h}} \tag{23}$$

where T_h and T_c are the hot and cold reservoir temperatures, respectively, and $\Delta T = T_h - T_c$.

From Equation (23), we understand that temperature directly affects the efficiency of a given material. Like all heat engines, the maximum power-generation efficiency of a thermoelectric generator is thermodynamically limited by the Carnot efficiency ($\Delta T/T_h$). If temperature is assumed to be independent and n-type and p-type thermoelectric properties are matched (α, σ, and κ), the maximum device efficiency is given by Equation (23) with $Z = z$ [4].

The materials and strategies that have achieved the highest zT values across different temperature ranges are reviewed in subsequent sections.

5 Strategies for High zT

In the previous sections, we demonstrated that the parameters governing the zT formula are correlated. This correlation limits the maximum zT we can achieve to values on the order of

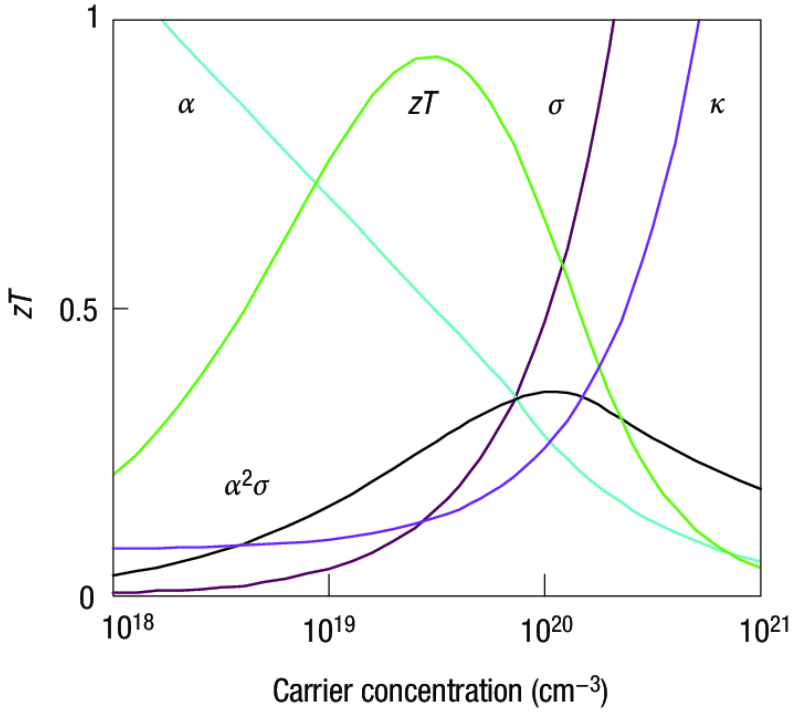

Figure 3: Optimizing zT through carrier concentration tuning. Maximizing the efficiency (zT) of a thermoelectric involves a compromise between thermal conductivity (κ), Seebeck coefficient (α), and electrical conductivity (σ). Good thermoelectric materials are typically heavily doped semiconductors with a carrier concentration between 10^{19} and 10^{21} carriers per cm^3. The thermoelectric power factor $\alpha^2\sigma$ maximizes at higher carrier concentration than zT. Trends shown were modelled from Bi_2Te_3. Reprinted by permission from Springer Nature: *Nature Materials* [4], copyright (2008).

unity.

We have mentioned throughout this paper that suitable thermoelectric devices are made from semiconductors, but have not yet discussed why. Metals have high electrical conductivity but also high thermal conductivity because of the Wiedemann-Franz law [2]. Insulators have low thermal conductivity but very low electrical conductivity due to their large band gap. Semiconductors lie in the middle: their thermal and electrical conductivity are not too high or too low, and both can be altered by strategies such as doping and adding defects. Therefore, we can design a semiconductor to optimize zT.

To understand how to improve thermoelectric efficiency, we return to the definition of the figure of merit:

$$zT = \frac{\alpha^2 T}{\rho\kappa} \tag{24}$$

where ρ is the electric resistivity ($\rho = 1/\sigma$) [4]. From this equation, zT can be increased by increasing the Seebeck coefficient, decreasing the electrical resistivity, and decreasing thermal

conductivity.

We have seen that reducing lattice thermal conductivity is essential for improving thermoelectric materials. This can be achieved through various engineering and materials design strategies. The most important approaches include nanostructuring, the phonon-glass-electron-crystal (PGEC) concept, and complex band structure materials.

We will first discuss mechanisms to reduce lattice thermal conductivity, followed by strategies to enhance the power factor and optimize the Seebeck coefficient and electrical conductivity.

5.1 Reducing Lattice Thermal Conductivity

Before we explain the strategies to improve the efficiency of a given thermoelectric material, familiarity with some solid-state physics concepts is helpful.

In a thermoelectric material, both charge carriers (κ_e) and lattice vibrations known as phonons (κ_{ph}) transport heat. Since the electronic part is related to electrical conductivity through the Wiedemann-Franz law, we cannot change it independently without affecting σ. Hence, we search for strategies to reduce heat transport by phonons in a semiconductor.

In a perfect crystal, lattice vibrations can be approximated using the simple harmonic oscillator model [6]. In reality, anharmonicity is responsible for finite thermal conductivity. Within this model, higher phonon frequency and lower atomic mass result in higher phonon transport. Additionally, various scattering processes such as Umklapp scattering and dipolar scattering lower the thermal conductivity. Umklapp scattering is responsible for reducing heat transport compared to the ideal (harmonic) case [6].

The lattice thermal conductivity is expressed by:

$$\kappa_{ph} = \frac{c_v v l_t}{3} \tag{25}$$

where l_t is the phonon mean free path, c_v is the specific heat, and v is the speed of sound, since only acoustic phonon modes contribute to thermal conductivity [2]. Optical phonons have higher energy but due to their very low group velocity, they carry little heat compared to acoustic phonons.

As Goldsmid mentions, it was first observed by Ioffe and Ioffe that lattice conductivity decreases when the atomic weight becomes larger in a group of materials with similar structure and bonding [2].

The following equation shows how anharmonicity of lattice waves affects the lattice thermal conductivity:

$$\kappa_{ph} = 3.5 \left(\frac{k_B}{h}\right)^3 \frac{M V^{1/3} \Theta_D^3}{\gamma^2 T} \tag{26}$$

where M is the mean atomic mass, V is the mean atomic volume, γ is the Grüneisen parameter

(a measure of anharmonicity), and Θ_D is the Debye temperature [2].

Equation (26) shows that at high temperatures, lattice thermal conductivity is inversely proportional to temperature ($\kappa_{ph} \propto 1/T$), decreasing as temperature rises. At very low temperatures, however, $\kappa_{ph} \propto T^3$ due to the temperature dependence of phonon specific heat [6]. Electronic thermal conductivity also depends on temperature through the Lorenz number, but its contribution is small in semiconductors because of the reasons we discussed.

At low temperatures, electron scattering by phonons becomes significant; this is known as phonon drag [2]. In this regime, electrons are scattered by low-energy phonons.

Lattice thermal conductivity can also be reduced by using materials with large unit cells or fine-grained structures [2].

Now that we are familiar with the heat transport mechanisms, properties, and structures, we can discuss the successful strategies for reducing lattice thermal conductivity.

5.1.1 PGEC (Phonon-Glass Electron-Crystal)

The PGEC approach [4] states that in suitable semiconductors, phonons should behave as they do in a glass (high scattering, low κ_{ph}), while electrons behave as they do in a crystal (high mobility, high σ). Reducing κ_{ph} is achieved through scattering processes such as point defects, grain boundaries, and rattling atoms [2].

Glasses alone are not suited for thermoelectrics because they have high electron-phonon scattering in addition to the desired phonon-phonon scattering. Crystals, on the other hand, have low electron-phonon scattering, allowing electrons to move freely, which results in high electrical conductivity and high Seebeck coefficient. The challenge is to reduce the phonon mean free path while preserving electron transport [4].

In the PGEC approach, the goal is to increase phonon scattering within the unit cell. Adding disorder to the structure helps achieve this. This is done by creating rattling structures or adding vacancies, point defects, interstitial defects, or alloying [4].

By rattling structure we mean containing loose atoms that do not have unique positions in the lattice. This leads to intense phonon scattering, and these materials exhibit large open cages [2].

As examples, rare-earth chalcogenides with the Th_3P_4 structure have low κ_{ph} because of the large number of vacancies present. Clathrates also contain rattling atoms in cages. Likewise, skutterudites such as $CoSb_3$ contain void spaces that may be filled with rattling atoms. These skutterudites have low electronegativity difference, resulting in a high degree of covalent bonding and therefore good electron-crystal properties. However, this strong covalent bonding also leads to high lattice thermal conductivity. The maximum zT achieved in these materials is as high as 1 [4].

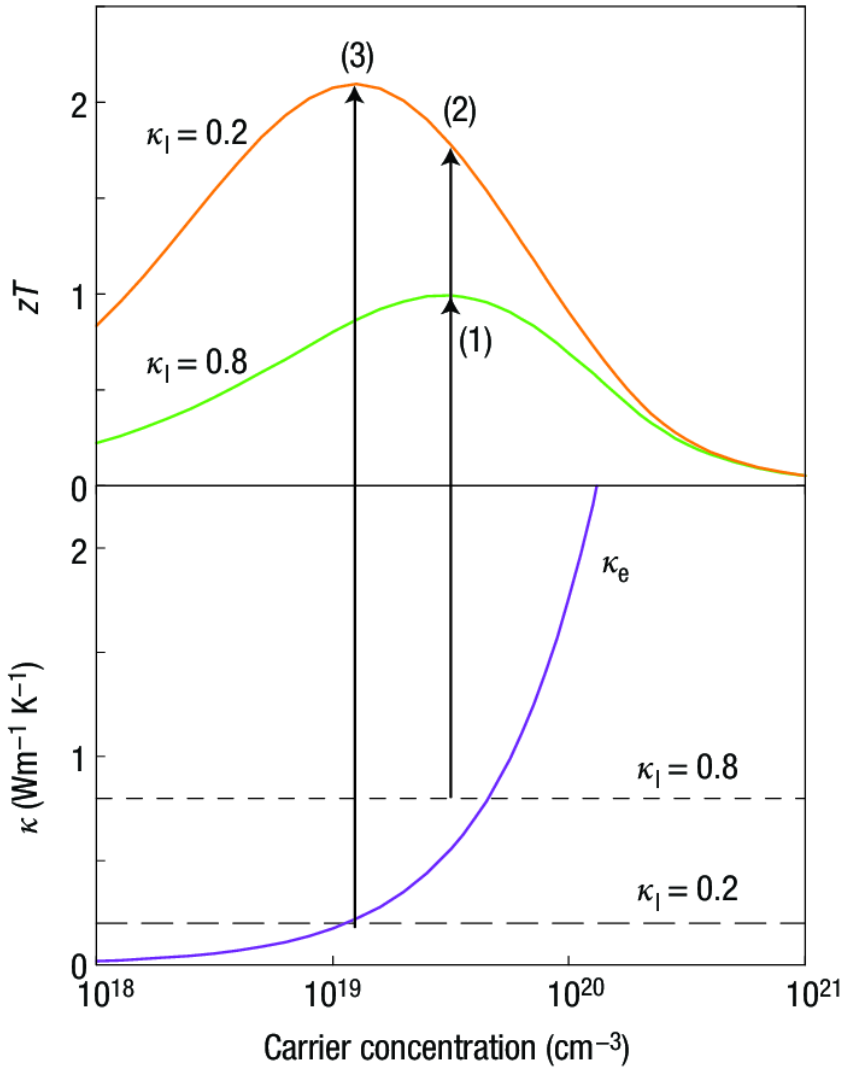

Figure 4: Reducing the lattice thermal conductivity leads to a twofold benefit for the thermoelectric figure of merit. First, reducing κ_{ph} to $0.2\,\mathrm{W\,m^{-1}\,K^{-1}}$ directly increases zT (from point 1 to point 2). Second, the lower κ_{ph} allows the carrier concentration to be reoptimized (reduced). This increases the Seebeck coefficient and decreases κ_e, further enhancing zT (point 3). Reprinted by permission from Springer Nature: *Nature Materials* [4], copyright (2008).

5.1.2 Nanostructuring

The concept of low-dimensional thermoelectric materials began with the theoretical work of Hicks and Dresselhaus in 1993 [7]. As Hosung Lee explains [3], nanostructuring creates quantum confinement in one or more dimensions (quantum wells, wires, or dots). This confinement leads to a higher density of states (DOS) and narrower energy bands. This means we have higher charge carrier concentration and mobility, which results in high σ, while the increased effective mass enhances the Seebeck coefficient.

However, what makes nanostructuring particularly effective for thermoelectrics is its effect on thermal conductivity. When the size of a material is reduced, phonons collide with boundaries and scatter more frequently, reducing κ_{ph}. This happens because the thin film thickness becomes comparable to the mean free paths of phonons or electrons. As Hosung Lee continues, in this case thermal conductivity cannot be defined in the usual way, and heat transports as radiative heat transfer (the Casimir limit) [3].

In nanostructured thermoelectric materials, electrons scatter along with phonons, which reduces electrical conductivity—an undesirable effect that leads to a limitation on the size of the thin film. Examples of reported materials such as Bi_2Te_3-Sb_2Te_3 and PbTe-PbSe films and Si nanowires have shown low κ_{ph} (0.2–0.5 $\mathrm{W\,m^{-1}\,K^{-1}}$), while having high zT values (> 2), but these results cannot be easily reproduced [4]. To prevent electron scattering, the material should be thermodynamically stable, coherent, and epitaxy-like [4].

5.1.3 Complex Crystal Structure

Another strategy to reduce lattice thermal conductivity is to use complex crystal structures to separate the electron-crystal from the phonon-glass. In this case, electrons are transported via the crystal region, and the structure exhibits phonon-glass behavior [4].

Large and complex unit cells also reduce lattice thermal conductivity. As an example, in Zn_4Sb_3, disordered Zn interstitials create a phonon glass, while the more ordered Sb framework is the electron transfer region [4].

Complex Zintl compounds are another type of complex thermoelectric material that will be discussed in detail later. These compounds are combinations of both ionically and covalently bonded atoms, such as $Yb_{14}MnSb_{11}$. This structure has very low κ_{ph} (0.4 $\mathrm{W\,m^{-1}\,K^{-1}}$) and zT on the order of unity at 900 °C [4].

5.2 Increasing the Seebeck Coefficient and Electrical Conductivity

The effect of these two properties is captured in the power factor, $\alpha^2\sigma$. Both the Seebeck coefficient and electrical conductivity depend on charge carrier concentration and Fermi energy [2]. Therefore, we must note the band structure and the Fermi energy of a given material.

The thermoelectric device should operate with only a single type of carrier. Mixed n-type and p-type conduction will result in both charge carriers moving to the cold end and canceling out the induced Seebeck voltages [4].

High mobility and low effective mass are found when the device consists of materials with small electronegativity differences. There is an optimum value for mobility and effective mass since they are related by the bandgap equations and Fermi level [4].

The electrical conductivity affects the Seebeck coefficient through the charge carrier concentration. For metals or degenerate semiconductors (high carrier concentration) with parabolic bands, the Seebeck coefficient is given by:

$$\alpha = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3} \tag{27}$$

where n is the carrier concentration and m^* is the effective mass of the carrier [4]. Charge carrier concentration is related to electrical conductivity by Equation (10) [4].

As shown in Equation (27), large effective mass and low carrier concentration lead to a high Seebeck coefficient. However, large effective mass reduces mobility, which decreases electrical conductivity. Semiconductors have rather small band gaps, which suggests a low Seebeck coefficient. Non-parabolic bands occur when the wave vector and energy of charge carriers have a linear relation, which increases the effective mass of the carriers and decreases mobility. The parabolic approximation, which suggests a quadratic relation between these two terms, is unfortunately not satisfied anywhere except close to the band edge [2].

5.3 Limitations: The Bipolar Effect

When a junction of p-type and n-type semiconductors exists in a thermoelectric material, there is a possibility that both carriers move in one direction. This leads to an additional term in electronic thermal conductivity known as the bipolar effect [2].

The bipolar effect occurs at high temperatures when both charge carriers (electrons and holes) transport heat. This increases the total thermal conductivity, which lowers zT.

When there is no bipolar effect, the electronic thermal conductivity is simply the sum of the conductivities of each carrier type [2].

After explaining how a thermoelectric device works and how to improve its efficiency, we now turn to the various materials and families that exhibit good thermoelectric properties.

6 Thermoelectric Materials

Thermoelectric materials are classified by their operating temperature range, as no single semiconductor works well at all temperatures. Table (1) summarizes the key families, including their general formulas, representative examples, zT values, and unique features [2].

Table 1: Important families of thermoelectric materials. Data from Goldsmid [2].

Family	General Formula	Example	zT	Temp. (K)	Unique Feature
Chalcogenides	A_2B_3 (A=Bi,Sb; B=Te,Se)	Bi_2Te_3	∼1	300	Layered structure, high band degeneracy
Chalcogenides	AB (A=Pb,Sn; B=Te,Se)	PbTe	0.8–1.0	500–800	Multiple valence bands, high thermal stability
Group IV Alloy	$Si_{1-x}Ge_x$ $(0 < x < 1)$	SiGe	0.6–0.7	900–1300	Extremely stable, high melting point
Skutterudites	MX_3 (M=Co,Rh,Ir; X=P,As,Sb)	$CoSb_3$	∼1.0	500–900	Empty cages with rattling atoms
Clathrates	X_8Y_{46} (X=guest; Y=Si,Ge,Sn)	$Ba_8Ga_{16}Ge_{30}$	0.7–1.35	600–1000	Cage-like structure, rattling atoms
Oxides	ABO_3 (A=Sr,Ca; B=Ti,Co)	$SrTiO_3$	0.37	800–1200	Chemically stable and inert
Half-Heuslers	MNiSn (M=Hf,Zr,Ti)	ZrNiSn	∼0.3–0.45	700–1000	High power factor, high effective mass

These materials fall into two classes: classical materials (Bi_2Te_3, PbTe, and SiGe) and advanced materials (skutterudites, clathrates, oxides, and half-Heuslers).

Another notable example, not listed in the table, is GeTe-based compounds. Their figure of merit has reached a high value of 2.7. Due to their high performance and efficient power generation, such materials have been of great interest for predicting suitable thermoelectric candidates. Synergistic optimization of electrons and phonons via high-entropy stabilization is the unique advantage of these materials [10].

Figure (5) illustrates some advanced compounds that exemplify the lattice thermal conductivity reduction strategies discussed earlier.

7 Computational Design of Thermoelectric Materials

Discovering new materials with higher zT remains a challenge because experimental methods are time-consuming and expensive. To suggest novel thermoelectric compounds, a reliable, well-defined method is required. Therefore, scientists use first-principles density functional theory (DFT) and machine learning (ML) methods as complementary approaches to accelerate the discovery process and identify potentially stable compounds.

Machine learning has proven capable of accurately predicting electrical and thermal transport properties, making it a powerful tool for identifying high-performance thermoelectric candidates, provided that large, high-quality datasets are available [10, 11]. Interpretable ML frameworks such as SHAP (SHapley Additive exPlanations) are particularly valuable, as they not only predict thermoelectric performance but also identify which physical descriptors—such as band gap or atomic mass—most strongly govern material behavior, thereby revealing structure-property correlations across large material databases [10, 11]. These descriptors are not arbitrary; meaningful input features such as band gap and Fermi energy are obtained from

DFT calculations, establishing a natural link between first-principles theory and data-driven prediction [10, 11].

While ML offers fast predictions, DFT provides the fundamental electronic structure calculations needed to understand why a material performs well. He et al. performed high-throughput DFT screening using the Vienna Ab initio Simulation Package (VASP) with the Perdew-Burke-Ernzerhof (PBE) functional [12]. They calculated electron transport properties (Seebeck coefficient and electrical conductivity) using the BoltzTraP code within the relaxation time approximation. Lattice thermal conductivities were calculated using the third-order phonon approach, solving the linearized Boltzmann equation with the ShengBTE package [12].

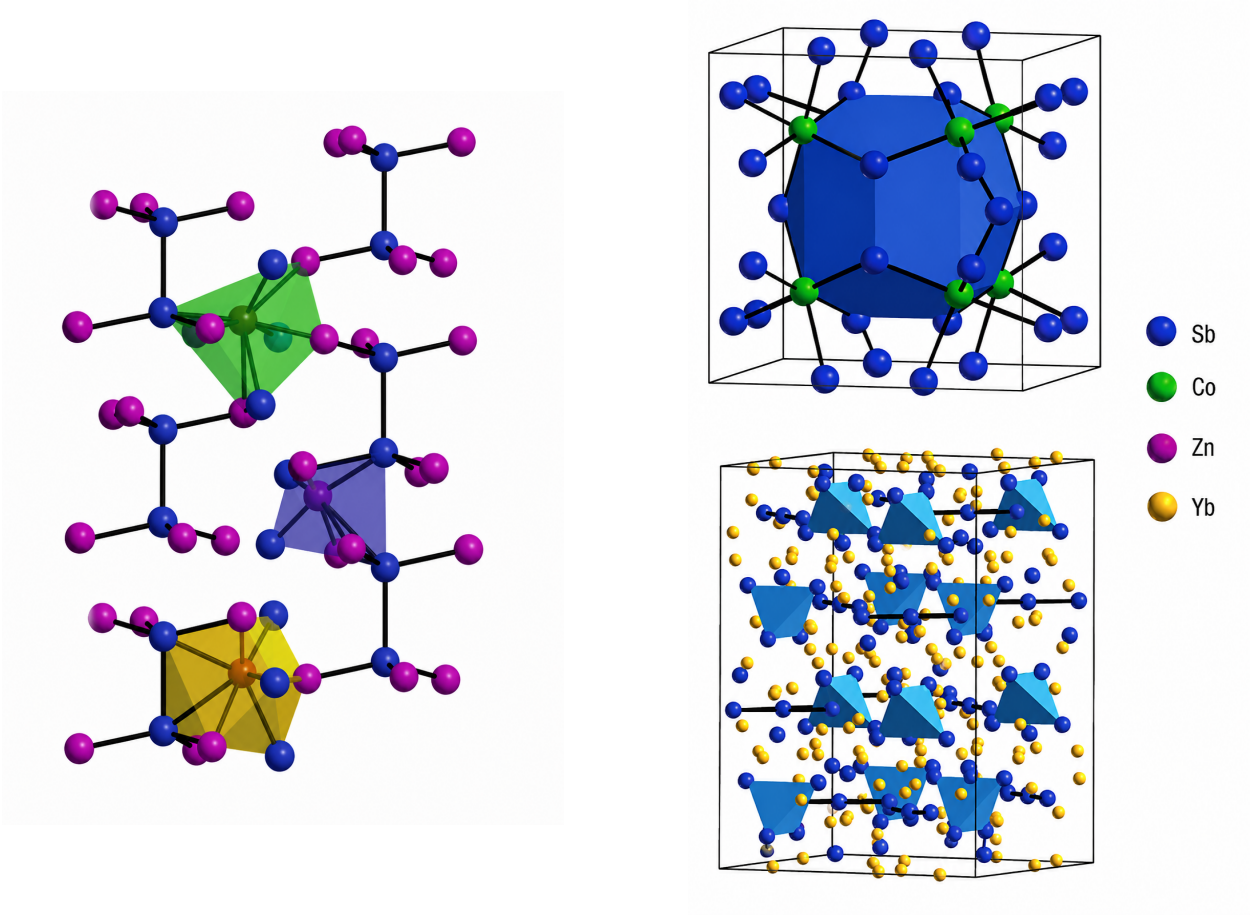

Figure 5: Three strategies to achieve low lattice thermal conductivity: disordered Zn sublattice with ordered Sb crystal in Zn_4Sb_3 (left), rattling atoms in skutterudite voids (top right), and complex covalent-ionic bonding in Zintl phase $Yb_{14}MnSb_{11}$ (bottom right). After Snyder and Toberer. Reprinted by permission from Springer Nature: *Nature Materials* [4], copyright (2008).

As another example of computationally driven discovery, Gholami et al. demonstrated that Ag_2PbGeS_4 achieves an exceptionally low lattice thermal conductivity of $0.15\,\mathrm{W\,m^{-1}\,K^{-1}}$, attributed to strong anharmonic phonon scattering within the crystal structure [13]. Fur-

thermore, its electronic structure features multiple degenerate valence bands that collectively enhance the power factor, resulting in a zT exceeding two [13].

Together, DFT and machine learning are transforming thermoelectric research by enabling the rapid screening of vast compositional spaces that would be prohibitive to explore experimentally.

8 Applications

Thermoelectric devices have applications in power generation, cooling, sensors, and temperature controllers in microelectronic devices and electronic manufacturing services [10].

Thermoelectric coolers (TECs) are used for temperature control, operate silently, and require little space. One way to save electrical energy is to combine air conditioning systems with thermoelectric effects. Thermoelectric coolers are used in electronic equipment and large instrument cooling.

Due to the thermoelectric effects, TECs generate Joule heat in addition to Peltier cooling; by reversing the current direction, they can function as heating devices as well. Their applications include thermoelectric heat pumps, which are a green, pollution-free method of heating with higher efficiency [14].

Thermoelectric devices can also be used as power generators. They are used in wearable electronics, photovoltaic power generation, and batteries. They operate with no moving parts [14].

In the automotive and aerospace sectors, thermoelectric generators recover waste heat from exhaust systems and convert it into usable electricity [15]. Thermoelectric devices are also used in self-powered, energy-autonomous wearable devices [15].

They are candidates for renewable energy applications and contribute to the sustainability of energy systems. When integrated with solar panels, thermoelectric generators can recover heat that photovoltaic cells cannot convert, improving the overall efficiency of hybrid energy systems [15].

As another example, thermoelectric materials function as heat flux sensors. These sensors provide active temperature control and accurate heat flow measurements. In this configuration, the Seebeck voltage generated across the thermoelectric element is directly proportional to the local heat flux, enabling precise and continuous measurement. In this application, thermoelectric materials are usually combined with existing heat flux sensors [14].

In summary, the unique advantages of thermoelectric materials, namely their pollution-free operation, localized temperature control, and quiet operation, make them highly valuable for a wide range of practical applications. As research into higher zT materials continues, even modest improvements in efficiency could broaden their impact across these sectors significantly.

9 Conclusion

This overview has traced the development of thermoelectric materials from their fundamental thermodynamic origins to their practical applications. We discussed the thermodynamics of thermoelectricity, including local entropy density and entropy production, following Callen's explanation of irreversible processes. The Seebeck, Peltier, and Thomson effects were presented and the Kelvin relations were derived.

The figure of merit zT was then introduced. Achieving high zT remains fundamentally challenging due to the interdependence of α, σ, and κ, further complicated by the Wiedemann-Franz law and the bipolar effect at high temperatures. To improve zT, we reviewed strategies for reducing lattice thermal conductivity, including the PGEC approach (using rattling atoms in skutterudites and clathrates), nanostructuring (quantum confinement), and complex crystal structures such as Zn_4Sb_3 and $Yb_{14}MnSb_{11}$. Increasing the power factor through band engineering and optimal doping was also discussed.

Classical materials including Bi_2Te_3, PbTe, and SiGe were surveyed, each suited for a specific temperature range. Advanced families such as skutterudites, clathrates, oxides, half-Heuslers, Zintl phases, and GeTe-based compounds were also reviewed, each offering distinct structural advantages.

DFT calculations were explained as a method for computing transport properties from first principles, while machine learning was presented as a tool for accelerating the search for high-performance thermoelectric materials.

Finally, we highlighted the applications of these materials in power generation and cooling. The ability of thermoelectric modules to provide precise, localized, and silent temperature control positions them as promising devices for next-generation medical and electronic applications [15].

In summary, thermoelectric materials offer a promising solid-state solution for waste heat recovery and cooling. The combination of DFT and machine learning is accelerating the discovery of high-performance candidates, while continued advances in nanostructuring and band engineering are pushing zT values beyond the long-standing barrier of unity. Future work on nanostructured, organic, and hybrid materials will continue to broaden the scope of thermoelectric research, bringing next-generation devices closer to widespread practical deployment [15].

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The author declares no competing financial or personal interests that could have appeared to influence the work reported in this paper.

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Data Availability

No new data were generated or analysed in support of this review. All data and results discussed are available in the cited literature.

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