

THE THERMOELECTRIC LIMIT $ZT \sim 1$: FACT OR ARTIFACT

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ABSTRACT

The dimensionless thermoelectric figure of merit, ZT , represents the relative magnitude of cross-effect transport. ZT has been recognized as an important material property for more than 100 years and has been extensively studied both theoretically and experimentally. Experimental results to date yield at best $ZT \sim 1$, which has been found for a number of different materials. Neither thermodynamics nor irreversible thermodynamics, however, place any upper limit on ZT and transport theory reveals nothing special about the region $ZT \sim 1$. Certain transport property models do place upper bounds on ZT for specific classes of materials, but even these bounds are typically much higher than has been observed. The discrepancy between the theoretical expectations and the experimental observations poses several basic questions: Why do many different materials have $ZT \sim 1$? Is $ZT \sim 1$ a fundamental limit or merely characteristic of the materials examined to date? If $ZT \gg 1$ is possible, how can it be achieved? These issues, which remain unresolved, are discussed in a context of their implications for both the basic understanding of transport phenomena in solids as well as for thermoelectric technology.

INTRODUCTION

Rumford supervised the machining of brass cannon at the Munich Arsenal in 1798 [1]. Watt built steam engines to remove water seeping into coal mines [2]. While primarily intended to fulfill specific and immediate needs, these efforts to improve the performance of engines played a crucial role in developing an understanding of heat, work and particularly entropy. Those engines have long since been replaced, but the resulting principles embodied in equilibrium thermodynamics are among the most powerful and enduring known.

Not all processes of interest, however, are equilibrium in nature and often a flux of some quantity (matter, charge, heat, etc.) is generated by a gradient of a corresponding thermodynamic quantity (such as chemical concentration, electric potential, temperature, etc.). Effects of this type are outside the realm of thermodynamics since they inherently involve non-equilibrium processes. Classic examples of 'non-equilibrium thermodynamics' (also called 'irreversible thermodynamics') [3] include Fick's Law for chemical diffusion in a concentration gradient, Fourier's (or Newton's) law of thermal conduction in a temperature gradient and Ohm's Law of electric conduction in a voltage gradient. Also to be considered are the so-called cross effects such as Soret's effect of chemical diffusion in a temperature gradient, the Seebeck effect [4] of an electric potential resulting from a temperature gradient, the Peltier effect [5] of heat

flow resulting from an electrical current, and the Thomson effect which modifies the Joule heating observed in an isothermal electrical conductor depending on the temperature gradient.

Thermoelectric effects play a special role in the development of irreversible thermodynamics because the physical quantities involved are relatively accessible experimentally. As early as 1855, for example, Thomson applied thermodynamic arguments to deduce relationships between the Seebeck, Peltier and Thomson effects [6]. While these 'Kelvin' relations are correct, Thomson's derivation was not and only much latter was irreversible thermodynamics placed on more firm grounds by, for example, Onsager [7] and Casimir [8].

Thermoelectric effects are distinguished by a coupling between the electrical (i) and thermal currents (Q) induced by an electric field (E) and temperature gradient ∇T :

$$\vec{i} = \sigma(\vec{E} - S\nabla T) \quad (1)$$

$$\vec{Q} = ST\vec{i} - \lambda\nabla T \quad (2)$$

where the electrical conductivity, σ , Seebeck coefficient, S , and thermal conductivity, λ have their usual meanings. The relative strength of the cross-coupling between electrical and thermal effects may be characterized by the dimensionless thermoelectric figure of merit:

$$ZT = \frac{\sigma S^2 T}{\lambda} \quad (3)$$

ZT occurs in any expression governing the optimum efficiency of a thermoelectric device, such as

$$\eta = \frac{T_h - T_c}{T_h} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_c / T_h} \quad (4)$$

for the efficiency of a thermoelectric generator and

$$COP = \frac{T_c}{T_h - T_c} \frac{\sqrt{1 + ZT} - T_h / T_c}{\sqrt{1 + ZT} + 1} \quad (5)$$

for the coefficient of performance of a single-stage thermoelectric cooler. Typically ZT varies relatively slowly with temperature and the appropriate value to use in the expressions above is some average ZT .

In all cases, as ZT becomes very large the conversion device

approaches the Carnot limits. Today, the performance of thermoelectric devices is limited to a small fraction ($\sim 10\%$) of the Carnot limits because for available thermoelectric materials $ZT \leq 1$. Therefore, doubling or tripling the performance of thermoelectric materials would qualitatively alter the economics of thermoelectric energy conversion technology.

ZT is not merely an engineering quantity, however, but is itself a true transport property representing the relative magnitude of cross-effect transport in materials. This may be illustrated by the following two examples. Consider that the electrical resistivity is defined as the ratio of the electric field to the current under isothermal conditions. An equally fundamental property is the ratio of the electric field to the current under conditions of zero heat flux, which may be called the adiabatic electrical resistivity.

The adiabatic resistivity must be greater than the isothermal resistivity and the ratio of the two resistivities is entirely governed by ZT :

$$\rho_{Q=0}/\rho_{VT=0} = 1 + ZT \quad (6)$$

Similarly, the thermal conductivities may be defined under conditions of zero current (the usual definition) or under conditions of zero electric field. In this case, the zero field thermal conductivity must be larger, and is given by

$$\lambda_{E=0}/\lambda_{i=0} = 1 + ZT \quad (7)$$

These two examples serve to highlight that ZT reflects in a rather fundamental way the difference between purely electrical and purely thermal transport.

Although the individual transport properties contributing to ZT (i.e. σ , S and λ) can each vary by many orders of magnitude, no material has been found with ZT even as large as 2. Moreover, there is no reason or principle limiting ZT to such small values. The complete absence of materials with large ZT , therefore, presents a challenge not only to the efficiency-conscious technologist but also a challenge to the theory of transport in solids.

Just as attempts to better understand the factors limiting the performance of steam engines had a profound impact on the development of science, attempts to better understand the factors limiting ZT can also be expected to have major benefits for science, technology, or both. If, however unlikely this prospect now seems, some underlying principle limiting ZT were discovered, the implications for irreversible thermodynamics and/or the theory of transport in solids could also be quite profound. If systems with larger ZT values can be found, then at the very least the understanding of transport in solids will be substantially expanded, with the potential for a major impact on energy-related technologies.

In either case, resolution of open questions in thermoelectricity seems certain to have valuable implications. A systematic study of the fundamentals of thermoelectric effects, particularly in novel materials or under novel conditions not previously considered, seems to be well justified. The purpose this paper is to focus attention on certain key aspects of thermoelectric effects in solids and to attempt to motivate renewed efforts in this area after many years of relative neglect.

STATUS OF THERMOELECTRIC TECHNOLOGY

A firm foundation in irreversible thermodynamics, coupled with rapid advances in the theory of solids and materials preparation techniques during the 1940's and 1950's, led to intense study of thermoelectric effects through about the mid-1960's as part of the

general advances being made in semiconductor technology. In 1961 Snyder [9] cited 19 companies, 8 universities, 4 research institutes, and 7 government laboratories with major thermoelectric research activities in the United States alone. At the time it seemed solid-state thermoelectric technology might eventually replace, for example, heat engines and refrigerators in much the same way that transistors and semiconductor diodes were replacing their vacuum tube technology counterparts. Such was the enthusiasm that Zener in 1959 described the Westinghouse program efficiency goal as for a thermoelectric power generator as 'only 35%,' explaining that "Frankly, I wish the goal to be one which we can attain [10]."

Needless to say, the optimism of the 1950's and 1960's has faded, largely because thermoelectric devices, shown schematically in Figure 1, never achieved the desired efficiencies. By the early to mid-1960's an unexpected pattern began to emerge, as illustrated in Figure 2: experimental ZT values never exceeded ~ 1 , even though much larger ZT values are theoretically possible.

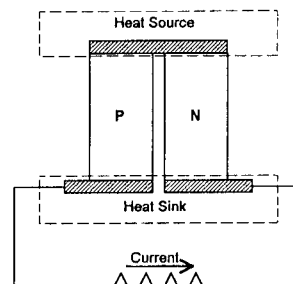


Figure 1. Schematic of typical thermoelectric power generator. Refrigeration is achieved by replacing the resistor with a current source, and reversing the current flow.

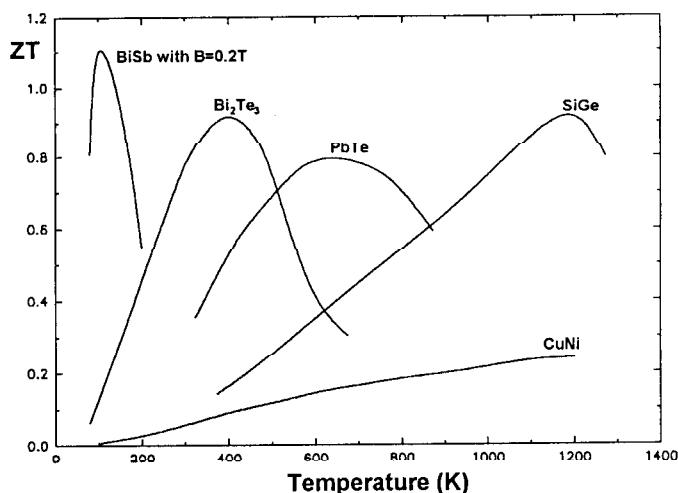


Figure 2. Dimensionless thermoelectric figure of merit as a function of temperature for selected n-type alloys.

The best thermoelectric materials, all of which were identified in this early period, are typically heavily doped semiconductor alloys. Through doping of semiconductors, an optimal trade can be achieved between the large Seebeck/small conductivity typical of low carrier concentration materials and the small Seebeck/large conductivity typical of metals. By alloying two isostructural semiconductors (such as Bi_2Te_3 - Bi_2Se_3 alloys or Si-Ge alloys), strong point defect scattering is introduced which substantially lowers the lattice contribution to the thermal conductivity (λ_p). These principles, first described in detail by Ioffe [11], are common to all of the best thermoelectric materials known today. It is illustrative to note, however, that certain transition-metal alloys, such as $\text{Cu}_{0.5}\text{Ni}_{0.5}$ shown in Figure 2, are within a factor of 4 of the maximum ZT values observed.

With $ZT \sim 1$, thermoelectric devices remain severely limited in performance, as illustrated in Figure 3, and to this day are restricted largely to applications where efficiency is not the primary consideration. The accomplishments of that early period of thermoelectric research were important and substantial, however. A variety of materials and practical devices were developed, for both power generation and refrigeration, which achieve up to about 1/10 of the ideal Carnot efficiency. And, the principles governing thermoelectric performance were sufficiently well understood to allow tailoring materials to meet the special requirement of specific applications.

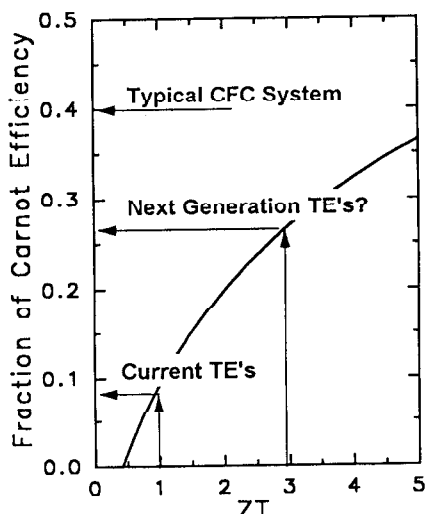


Figure 3. Effect of the Thermoelectric Figure of Merit on the Performance of a Thermoelectric Cooler.

While less efficient than their mechanical analogs, thermoelectric devices have delivered on the promises of simplicity, reliability, small size and long lifetime typical of solid-state devices. Perhaps the earliest example, described by the Soviet pioneer Ioffe, is a kerosene-powered device used in remote areas of the Soviet Union to provide power for a small radio receiver [11].

Rowe and Bhandari [12] describe a variety of applications for thermoelectric power generators from remote oil pipelines, maritime buoys, automatic meteorological stations and even cardiac pacemakers to military situations where silent operation is important. Thermoelectric refrigerators are commercially available from a few small, specialty businesses and, since their coefficient of performance is independent of size, are particularly attractive for miniature applications such as detectors and electronic components. Large scale applications are also possible, of course, and as an example a prototype passenger railway coach with thermoelectric air-conditioning has been operating continuously in France for ten years without a single thermoelectric-related failure [13].

Certainly the most widespread application for thermoelectric devices is as a temperature sensor, the common thermocouple. These are cheap, flexible and (with proper care) accurate devices. With the advent of thin-film technologies, which allows forming up to hundreds of thermocouples in a very small area, a number of new applications are beginning to be discussed in the literature. Thin film microcalorimeters [14] and radiation detectors [15,16,17,18] as well as miniature, thin film thermoelectric generators [19] have been described recently.

Thermoelectric technology really comes into its own, however, in space power applications where radioisotope-powered thermoelectric generators (RTG's) continue to provide the only viable source of electrical power for deep space missions [20]. Now 15 years since their launch, the spectacularly successful Voyager I and II

spacecraft have left the solar system and accumulated over 2.5×10^8 device-hours on the thermoelectric power supplies without a single failure [21]. This is all the more impressive when considering that these thermoelectric devices operate between about 1275 K and 575 K and have therefore been literally 'red-hot' the entire time.

These specialized applications will certainly continue, and may expand to some extent. A recent feasibility study in France, for example, on small household refrigerators has concluded [22] that even the current generation of thermoelectric technology is economically competitive (within 20%) with CFC-based technology. A second study, performed under a USDOE-sponsored Energy-Related Inventions Program grant, concluded that current thermoelectric generator technology is economically feasible as the electrical power source for certain diesel truck applications [23].

Given the inherent simplicity and reliability of thermoelectric technology, even modest improvements in the fundamental materials should significantly expand the range of practical thermoelectric applications. The key, as with so many technologies, is to develop new materials. Today, materials science is a rich and a rapidly expanding field. Thousands of electronic materials available today were unknown in the 1960's: superlattices, ceramics, organic and polymer conductors, and of course the copper oxides so important to high temperature superconductivity. Modern preparation techniques allow preparation of materials with modulated compositions and/or doping levels almost at will. But virtually none of these materials have been seriously or systematically examined for thermoelectric applications.

THE ROLE OF ZT

In metals, S is ordinarily so small, due to degeneracy, that $ZT \ll 1$. In electrical insulators, the electrical conductivity is negligible and again $ZT \ll 1$. The smallness of ZT for almost all materials is quite fortuitous for the theory of transport because the difference between adiabatic and isothermal transport becomes rather less important in this limit and may be treated as a small perturbation. If ZT becomes very large, assumptions about local equilibrium between electrons and phonons must be treated with somewhat more care.

The distinction between an adiabatic and isothermal resistivity has long been recognized as a subtle point in the theory of metals. In their seminal paper, for example, Kohn and Luttinger [24] develop a density matrix procedure for calculating the electrical resistivity from first principles, but their treatment assumes the electronic system is thermally isolated and the calculated resistivity is more properly an adiabatic one, not the experimentally determined isothermal one.

Formal inclusion of a heat bath to maintain a true steady state in transport calculations can be accomplished by a number of methods, but even today questions of interpretation continue to arise. Methods based on the Boltzmann equation, for example, yield resistivity expressions for the electrical resistivity like

$$\rho = 1/en\langle\tau\rangle \quad (8)$$

while methods based on the force-balance approach sometimes yield expressions like

$$\rho = \langle 1/\tau \rangle / en \quad (9)$$

The difference between these two approaches has been attributed to the former representing an adiabatic resistivity and the latter representing an isothermal resistivity [25]. The two approaches, however, typically produce similar temperature and doping dependencies and differ only somewhat in magnitude. Comparison

with experimental results will therefore typically be ambiguous since minor differences in magnitude can usually be absorbed in the adjustable constants of the theories.

In spite of any minor ambiguities which may remain regarding this or that formal method for calculating transport properties, there is no intention to suggest here that modern theory is seriously deficient in any fundamental way. Indeed, the quantitative success in describing the transport properties of real thermoelectric materials with $ZT \sim 1$ argues quite the opposite: that transport theory is completely adequate for consistently describing known thermoelectric materials. Instead, the point to be emphasized is that the magnitude of ZT has a direct bearing on even the most fundamental assumptions of transport theory.

The typically small values of ZT in known materials justifies, as a practical matter, neglect of the difference between adiabatic and isothermal transport. But existence of a *rigorous* limit near $ZT \sim 1$ would have significant consequences, possibly including bounding relationships between transport coefficients which today are unknown. Boltzmann [26], perhaps the first to consider relationships between transport coefficients, derived using thermodynamic arguments

$$[\Pi - ST]^2 \leq 4 \frac{\lambda T}{\sigma} \quad (10),$$

where Π , the Peltier coefficient, is the coefficient relating the heat current to the electrical current. Irreversible thermodynamics requires only that $\Pi = ST$, which automatically satisfies Boltzmann's thermodynamic criteria and even a careful treatment of irreversible thermodynamics leaves the rather unrestrictive and unsatisfying condition [27]

$$ZT < \infty \quad (11),$$

in striking contrast with the experimental result $ZT_{\max} \sim 1$.

Transport theory is more illuminating and several authors (see Wood [20] for a recent review) have placed various limits on ZT using specific models more or less appropriate for the type of semiconductor alloys known to have $ZT \sim 1$. The general outline of the problem can be illustrated as follows. The thermal conductivity can be considered to be made up of an electronic and a lattice contribution. The electronic contribution is related to the electrical conductivity via the Weidemann-Franz law,

$$\lambda = \lambda_{el} + \lambda_{ph} = L_o \left(\frac{k_B}{e} \right)^2 \sigma T + \lambda_{ph} \quad (12)$$

where L_o is between 2-4 for the most common scattering mechanisms.

In the limit where the lattice contribution to the thermal conductivity is negligible,

$$ZT = \frac{S^2}{L_o \left(\frac{k_B}{e} \right)^2} \quad (13).$$

Only a large Seebeck is required for a large ZT in this case. For a single band, nondegenerate semiconductor,

$$S = \left(\frac{k_B}{e} \right) \left[2 + r - \ln \left(\frac{n}{n_o} \right) \right] \quad (14)$$

$$n_o = 2 \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2}$$

and a large Seebeck can be achieved merely by decreasing the carrier

concentration. For the most common carrier scattering mechanisms r is between 0 and 2. In this limit, both S and ZT will diverge for small n .

An actual divergence will never be observed of course. Minority carriers will eventually make a significant contribution, reducing the magnitude of S and eventually the lattice thermal conductivity will no longer be negligible, so this model is much too simple.

Taking the opposite limit, where the lattice thermal conductivity dominates, we have

$$ZT = \frac{S^2 \sigma T}{\lambda_p} \quad (15).$$

Again taking the non-degenerate limit, we can optimize with respect to the carrier concentration (ignoring any dependence of the mobility, μ , or λ_p on the carrier concentration) with the well known result

$$ZT = 4\beta e^r, \quad \text{where} \quad \beta = \left(\frac{k_B}{e} \right)^2 \frac{en_o \mu T}{\lambda_p} \quad (16)$$

Any limit on ZT would, in this case, imply a relationship between the lattice thermal conductivity, the mobility and the density of states effective mass. In neither limit is there any compelling upper bound on ZT , nor even any special reason why ZT should be on the order of unity.

The illustrations above are clearly very crude and overly optimistic since contributions which tend to reduce ZT have been neglected. They serve to illustrate, however, that the problem of large ZT values cannot be adequately treated by overly simple models. Therefore, attempts have been made to include more and more details into the models. Mostly, theoretical limits estimated in this manner remain relatively large, say $ZT \sim 10-50$. As the models are more and more tightly constrained to be appropriate for the particular material under consideration, the predicted ZT values naturally converge toward the values actually observed.

Results from this type of highly constrained calculation have lead a few authors to suppose $ZT \sim 1$ is an actual limit. But virtually all such models are at most appropriate to only a very narrow class of materials: usually covalent semiconductors with ellipsoidal Fermi surfaces. Restrictive assumptions about the character of the carrier and phonon dispersion relations and scattering rates have invariably been made. By including more and more details about a particular material system, a model can become more and more accurate for a given material, but at the sacrifice of implying less and less about other classes of materials. The most recent of this type of effort appears to be due to Mahon [28] who concludes "when we choose values for β appropriate for good thermoelectric materials, our theory predicts the maximum value of ZT to be about 1-2."

Transport in real materials is quite complex and additional contributions which might be important are numerous. One contribution to ZT which certainly requires more careful attention arises from consideration of the phonon scattering rate. Slack [36] has suggested that overly large phonon scattering rates are simply unphysical, with the implication that the lattice thermal conductivity has a minimum value, λ_{\min} , which can be reduced no further. Slack's procedure for estimating λ_{\min} involves inserting a cutoff for the phonon mean free path at one phonon wavelength. A slightly more optimistic procedure (with regard to ZT) is to cut off the phonon mean free path at one interatomic spacing.

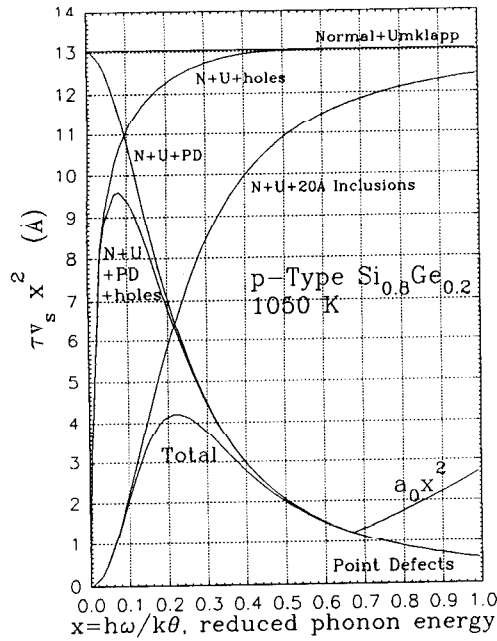


Figure 4. Phonon relaxation time illustrating the effect of normal (N) and umklapp (U) scattering, point defects (PD), holes, inclusions and the minimum mean free path cutoff on λ_p , which is given by the area under the respective curves [33].

Experimental results on highly disordered solids, recently reviewed by Cahill and Pohl [29], essentially confirm this concept of a minimum lattice thermal conductivity and the impact on ZT can be significant. Models have therefore been developed by White and Klemens [30] for n-type SiGe and by Vining [33] for p-type SiGe which incorporate the minimum lattice thermal conductivity concept explicitly. The lattice thermal conductivity has been calculated using the usual Boltzmann's equation method, estimates for the various scattering rates, and taking an appropriate average of the total relaxation time.

The areas under the curves in Figure 4 represent weighted averages of the relaxation time appropriate for calculating the lattice thermal conductivity. The total thermal conductivity due to the distinct phonon scattering mechanisms is determined from the areas under the various curves. The thermal conductivity of ordinary SiGe, for example, is represented by the curve labeled 'N+U+PD+holes' and the effect of adding 2 nm (20 Å) inclusions is indicated by the curve labeled 'total.'

The curve labeled ' $a_0 x^2$ ' represents the lower bound on the mean free path, i.e. the scattering rate required to make the phonon mean free path from exactly one interatomic spacing, a_0 . In fact, the majority of the heat is carried by low frequency, long wavelength phonons and the actual lattice thermal conductivity is 3-4 times greater than this minimum possible value. If some method could be found to prepare materials with the minimum lattice thermal conductivity, but electrical properties similar to existing materials, then higher ZT values would result. Slack and Hussain [31] provide the most thorough discussion of this point and from their results one can conclude that the average ZT for SiGe would improve by a factor of about 2.6 under these conditions, although most of the improvement is expected at temperatures where ZT was well below 1 to start with.

Similar attention to the electrical properties has resulted in detailed material-specific models have recently been developed, for example, by Vining for n-type [32] and p-type [33] SiGe alloys. These calculations, for the first time, established that all of the

observed transport properties were quantitatively consistent with each other and with conventional transport theory. Typical agreement is shown in Figures 5 and 6, which illustrate the good agreement ($\pm 10\%$) between experimental and calculated temperature and doping level dependencies for the properties of p-type SiGe. Previous calculations had generally focused on a single transport coefficient, rather than attempting to calculate all the coefficients self consistently. While the agreement between experiment and conventional transport theory was not unexpected, a quantitative model for the experimental results was not previously available and the results were therefore reassuring.

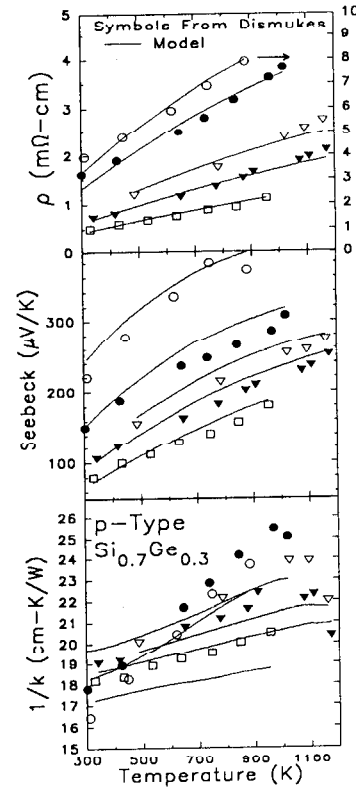


Figure 5. Resistivity, Seebeck and thermal conductivity for p-type $\text{Si}_{0.7}\text{Ge}_{0.3}$. The points are experimental results and the lines are calculated [33].

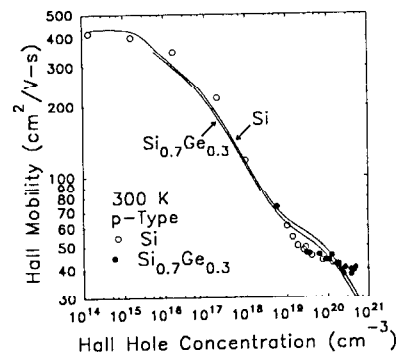


Figure 6. Hall mobility as a function of the Hall hole concentration for p-type Si and $\text{Si}_{0.7}\text{Ge}_{0.3}$. The points are experimental and the lines are calculated [33].

Rather than support the hypothesis that ZT~1 has some fundamental basis, however, even these quantitative and highly specific models indicate quite the opposite, as illustrated by the following two examples. First, suppose that nature had provided an isotope of Ge, called Ge^* , with a very large atomic mass of about 200 grams/mole. Such an isotope would be expected to behave chemically the same as ordinary Ge and we could expect to be able to prepare a Si- Ge^* alloy by methods similar to current methods used for ordinary Si-Ge.

The heavy mass of Ge^* would alter the properties of the alloy considerably, but all of the effects are reasonably well understood. The melting point and speed of sound would be lower, and the various scattering rates would be altered. Effects of this type have been taken into account in models for ordinary SiGe alloys described by Vining [32, 33]. It is therefore a straight-forward task to calculate ZT for this hypothetical Si- Ge^* alloy, the results of which are shown in Figure 7. For high atomic mass, ZT values up to 2 are expected even for a material nearly identical to actual SiGe alloys.

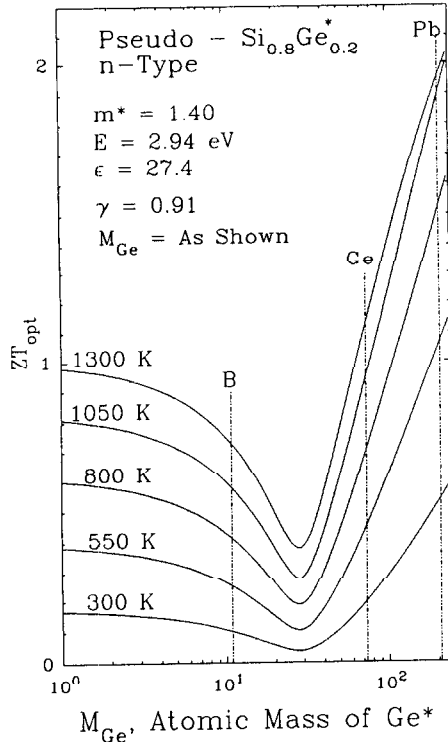


Figure 7. Effect of atomic mass on ZT for n-type SiGe [34]

The effect of physically reasonable variations of other microscopic materials properties have been examined in the same system [34]. Figure 8 shows the thermoelectric figure of merit calculated as a function of the deformation potential, a microscopic parameter characterizing the interaction between electrons and phonons in a solid. The other parameters have been chosen to reflect the actual properties of SiGe and the vertical line labeled 'A' (for 'actual') comes very close to the observed ZT values for SiGe. The vertical line labeled 'L' (for 'low') represents the low end of the range of deformation potential values actually observed in compounds similar to SiGe. The point of Figure 8 is to demonstrate that ZT values of 3 or even higher are well within the range of current theory and that there is no special reason for $\text{ZT} \sim 1$ to occur as a natural limit.

Classical versus Quantum Composites

A tempting approach to increasing ZT is to prepare some type of composite of two or more materials in the hopes of achieving an average, composite ZT which is greater than the ZT for any of the individual components. Like many questions regarding the properties of composites, this apparently simple problem is quite stubborn and only recently has a rigorous analysis been performed, by Bergman and Levy [35], and then the analysis is rigorous only for a two component composite. The disappointing, but not unexpected, result is that the composite can never have ZT greater than the largest ZT of the components. A remarkable point about Bergman and Levy's method is that the results are exact and quite general, independent of the geometry or length scale of the composite. The general case of a composite composed of three or more materials remains, formally,

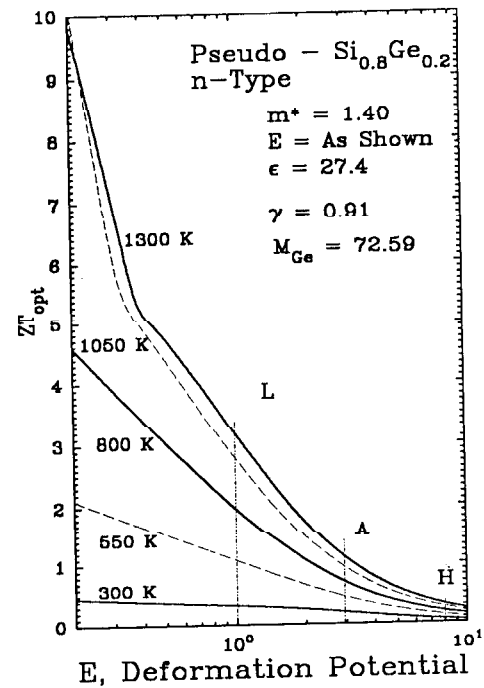


Figure 8. Prediction of high ZT values [34].

an open question, although approximate solutions suggest the limit on ZT may be true for any number of components.

Upon reflection, Bergman and Levy's result for composites presents a conceptual difficulty: alloys, which may be thought of as 'quantum composites' where the mixing is on an atomic length scale, typically have ZT much greater than either of the components. All of the alloys in common use today as thermoelectric materials (SiGe, Pb(Te,Se), $\text{Bi}_2(\text{Te,Se})_3$) have much higher ZT than either of their respective components. Clearly quantum effects are important in these alloys, since no 'effective medium' model can account for the enhanced ZT values, and a kind of quantum mechanical generalization of Bergman and Levy's result is needed to address very small length scale composites.

With modern, thin-film techniques, however, the question can be addressed experimentally. Deposition techniques can be used to prepare 'composites' of well defined geometry and on a length scale never before possible. Experimental results on thermoelectric effects in such 'quantum composites' can directly test Bergman and Levy's results for large length scale and, as the composite length scale is reduced, systematically demonstrate the cross-over to the quantum-dominated regime.

Minimum Lattice Thermal Conductivity

Perhaps the most obvious and common approach to improving ZT is to find materials with very low lattice thermal conductivity values. Alloys of semiconductors have been particularly successful in this regard because the introduction of neutral point defects increases the phonon scattering rate much more than the charge carrier scattering rate. Mechanisms might be sought to increase the phonon scattering rate further, particularly mechanisms that leave electron scattering rates nearly unaffected.

There may be limits on this approach, however, because the lattice contribution to the thermal conductivity can never be reduced to zero, although it may be very small in glasses and metals where disorder or carriers, respectively, scatter phonons extremely well. As new scattering mechanisms are introduced and phonon scattering rates (τ^{-1}) become larger, the phonon mean free path ($l = v\tau$) may

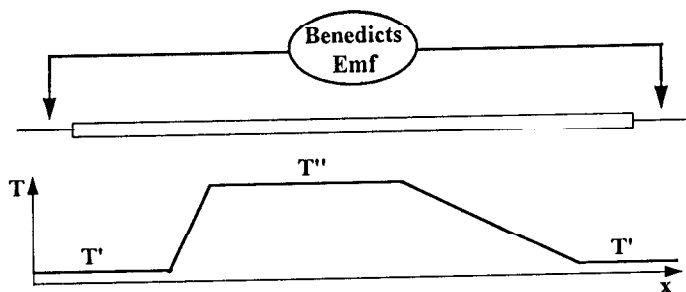


Figure 10. Conditions for observing Benedicks effect in homogeneous materials.

Effects of this type have been studied in homogeneous materials and can be substantial in magnitude, as discussed by Tauc [45]. In inhomogeneous materials, such as p-n junctions, these effects can be even larger and cannot be neglected even to first order.

CONCLUSION

ZT plays a special role in the theory of transport and the discrepancy between the experimental limit $ZT \sim 1$ and the theoretical expectation of $ZT \gg 1$ deserves closer attention after several decades in relative obscurity. Even specific transport property models constrained to accurately describe real materials indicate that substantially larger ZT values are to be expected. Moreover, the region $ZT \sim 1$ appears to play no special role in the theory of transport and extrapolations (either simple or complex) pass through this region to much larger values without hesitation. It would be surprising indeed if, in the absence of a general principle limiting ZT, the very best possible materials were exhausted nearly 30 years ago.

Further, estimates of ZT_{\max} based on material-specific models beg the question, in much the same way that estimates of the maximum T_c for superconductors of 25-30 K were begging the question. If one selects a reasonable model, and inserts parameters appropriate to the material under study, the model *must* predict the ZT actually observed. Any other result would force an iteration of the analysis until the theory and experiment converged. Such efforts convincingly demonstrate consistency between current theory and current experimental results, but no *general* conclusions about ZT_{\max} can be drawn at all.

It would be presumptuous to press the analogy to superconductivity to the point of predicting that $ZT=10$ or 50 (say) must eventually be found, but in the long run there nevertheless appear to be only two real possibilities:

1) $ZT \gg 1$ is possible and will be demonstrated experimentally

or

2) $ZT \sim 1$ represents some as yet unstated principle.

ZT is not merely an engineering quantity, however, but is itself a true transport property representing the relative magnitude of cross-effect transport in materials. The complete absence of materials with large ZT, therefore, presents a challenge not only to the efficiency-conscious technologist but also a challenge to the theory of transport in solids.

Most recent effort on thermoelectric materials has been narrowly focused on incremental improvements in existing materials, largely because even modest improvements in these materials have immediate, practical benefits. As a result, a great many distinct approaches enabled by modern preparation methods have simply not been examined. Today, flexible preparation methods such as molecular beam epitaxy and metallo-organic chemical vapor deposition are available for the fabrication of crystalline thin films,

layered structures, and superlattices. Structures and devices have been demonstrated by these preparation methods with a variety of novel properties not possible with bulk materials, particularly in the fields of electronics and optoelectronics. Perhaps these techniques can allow realization of effects beneficial to thermoelectricity such as thermal conductivity reduction and mobility enhancement.

However, this sort of sophisticated engineering of materials has not been applied to thermoelectric materials to date. By emphasizing basic transport studies in mature and well understood materials, but under conditions ordinarily not encountered or studied experimentally, there appears to be some opportunity today to resolve the issue of why no material has been found with ZT significantly greater than unity.

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