LECTURE 2

THERMOELECTRIC FUNDAMENTALS
AND
PHYSICAL PHENOMENA

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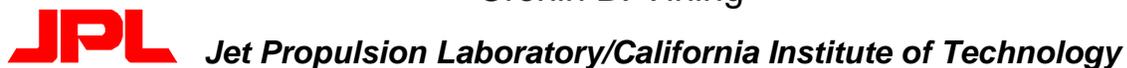**JPL** *Jet Propulsion Laboratory/California Institute of Technology*

1. INTRODUCTION

This portion of the course describes the physical origins of thermoelectric effects in solids. Key concepts and physical principles governing thermoelectric phenomena are discussed and concepts, rather than equations, are emphasized. The intent is to present the vocabulary in a straightforward form so that people from diverse backgrounds, from materials scientists to systems engineers, can communicate with a common language.

A full appreciation of the science of thermoelectricity requires some understanding of a great many disciplines. Equilibrium thermodynamics, non-equilibrium thermodynamics, quantum mechanics, statistical mechanics, transport theory, crystallography and solid state physics are all needed to understand the physics of thermoelectric phenomena. Clearly, a single lecture cannot hope to cover all of the important material. Also, some people will require only a conceptual overview, while others may need a much more detailed discussion. Therefore, this lecture will provide an overview of some of the main concepts which, combined with the suggested reading list, may provide a reasonable basis for a self-study course suitable for even a relatively advanced understanding.

The first lecture in this course provided an introduction to thermoelectricity and the basic ideas are familiar to any specialist in the field. Still, some discussion of the commonly used terms is useful to provide a common language for further discussions. First, the term "thermoelectric" itself implies that both thermal and electrical phenomena are involved. While the term can be used in a more general context, for the purposes of this lecture it refers specifically to effects which occur in solids.

2.   THERMOELECTRIC MATERIAL

The term "Thermoelectric Material" is usually understood to refer to a material which exhibits substantial thermoelectric effects. Neglecting superconductors for the moment, every material exhibits *some* thermoelectric effects. Although the best electrical conductors are perhaps 20 orders of magnitude better than the best electrical insulators at conducting electricity, all materials conduct to some extent. Similarly, all materials conduct heat to some extent. It should be no surprise, therefore, to find that all materials also generate a thermal EMF.

3.   PHENOMENOLOGY

In order to really understand the origins of these effects, however, a certain amount of background is required. The following sections attempt to outline the essential points of thermoelectric phenomena, starting from the most fundamental concepts of heat and charge and finishing with much more advanced topics such as the Boltzmann equation and scattering mechanisms. The emphasis, however, is on the concepts involved and relatively few equations are employed.

3.1. Heat, Temperature and Thermal Equilibrium

The concepts of heat, temperature and thermal equilibrium are among the most fundamental and important concepts in science. Two isolated objects are said to be in *thermal equilibrium* if nothing happens when they are brought into contact with each other. It is an *experimental fact* that any other object which is shown to be in thermal equilibrium with one of the first two objects will also be in thermal equilibrium with the other. This intuitively appealing result is the so-called *Zeroth Law of Thermodynamics* and is the basis for the establishment of a *temperature* scale. Objects in thermal equilibrium are said to be at the same temperature.

Isolated objects at different temperatures, if brought into contact with each other, will exchange energy in an attempt to establish thermal equilibrium. This too is an *experimental fact* and we call the energy exchanged *heat*. Any *work* performed during this process is equal to the difference between the heat lost by one object and gained by the other object. This is the *First Law of Thermodynamics*, i.e. energy is always conserved.

3.2. Charge, Potential and Electrical Equilibrium

The concepts of electrical charge and electrical potential are also very fundamental. Material objects are composed of *positive and negative charges*. Opposite charges attract and like charges repel each other. These are *experimental facts*. Material objects may be said to be in *electrical equilibrium* if there is no exchange of charge when they are brought into contact with each other. Such objects are said to have the same *electrical potential*.

Objects with different electrical potentials, if brought into contact with each other , will exchange charge in an attempt to establish electrical equilibrium. For this reason, most bulk materials have either zero or only a very small net electrical

charge. The unit for electrical charge is the Coulomb and the unit for electrical potential is the Volt. As a consequence of the exchange of charge there is also an exchange energy which we call *work*. Exchange of one Coulomb of electrical charge through a potential of one Volt results in the exchange of one Joule of work.

3.3. Currents, Forces and Equal Treatment

An electrical current is the quantity of electrical charges which passes through a boundary (either a real or an imaginary boundary) each second. An electrical force is related to the change in electrical potential per unit of distance, i.e. the electrical gradient.

Similarly, a heat current is the quantity of heat which passes through a boundary each second. And by analogy a "thermal force" is related to the change in temperature per unit distance, i.e. the temperature gradient.

The thermal and electrical properties have been described above in a manner intended to emphasize the importance of treating both phenomena on an equal footing. Each thermal property has an analogous electrical property, as illustrated in Table 1.

Table 1 Correspondence Between Thermal and Electrical Quantities.

	Thermal	*Electrical*	*Type*
Quantity	Heat	Charge	Reversible
Potential	Temperature	Potential	Reversible
Current Type	Heat Current	Electrical Current	Irreversible
Driving Force	Potential Difference	Temperature Difference	Irreversible

3.4. Irreversible versus Reversible Thermodynamics

The term "dynamics" often implies some type of motion or change with time. In the word "*thermodynamics*" the term refers to changes in properties with temperature (or heat) and in fact any changes in time are *assumed* to be negligible. If an object changes from one thermal (and electrical) equilibrium state to another, thermodynamic principles can be used to study the change in the object's properties from before the change to after.

But thermodynamics can say nothing about the rate of change. If two objects are in contact, thermodynamics tells us that heat will leave the hotter object and enter the colder one, but it cannot tell us how fast this process will occur. Processes which occur at a non-zero rate between two objects not in thermal (or electrical) equilibrium are beyond the scope of thermodynamics alone. Such processes are the subject of *irreversible thermodynamics* (also called *non-equilibrium thermodynamics*).

When electrical potential differences or temperature differences become large enough to cause significant electrical currents or heat currents, factors beyond ordinary thermodynamics must be considered. Since thermoelectric effects inherently involve significant forces and/or currents, *all thermoelectric effects are beyond thermodynamics*.

3.5. Ohm's Law and Linear Response

Ohm's law says that the electrical current will be proportional to the electrical force and the proportionality coefficient is called the electrical conductivity. Ohm's law is just one example of a "*linear response.*" The term implies only that one quantity changes linearly "in response to" a change of another quantity. For virtually all thermoelectric problems of interest, linear response is an excellent approximation and each of the thermoelectric properties may be defined by simple equations similar to Ohm's Law, as shown in Table 2.

Table 2 Definitions of Transport Coefficients of Interest in Thermoelectricity.

Thermoelectric Property	Definition	Under Condition	Type
Electrical Conductivity	$i = \sigma E$	$\nabla T = 0$	Direct
Thermal Conductivity	$Q = -\lambda \nabla T$	$i = 0$	Direct
Seebeck Coefficient	$E = \alpha \nabla T$	$i = 0$	Cross
Peltier Coefficient	$Q = \Pi i$	$\nabla T = 0$	Cross

The first relation connects the electrical current to the electrical force while the second relation connects the thermal current to the thermal force. The electrical and thermal conductivities are therefore called *direct effects* since they connect currents with the related force. The electrical conductivity indicates how well a material conducts electricity and the thermal conductivity indicates how well a material conducts heat.

The Seebeck and Peltier coefficients, however, are called *cross effects* since they connect an electrical response to a thermal force or a thermal current to an electrical current. The cross effects are the basis for utilizing thermoelectric materials for energy conversion applications. The Seebeck coefficient indicates how large a voltage a material generates in a temperature gradient and the Peltier coefficient indicates how much heat passes through a material for a given current.

3.6. Equal Treatment Revisited

The definitions of the thermoelectric coefficients, given above, are historical and were defined for experimental convenience. Zero electrical current or zero temperature gradient are relatively easy to achieve experimentally. Linear response coefficients could also be defined under conditions of zero heat current or zero electrical gradient, but such conditions are much more difficult to control experimentally.

In order to include the cross effects into the currents under arbitrary gradients, we need to add the effects together:

$$i = \sigma(E - \alpha \nabla T), \text{ and} \tag{1}$$

$$Q = \Pi i - \lambda \nabla T \tag{2}$$

These expressions are perfectly correct and often convenient to use, but they are not symmetrical and in order to treat everything equally it may be preferred to re-write the expressions as:

$$i = \sigma E + \sigma\alpha(-\nabla T), \text{ and} \tag{3}$$

$$Q = \sigma\Pi E + \lambda(-\nabla T) \tag{4}$$

In this form, the expressions represent a generalization of Ohm's Law. In general a force (such as E or $-\nabla T$) can generate a current (such as i or Q).

Lord Kelvin first suggested that the Peltier coefficient and the Seebeck coefficient had a definite relationship: $\Pi = \alpha T$. While Kelvin's relationship is correct, his derivation was incorrect since it was based on purely thermodynamic arguments. Not until 1931 did Onsager derive this relationship (and indeed a wide variety of other cross-effect relationships) correctly, using a technique based on thermal fluctuations. This result shows that the Seebeck and Peltier effects are not really independent effects, but more accurately are both manifestations of the same thing. This unification is comparable to the development of Maxwell's equations, which show that electricity and magnetism are really just distinct manifestations of a single electromagnetism.

3.7. A Note on the Thompson Coefficient

In addition to the Seebeck and Peltier effects, it is sometimes asserted that there is a third effect, called the Thompson effect. This effect asserts that when an electrical current flows through a material which is also subject to a temperature gradient that heat is generated at a rate proportional to the electrical current and also proportional to the temperature gradient, thus

$$\dot{Q}_{Thompson} = \tau i(-\nabla T) \tag{5}$$

where τ is the Thompson coefficient.

The total rate of heat generation *within* the material is then given by the sum of three terms: 1) $i^2\rho$, the Joule heating, 2) $-\nabla[\lambda(-\nabla T)]$, the rate that heat is conducted into the material, and 3) $\tau i(-\nabla T)$, the Thompson heat:

$$\dot{Q}_{Total} = i^2\rho - \nabla[\lambda(-\nabla T)] + \tau i(-\nabla T) \tag{6}$$

This, in fact, is just the usual heat balance equation. Thompson (who later was named Lord Kelvin) was able to show that the coefficient τ was related to the temperature dependence of the Seebeck coefficient:

$$\tau = T\frac{d\alpha}{dT}. \tag{7}$$

Basically, the Thompson effect represents the heat generated (or absorbed) due to the fact that the Peltier heat changes with temperature. This result can be derived from the usual thermoelectric expressions (1) and (2) given above.

In experimental analysis and device design, some care must be exercised to account for the Thompson effect. A consistent approach must be taken. If the analysis ignores the temperature dependence of the Seebeck coefficient, an the Thompson term may need to be added explicitly to get the correct heat balance. On the other hand, modern analysis techniques such as finite-element thermal models can often account explicitly for the temperature dependence of the transport coefficients and in this case explicit addition of a Thompson term could cause a

double-counting effect in the heat balance, since the entire effect is already contained in the basic equations.

In reality there is only one thermo-electric cross effect and the Seebeck, Peltier and Thompson effects are merely manifestations of the same basic phenomena.

4. THERMOELECTRIC THEORY OF SOLIDS

Up to this point, we have only described the phenomena of thermoelectric effects. Virtually all materials exhibit currents which respond linearly to applied forces. The only real question which varies widely from material to material is the particular values of the thermoelectric coefficients σ, λ and α. A notable exception is superconducting materials which may not be described in this way at all. For *superconducting* materials, electrical currents may flow *with no driving force at all*. Ohm's law fails entirely in this case and superconducting materials are therefore entirely beyond the scope of the present discussion.

But what is it about a material which determines the transport coefficients? Why are some materials good conductors and others bad? Under what conditions is the Seebeck or thermal conductivity large or small?

To address these questions we need a theory of solids which can connect the structure and makeup of solids to the thermoelectric properties. This is an ambitious task, so in order to be definite most of the remaining discussion will actually apply to a kind of idealized material and many approximations will be assumed. Nevertheless, the concepts depicted are generally well established and the overall picture is useful as a starting point, even if it does not tell the whole story.

A solid material is made up of a collection of atoms. The ideal theory would be able to take as input the geometrical arrangement and type of atoms and predict all the important properties. In principle, modern solid state theory is capable of doing exactly this and in a few special cases these so-called "first-principle" calculations are remarkably accurate. For most real materials of interest, however, the calculations are far too complex to perform reliably, even though all the fundamental principles are well known. An analogy can be made to complex games such as chess or go or shogi, where all the fundamental rules are well known but completely accurate play is seldom achieved.

5. CRYSTALS

We will consider crystalline materials with a definite arrangement of atoms. Figure 1 shows a two of the simpler crystal structures. Each atom has a definite geometrical relationship to all of the atoms around it.

It is traditional to make a distinction between the properties of the *lattice* and the properties of the *electrons*. The lattice refers to the positions of the atoms themselves. The atoms are not stationary, but the are considered to move only very

slightly compared to the distances between the atoms. This is to say that they vibrate about their average position, but the do not move throughout the crystal. We will neglect here any larger motions which atoms might make in real materials.

Most of the electrons are considered to be localized, always remaining associated with the same particular atom. Localized electrons do not car ry any current, even when a force is applied, and may be considered to be part of the lattice. Some of the electrons, however, are essentially "free" and will move throughout the solid. It is these "free" electrons which determine the ability of a material to carry an electrical current.

(a)   (b)

Fig. 1 Diamond (a) and Sodium Chloride (b) Crystal Structures. Si and Ge form with the Diamond Crystal Structure, in which Case all the Atoms are Identical. PbTe and PbSe Occur in the Sodium Chloride Crystal Structure.

It is customary and usually convenient to speak of the properties of the lattice and the properties of the electrons (taken to mean the free electrons), but this division of properties is somewhat artificial. Sometimes it is important to remember that the lattice influences the behavior of the electrons and the electrons influence the behavior of the lattice. At the minimum, it is important to treat both systems on an equal footing for a reliable description of thermoelectric effects.

6.   THE IDEAL MATERIAL IN EQUILIBRIUM

This section will describe an ideal crystal in thermal equilibrium. First the lattice and then the charge carriers will be discussed. Keep in mind that this is just the beginning. At this point there are no net forces and no net currents in the solid.

The next section will generalize these concepts to the case when there are net forces and net currents in the solid.

6.1. The Lattice and Phonons
6.1.1.   Main Features

Many of the main features of a lattice may be illustrated by a simple mass and spring model where the atoms are represented as point masses and the bonding between the atoms is represented by very small springs:

Undisturbed Mass and Spring Model

Transverse Phonon

One Wavelength

(Displacements have been greatly exagerated for clarity)
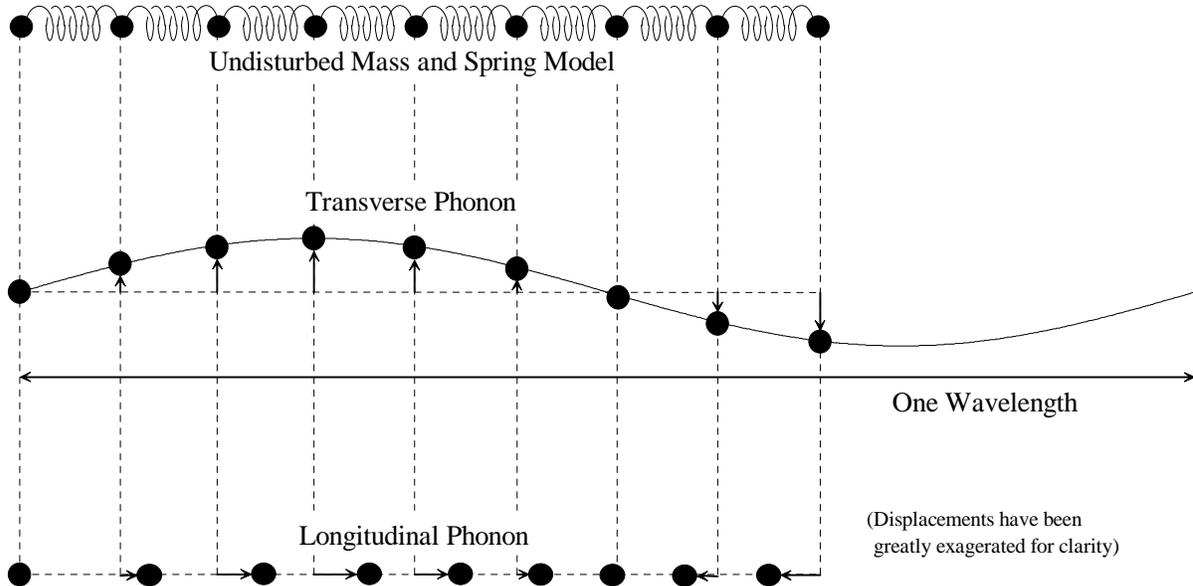
Longitudinal Phonon

Fig. 2 Mass and Spring Model for a One-Dimensional Crystal of Ions (Represented by the Masses) Held in Place by Bonds (Represented by the Springs). Two Possible Types of Disturbances from Equilibrium are Represented by the Transverse and Longitudinal Phonons Shown.

In the undisturbed lattice (at top in Figure 2) the atoms would be regularly spaced apart with a distance corresponding to a unit cell repeat distance. In fact the atoms will vibrate about their equilibrium positions due to thermal agitation. This motion is not entirely random, however, since the movement of one atom stretches or compresses the springs connecting it to neighboring atoms.

Vibrations, even if initiated at a single atom, will propagate throughout the crystal. Rather than describing the vibrations of the each atom individually, it has been found to be both more convenient and more accurate to speak about regular, sinusoidal disturbances of entire groups of atoms, as suggested by the middle and lower portions of Figure 2. Such a sinusoidal disturbance is called a *phonon*. The word phonon means "particle of sound" and is used because sound is precisely an elastic wave of compression and extension which propagates through a solid.

A solid with only a single phonon in it, therefore, would exhibit a particularly regular pattern of atomic displacements such as shown in the lower two portions of Figure 2. It can be shown, using mathematical techniques almost identical to ordinary Fourier analysis, that any configuration of atomic displacements - no matter how complex - can be accurately represented by an appropriate summation of many sinusoidal disturbances. Since a collection of phonons can represent *any possible* configuration of disturbances from equilibrium, and since individual phonons represent particularly simple motions which actually do occur in solids, the phonon description has become the most common tool for describing the properties of solids.

There are several terms used to describe a phonon. First, each phonon has a characteristic wavelength, as shown in Figure 2. The phonon wavelength may be very long, but a wavelength less than the distance between the atoms does not make sense. A phonon represents a disturbance in the positions of the atoms, and there can be no disturbance where there are no atoms. So, the minimum wavelength (*1*) allowed is one interatomic distance (*a*).

Now, quantum mechanics tells us that a wave will carry a momentum given by *h/*λ, where *h* is Plank's constant. This principle was first described by de Broglie and it is a very powerful concept indeed. Note that this momentum is not the same as the phonon velocity. It is common to speak of *phonon wavenumber* defined by *2p/1*. Since there is a minimum allowed wavelength, there is also a maximum allowed momentum (*h/a*) and a maximum allowed wavenumber (*2p/a*). Except for a factor related to Plank's constant, the *momentum* and *wavenumber* can be used interchangeably.

A crystal with a phonon in it must have a greater energy than a crystal without any phonons. Bonds are being stretched and atoms moved, so there is both kinetic and potential energy associated with each phonon. The energy associated with a single phonon is typically very small, representing only a fraction of an electron volt. As suggested in Figure 2, however, there may be several different types of atomic motion allowed for a given wavelength and in general each type of allowed motion will have a different amount of energy associated with it.

Each type of phonon travels through the crystal at a velocity characteristic of that type of phonon. "Velocity" refers to the speed of a crest of one of the waves shown in Figure 2. There may be several types of phonon with the same wavelength, each of which have different energies and different speeds. Indeed, some phonons hardly move at all and just represent a kind of standing wave.

There are two major issues to be determined regarding phonons: 1) what types of phonons are actually allowed in crystals (only two types are shown in Figure 2) and 2) which ones are actually present under the conditions of interest? If both questions are known, then one should be able to predict a wide variety of p roperties of the lattice.

6.1.2. Phonon Dispersion Relation

The first question (what phonons are allowed?) is a mechanics question. If the single-chain of masses and atoms shown in Figure 2 is not good enough, you simply work up a more accurate representation of the geometry using the full crystal structure (such as shown in Figure 1). Since the masses and distances are very small, quantum mechanics is required to get reasonable answers. It can be particularly difficult to accurately calculate the strength of the springs (i.e. the chemical bonds), but this has been done for many crystals. Calculations become more difficult as the crystal structure becomes complex.

The energies of the allowed phonons vary with the direction the phonon moves through the crystal and the momentum (or wavelength) of the phonon. Fortunately, individual phonons may be studied experimentally using neutron scattering techniques. Experimental energy/momentum relationships, called the *phonon dispersion relation*, can then be compared to the calculated relationships, such as shown for silicon in Figure 3. Thus, the allowed phonons may be determined rather precisely.

Sometimes the full dispersion relation must be used, but very often a much simpler description is sufficient. The two most common models for how phonons move are the *Debye Model* and the *Einstein Model*, represented in Figure 4. In the Debye model phonons all have the same speed and have an energy which is directly proportional to the wavenumber (i.e. inversely proportional to the wavelength). The speed of these phonons is just the speed of sound through the solid. The term *acoustic phonon* is associated with this type of phonon to remind you that the acoustic (and elastic) properties of solids are associated with this type of vibration.
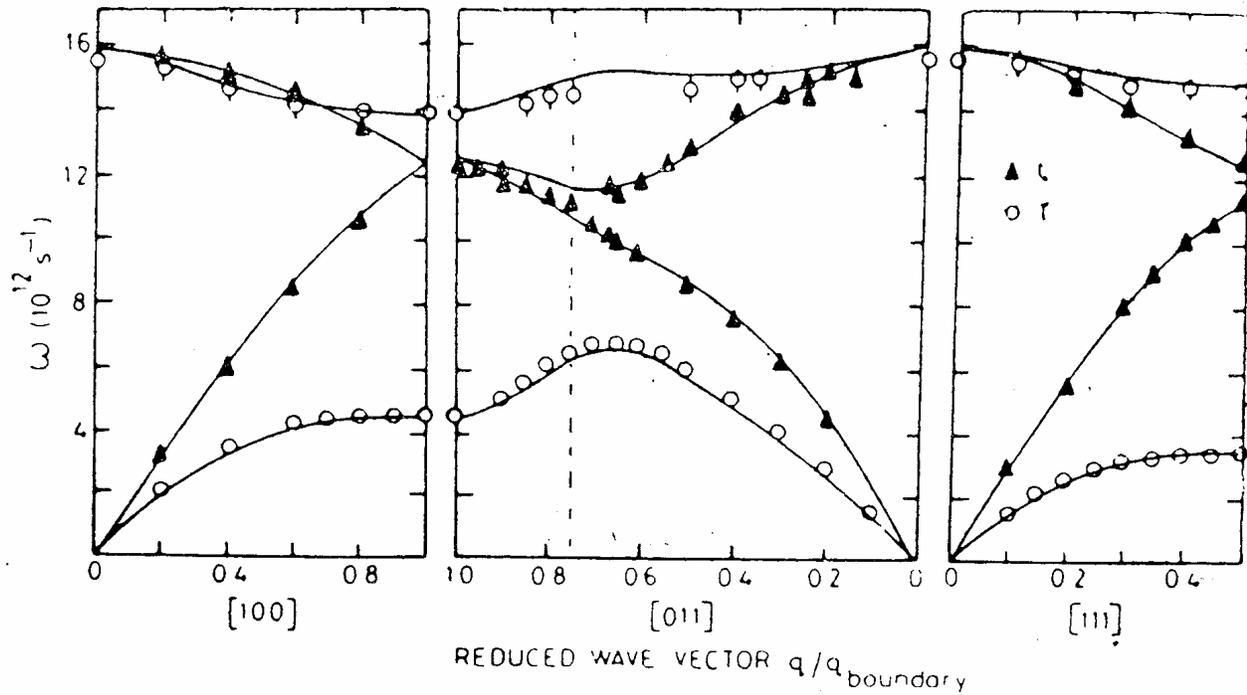

Fig. 3 Phonon Dispersion Relation (Energy as a Function of Momentum) for Silicon. Symbols are Experimental and Lines are Calculated. Note the Variation with Direction and that there are Several Different Branches (After Dolling[1]).
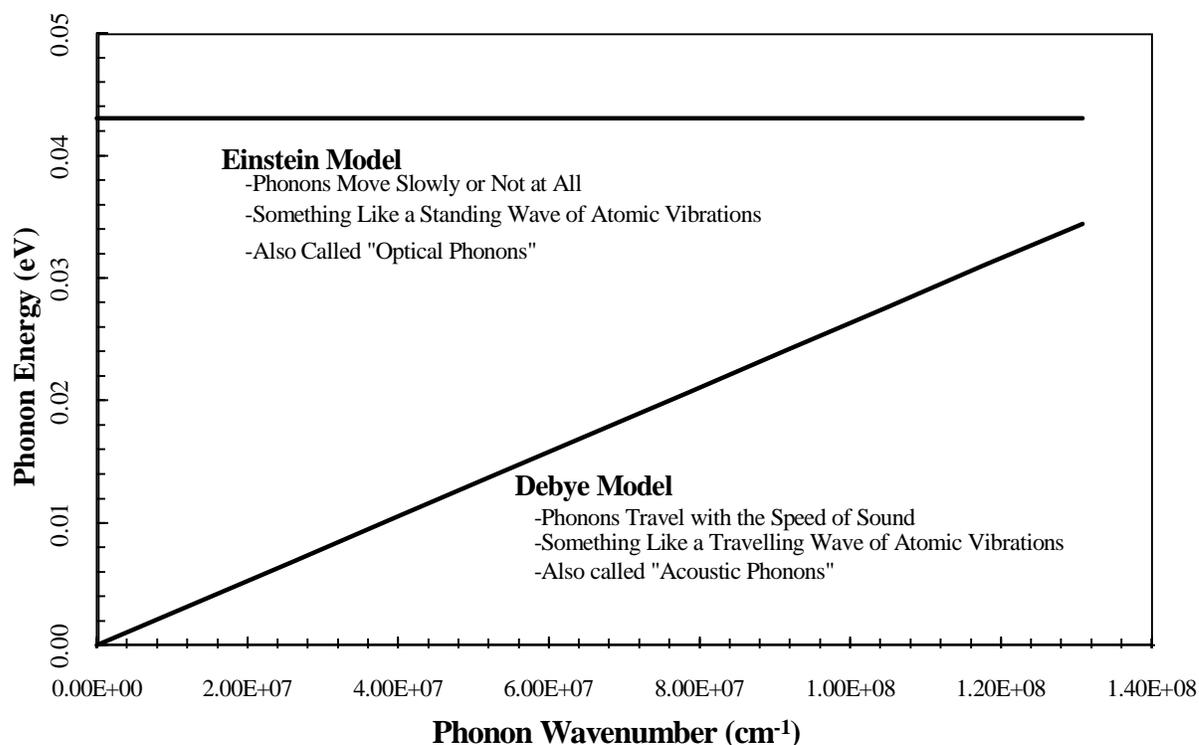
Fig. 4 Idealized Phonon Dispersion Relations for the Einstein and Debye Models of Lattice Vibrations.

A second model is the Einstein model, in which the phonons are considered to be standing still, which is to say that the crest of the vibration wave does not move through the crystal, but only oscillates back and forth. All phonons, in this ideal model, have exactly the same energy. Such a phonon is also called an *optical phonon* because in ionic crystals the standing wave vibrations of charged ions represents an oscillating electrical dipole which can interact with electromagnetic radiation. Many optical properties of solids are determined by interaction between light and these "optical phonons."

The phonons actually allowed in a real crystal (such as shown in Figure 3) seem to bear little resemblance to the idealized models shown in Figure 4. Nevertheless, careful use of the idealized models can often capture the essential features and provide surprisingly reliable estimates of many physical properties.

6.1.3.   Phonon Distribution: Equilibrium

The second question of interest was: which phonons are actually present? At low temperatures, the atoms clearly vibrate very little corresponding to very few phonons. Near the melting point of the solid, the atoms are vibrating very severely corresponding to very large numbers of all kinds of phonons. Fortunately, the number of each type of phonon present in equilibrium at a given temperature may be calculated using the well known *Bose-Einstein distribution* function. This is an application of *statistical mechanics*. Statistical mechanics provides a systematic framework for describing the properties of a system consisting of a large number of components. Little more is required in principle than a knowledge of which energy levels are allowed (i.e. the dispersion relation). While the calculations can become quite complex, part of the power of statistical mechanics is that the techniques can handle both equilibrium and non-equilibrium conditions. Under non-equilibrium

conditions there is still a distribution function, but it is not quite the Bose-Einstein function.
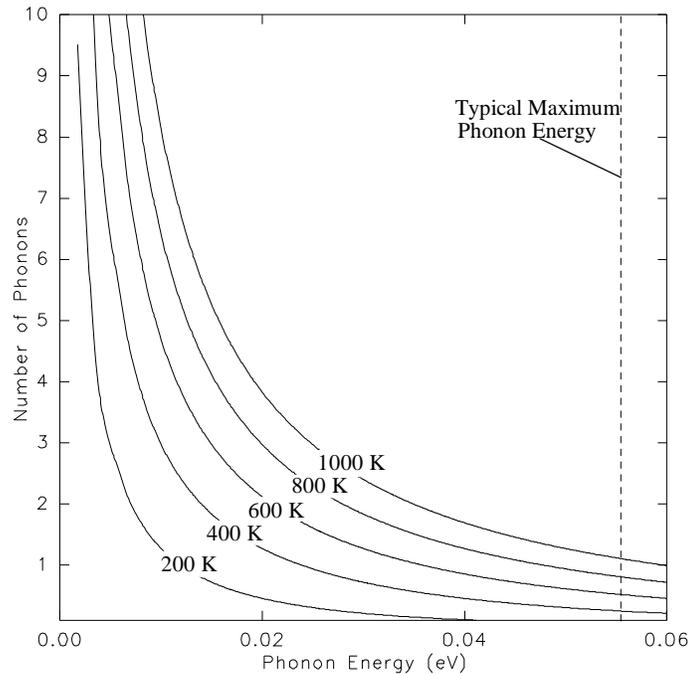

Fig. 5 The Number of Phonons of a Particular Type and Particular Energy is Given, in Equilibrium, by the Bose-Einstein Distribution Function as Shown for Several Temperatures.

Do not be concerned that the distribution function calls for less than one phonon under many conditions. What, does it mean to have less than one phonon? This is a part of *statistical mechanics*, where properties are calculated as averages over large numbers of particles and long periods of time. Imagine that sometimes a phonon is present and sometimes it is not present, which is to say that phonons are constantly being created and destroyed.

6.1.4. Statistical Mechanics: Calculating Properties

Now that we know which phonons are allowed (given by the *dispersion relation*) and which ones are expected to be present (given by the *distribution function*) we are in a position to calculate many properties of the crystal. The general procedure can become mathematically quite complex, but conceptually it is very simple and isi summarized in Table 3. First determine how much each type of phonon contributes to the property of interest, then multiply by the distribution function to account for how many of each type of phonon are expected to be present and finally add up the contribution counting every type and wavelength of phonon allowed.

Table 3 Procedure for Calculating the Total Energy Associated with Phonons.

Total Property	Sum over allowed types of phonons, i	Sum over allowed wavenumber, k	Contribution of each phonon	x Distribution Function

$$
\text{Energy} = \begin{array}{l} i=1 \Rightarrow \text{Longitudinal Acoustic} \\ i=2 \Rightarrow \text{Transverse Acoustic \#1} \\ i=3 \Rightarrow \text{Transverse Acoustic \#2} \\ i=4 \Rightarrow \text{Optical \#1} \\ i=5 \Rightarrow \text{Optical \#2} \\ i=6 \Rightarrow \text{Etc.} \end{array} \qquad \begin{array}{l} k \geq 0 \\ k \leq 2\pi/a \end{array} \qquad \varepsilon(i,k) \quad x \quad N(i,k)
$$

Properties other than the energy (such as heat current) may be evaluated using the same procedure and a variety of notations have been developed to make it easier to write down the expressions. Usually the summation over wavenumbers is treated as an integral and in three dimensions the wavenumber becomes a *wavevector*, indicating not only the wavelength of the phonon but also the direction it is traveling through the crystal. Evaluation of such expressions (which we will not discuss here) can be very tedious, but writing them down is simple:

$$
E = \sum_{phonon,\, i} \left\{ \int_{allowed\, k} e(i, \vec{k})\, d^3 k \right\}. \tag{8}
$$

6.2. Charge Carriers

Up to this point we have described only a crystal with no charge carriers. Recall that an isolated atom has two types of electrons: an inner core of electrons (corresponding to the number of electrons in the next-lighter noble gas) which are very tightly bound to the atom and an outer shell of less tightly bound electrons called the valence shell. If, in a solid, all of the outer shell electrons are exactly consumed in bonding, then there are no charge carriers at all. Such a material is called an electrical insulator and ideally has no electrical conductivity at all. Thermoelectric materials must have some charge carriers in order to exhibit electrical conduction phenomena.

6.2.1. The Origin of Charge Carriers

Charge carriers can result from a variety of mechanisms. In a classical metal, one or more of the outer shell electrons are not localized in bonds between specific atoms, but are more or less free to move throughout the crystal. The alkalis (Na, K) and alkali earths (Li, Mg) are classic examples of simple metals.

Of more interest for thermoelectric energy conversion is the creation of charge carriers in insulators. Since insulators ideally have no charge carriers, any defects that are present can be said to be due to defects. Figure 6 illustrates the production of carriers by substitutional defects. When a host atom is replaced by an atom with more valence electrons than the host has, the extra electron is not needed for bonding and enters the next higher available energy state. There is some attraction between the negative electron and the positively charged donor atom left behind, but often the attraction is very weak and the electron is free to move throughout the crystal, much like the electrons in a metal.
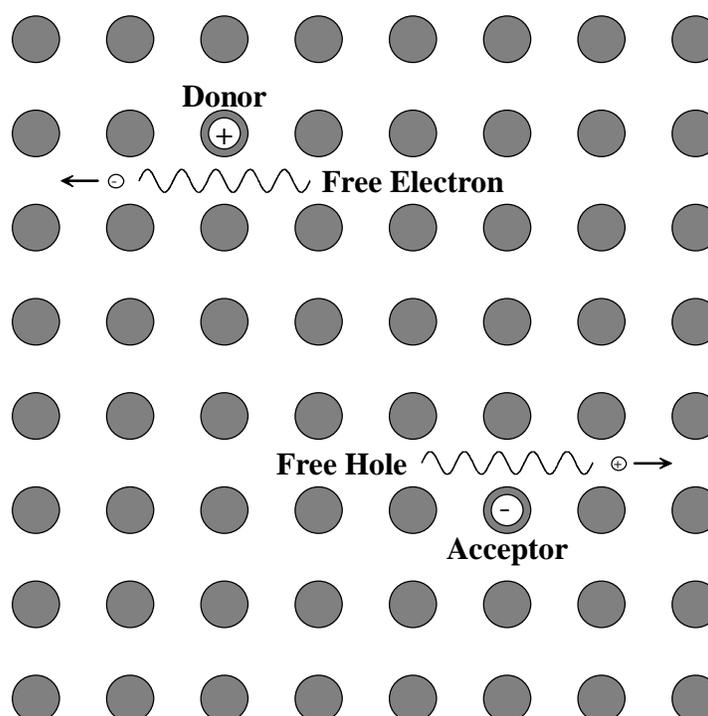
Fig. 6. Lattice Showing Atomic Substitutions by a Donor, Creating a Free Electron, and by an Acceptor, Creating a Free Hole.

When a host atom is replaced by an atom with fewer valence electrons than the host has, a bond is left one short of the ideal. This "shortage" is called a hole and there is some attraction between the hole and the negatively charged ion left behind, which is called an acceptor. The hole is literally the absence of an electron in one of the bonds and often the attraction is very weak, allowing the hole to move freely from bond to bond throughout the crystal.

Even in an otherwise perfect crystal, where all the bonds are exactly filled, electrons and holes are created thermally. A few electrons in the bonding states will occasionally acquire enough energy to leave the bonding state (leaving behind a hole) and enter one of the anti-bonding states (creating a free electron). These electron-hole pairs are constantly being created and destroyed.

There are several other mechanisms to create free charges or holes other than the simple substitution of dopants just described. Defects such as the absence of atoms (vacancies) or extra atoms occupying positions between the usual lattice sites (interstitials) can also create carriers. The precise origin of free charge carriers varies greatly from material to material and the control of doping levels is a major technical challenge beyond the scope of the present discussion.

6.2.2.   Charge Carriers as Waves

In the discussion of the lattice above, phonons were introduced as a convenient concept for describing atomic displacements. We also find a wave-like description convenient for the free charge carriers. Rather than imagining electrons as localized within a small region of space, the usual description in solids is to imagine electrons as waves with wavelengths longer than an interatomic distance.

In this case the amplitude of the wave does not represent atomic displacement at all, but instead the amplitude represents the charge density. More accurately, the

amplitude of the wave represents the quantum mechanical probability of finding a charge at that position. And we assign to each charge carrier a wavevector (k), the direction of which indicates the direction of propagation of the wave and the amplitude of which ($k=2p/l$) is inversely proportional to the wavelength of the wave. As usual, quantum mechanics tells us that such a wave carries momentum, given by Plank's constant divided by the wavelength, $p=h/l$.

As with phonons, the wave-like description represents no loss of generality because any spatial distribution of charge carriers can be represented using an appropriate summation of waves. Just keep in mind that this concept is used for convenience, largely because the mathematics are simpler this way.

So, charge carriers are imagined as waves and, whatever their origin, there are two major issues to be determined: 1) what types of charge carriers are actually allowed in crystals and 2) which ones are actually present under the conditions of interest? Although the answers are different, the questions are the same ones asked about phonons above.

6.2.3.   Electron Dispersion Relation: Electronic Energy Bands

To answer the question regarding the allowed charge carriers, the concept of *energy bands* must be introduced. Isolated atoms have discrete energy levels which may be occupied by electrons or may be empty. When two atoms are brought together, these energy levels mix to some extent. All of the valence electrons are consumed by filling the new "molecular energy levels," the lowest energy levels being filled first. The energy levels below the energy of the isolated atoms are called bonding levels and the higher energy levels are called anti-bonding levels. It is important to note that there are just as many energy levels in the molecule as there were in the two original, isolated atoms. The allowed energies have shifted, but there is a correspondence in number of levels to the original atoms.

As more and more atoms are brought together, the atomic energy levels become more and more mixed, but each energy level in the original isolated atoms is still represented in the final energy state-scheme. The individual energy levels of the individual atoms, form bands of allowed energies in the final solid. This idea is represented schematically in Figure 7.
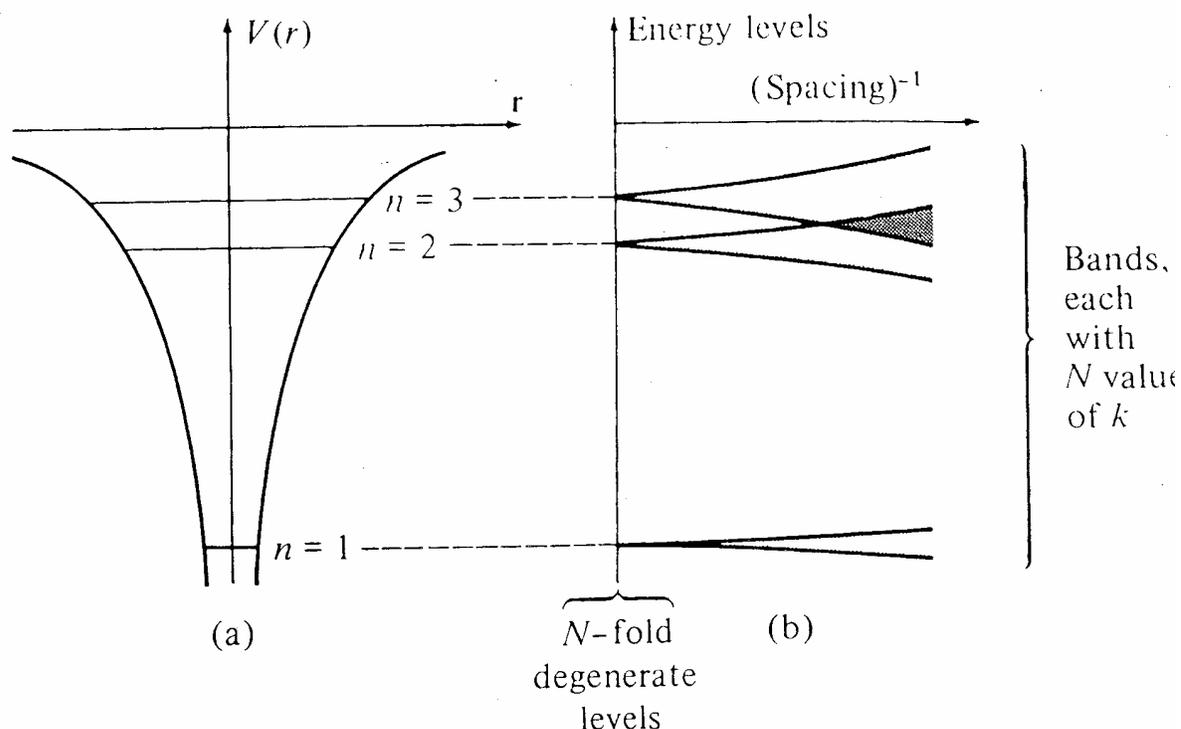
Fig. 7. Schematic Representation of Energy Levels in an Isolated Atom (a) and the Formation of Energy Bands from N such Atoms Brought Together into a Solid (After Ashcroft and Mermin).

Quantum mechanical techniques are required for calculating these energy bands. Conceptually, these calculations are not more difficult than calculating, say, the allowed energy levels of a hydrogen atom. The large number of atoms in a solid, however, means that the mathematics become considerably more complex and the number of energy levels to be calculated is as large as the number of atoms. A variety of techniques have been developed to perform these calculations, but they are beyond the present discussion.

Recall that there are several different types of phonons (longitudinal, t ransverse, etc.) and that the energy depends on both the wavevector and the type of phonon. So too with electrons, but each type of electron is called a band and the energy of the electron depends on both the wavevector and the band. The wavevector can point in any direction and can vary from a magnitude of $k=0$ (corresponding to an infinite wavelength) up to $k=2p/a$ (corresponding to a wavelength of one interatomic spacing). Figure 8 shows the full band structure for an alloy of 50% Si and 50% Ge, as an example.

This relationship between the allowed energy levels and the momentum of the electrons is called the charge carrier dispersion relation. The terms "band structure" and "dispersion relation" mean the same thing with regard to electrons. Fortunately, just as with phonons, simple approximations to the full band structure are usually

sufficient. Often, only the energy states just above or just below the band gap are really important.

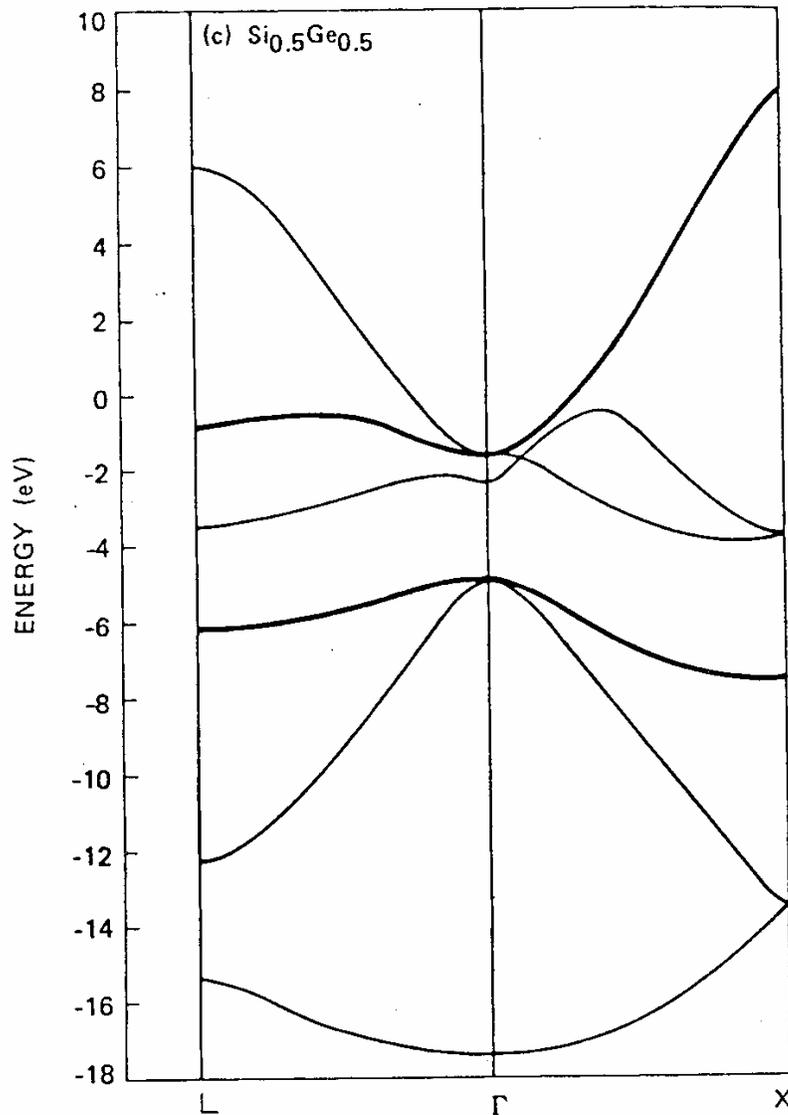Fig. 8: Electronic Energy Band Structure Calculated for $Si_{0.5}Ge_{0.5}$ (After Krishnamurthy and Sher[2]). The Energy Gap is Seen Between about -4 and -5 eV. States Below the Gap are FIlled and States Above the Gap are Empty, at Least in Undoped Material.

Electron Energy

Energy Band Structure

Approximate

$$\varepsilon \cong \frac{\hbar^2 k^2}{2m^*}$$

Electron Energy

Band Gap

Full Structure

e(i,k)
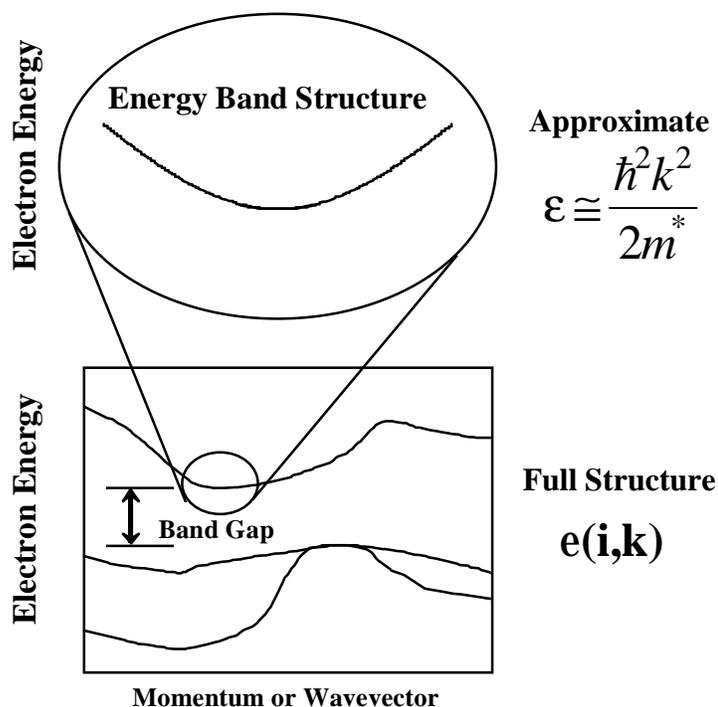
Momentum or Wavevector

Fig. 9 The Lowest Energy Levels of a Single Band are Nearly Parabolic in Shape.

If we magnify the energy states just above the band gap, we see that the energy dispersion relation is nearly parabolic, as suggested in Figure 9. Using a simple parabola to describe the relationship between the energy and wavevector (or momentum) is called the *effective mass* approximation. Indeed, the curvature of the dispersion relation *defines* the effective mass.

For phonons, the Debye model is typically used rather than the full spectrum of allowed phonon energies. For carriers, typically the effective mass model is used rather than the full band structure. The idea is that charge carriers in a solid really are very different from totally free electrons and should be described by their band structure. But for many purposes charge carriers in a solid behave just like totally free electrons, except that they *appear* to have a different mass.

Indeed, one uses a different mass for each band that must be considered. It is not unusual in thermoelectric materials to consider one band of electrons and another band of holes. Sometimes several bands must be considered to get a good description of a particular materials behavior. Still, it is a remarkable fact that very often one only needs to know the band gap and a few eff ective mass values in order to have a satisfactory approximation to the full band structure.

6.2.4. Electron Distribution Function

The previous section described which charge carriers are allowed in a solid. Now we need to turn to the question of which of the allowed states are actually occupied. Fortunately, this is also a relatively simple calculation is given by the *Fermi-Dirac Distribution Function*, as shown in Figure 10.

Fig. 10 The Number of Charge Carriers Which Occupy the Energy Levels of a Particular Energy Band is Given, in Equilibrium, by the Fermi-Dirac Distribution Function as Shown for Several Temperatures.

The principle difference between the phonon distribution function and the electron distribution function is that no more than one electron is ever allowed to occupy any given energy state. This is the famous *Pauli Exclusion Principle*, which is most important at low temperatures and/or high doping levels.

6.2.5.   Statistical Mechanics: Calculating Properties

Calculating the overall properties of a collection of charge carriers follows precisely the same pattern described above for phonons. Now that we know which charge carriers are allowed (given by the *dispersion relation*) and which ones are expected to be present (given by the *distribution function*) we are in a position to calculate many properties of the charge carrier system. Following the pattern used for phonons above, Table 4 outlines the procedure for calculating the energy associated with the charge carrier system.

Table 4: Procedure for Calculating the Total Energy Associated with Charge Carriers.

Total Property	Sum over allowed types of charge carrier, i	Sum over allowed wavenumber, k	Contribution of each carrier	x	Distribution Function
Energy	= i=1$\Rightarrow$First Conduction Band i=2$\Rightarrow$Second Conduction Band i=3$\Rightarrow$First Valence Band i=4$\Rightarrow$Second Valence Band i=5$\Rightarrow$Etc.	$k \geq 0$ $k \leq 2\pi/a$	$\varepsilon(i,k)$	x	$f(i,k)$

7. NON-EQUILIBRIUM PROPERTIES OF SOLIDS

Having discussed the equilibrium properties of solids we are finally in a position to discuss solids with driving forces and currents present. Fortunately, most of what has been discussed can still be retained under non-equilibrium conditions.

The first point to make clear is that the allowed energy levels are not altered at all in the presence of electrical potential gradients or temperature gradients. Phonons which were not allowed in equilibrium are still not allowed. All phonons which were allowed are still allowed. And similarly for charge carriers.

This means we can still use the same dispersion relations as before. If the Debye model for phonons and the effective mass approximation for charge carriers were good enough to calculate equilibrium properties, then they are probably sufficiently accurate for non equilibrium properties as well. And if necessary, the full phonon and electron structures can be used. These, at least, do not need to be recalculated for non-equilibrium conditions.

The main thing needed to calculate non-equilibrium properties is the non-equilibrium distribution function. Energy states which were occupied in equilibrium become unoccupied and states which were unoccupied become occupied. There are certain features we expect of the non-equilibrium distribution function. We will not prove these features here, but merely suggest that they are reasonable expectations.

First, we expect any deviations from equilibrium to be relatively small. Whatever the equilibrium distribution function is, we don't expect it to change much just by applying a small electrical or thermal gradient. Second, we expect the change in the distribution function to be proportional to the applied fields (electrical or thermal). We are looking to describe linear phenomena, like Ohm's law, so if we got any other result, we would throw out the calculation and try again.

Finally, we have one more expectation. In equilibrium there are no currents since there are just as many waves moving to the right as are moving to the left. By definition, a current means there are more waves moving one direction than are moving in the opposite direction. Therefore, we expect the deviations from equilibrium to be different for waves moving in opposite directions.

7.1. Mean Free Time and Mean Free Path

The equilibrium distribution functions provide only a statistical probability that a particular energy is occupied. Any particular energy state, however, will not remain

as it is forever. If the occupancy never changed, for example, it would be impossible even to heat up or cool off the material. Implicit in the very idea of a distribution function is that the occupancy of energy states are constantly changing, and changing at rates very fast compared to the rate of change of any external forces.

For each energy level, then, there is an average time between changes of occupancy. This time is called the *mean free time* and it is usually represented by the Greek letter tau, τ. When speaking of a wave (either a phonon or a charge carrier or whatever), τ is the average time the wave moves until it hits something or otherwise changes into some other type of wave. The same quantity is also called the *relaxation time* or the *collision time*. The inverse, τ^{-1}, is variously called the *collision rate* or *scattering rate*. All these terms mean the same thing.

Closely related to the mean free time is the mean free path. This is just the distance (*l*) the wave travels during the time τ, or *l=vt*. Before discussing how to estimate the scattering rate, we will examine some of it's consequences.

7.2. Boltzmann's Equation: Balancing In and Out

The scattering rate is the first piece needed for calculating the non-equilibrium distribution function. The actual value of the scattering rate is not important in equilibrium because it represents both how fast a state becomes occupied as well as how fast it becomes unoccupied. If occupation changes for any reason, scattering will tend to bring the distribution function back to the equilibrium value.

Boltzmann's equation provides a systematic method for accounting for the effects of forces, currents and scattering on the various distribution functions. Boltzmann's equation refers to the rate at which the distribution function changes and solving Boltzmann's equation is the most common method for computing the non-equilibrium distribution function. So long as all external forces are steady, the occupancy (on average) of *every* energy level will also be steady. The average rate of change of the distribution function is zero, so all you have to do is balance out the various effects.

There are three main contributions to consider. The first contribution is that due to scattering already discussed. The second contribution is due to waves "drifting" into the region of interest from other parts of the material where the distribution function is different. The third contribution is due to presence of forces which directly increase the momentum of a wave (which is the definition of a force) and thereby move the particle to a different energy state.

This balancing act is illustrated in Figure 11. All of these terms are zero in equilibrium and as a rule only first order contributions are included in the balance. Various approximations and mathematical techniques are available to solve Boltzmann's equation, but all of the solutions satisfy each of our expectations described above. The only thing we need to know about the material to calculate the non-equilibrium distribution function is the scattering rate.
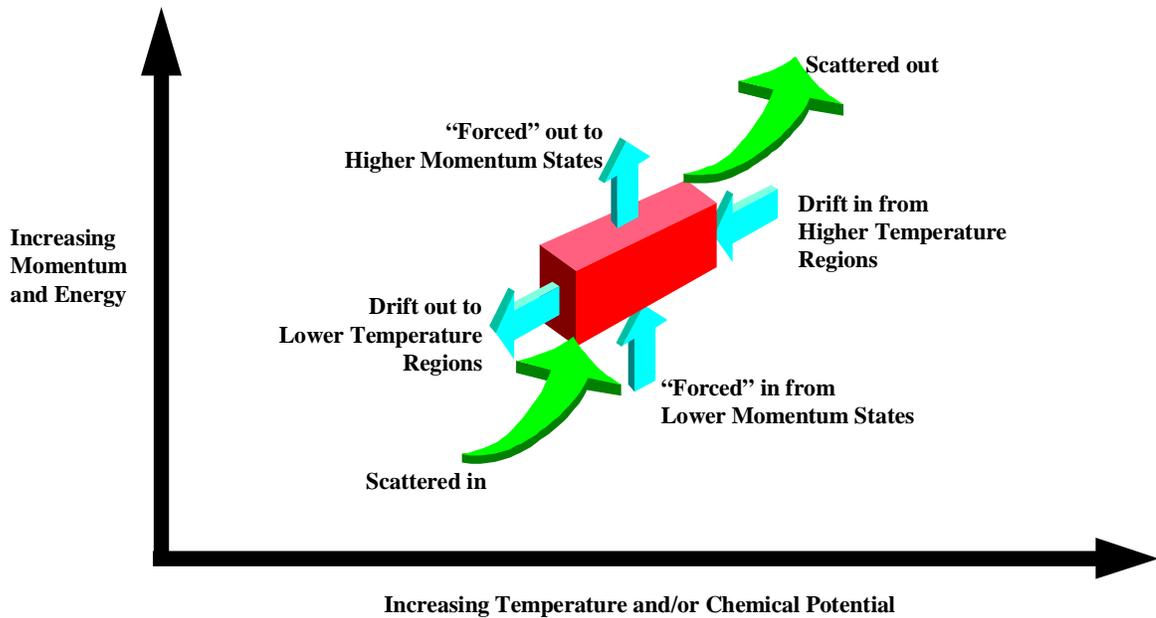
Figure 11. Boltzmann's Equation Determines the Non-Equilibrium Occupation of an Energy State by Balancing the Effects of Scattering, Forces and Drift on a Small Group of Energy States, in a Small Region of the Material.

7.3. Statistical Mechanics: Calculating Properties

Finally we are in a position to calculate an electrical current or a heat current in a solid. The procedure is very similar to calculation of an equilibrium property. Table 5 shows the calculation of a heat current through a lattice.

Table 5: Procedure for Calculating the Heat Current Associated with Phonons.

Total Property	Sum over allowed types of phonons, i	Sum over allowed wavenumber, k	Contribution of each phonon	x	Distribution Function
Heat Current =	i=1⇒Longitudinal Acoustic i=2⇒Transverse Acoustic #1 i=3⇒Transverse Acoustic #2 i=4⇒Optical #1 i=5⇒Optical #2 i=6⇒Etc.	k≥0 k≤2π/a	$\varepsilon(i,k)$ x $v(i,k)$	x	N(i,k)

Very simple, really. Each phonon carries an energy $\varepsilon(i,k)$ at a velocity $v(i,k)$. Multiply the energy by the velocity and you have the energy carried by a single phonon. Multiply this by the distribution function and add the contributions for each type of phonon and wavelength. Now you have the total heat current due to all the phonons. For phonons in a temperature gradient, the distribution function looks like

$$N(i,k) = N_0(i,k) + \left(-\frac{t(i,k)v(i,k) \cdot \nabla T}{T} \right) e(i,k) \frac{\P N_0(i,k)}{\P e(i,k)},$$

which has all the features we expected.

The first term is just the equilibrium distribution function and can be safely ignored when calculating currents. Most of the information of direct interest to thermoelectrics is in the second term, the deviations from linearity. The heat current will, as expected, be proportional to the temperature gradient and, using the definition of the thermal conductivity, the proportionality constant is identified as the thermal conductivity.

All of the transport coefficients can be calculated in a similar manner. The key is to know the dispersion relations for the type and the appropriate relaxation times, τ. Now we turn our attention to calculating scattering rates (or τ^{-1}).polarons and hopping conduction, etc. thermal conductivity (electronic and lattice), phonon drag,

7.4. Calculating Scattering Rates

Although quantum mechanical techniques are usually used to accurately calculate mean free times and scattering rates, the ideas are basically classical and most easily visualized for particles. A simple visual illustration may help, as shown in Figure 12. Consider a continuous stream of particles, all moving in the same direction and with the same velocity. If an obstacle is placed in the path of this stream, it is a simple matter of geometry to calculate how many particles strike the object per second. We don't really care at this point what happens to the particles after striking the object, just the rate.

$$N = \text{\# particles/cm}^3$$
$$\text{Moving at velocity} = v \text{ cm/s}$$

Obstacle casts shadow of area$= \pi r^2$

$$\text{Scattering rate} = \text{\# particles which hit obstacle/sec}$$
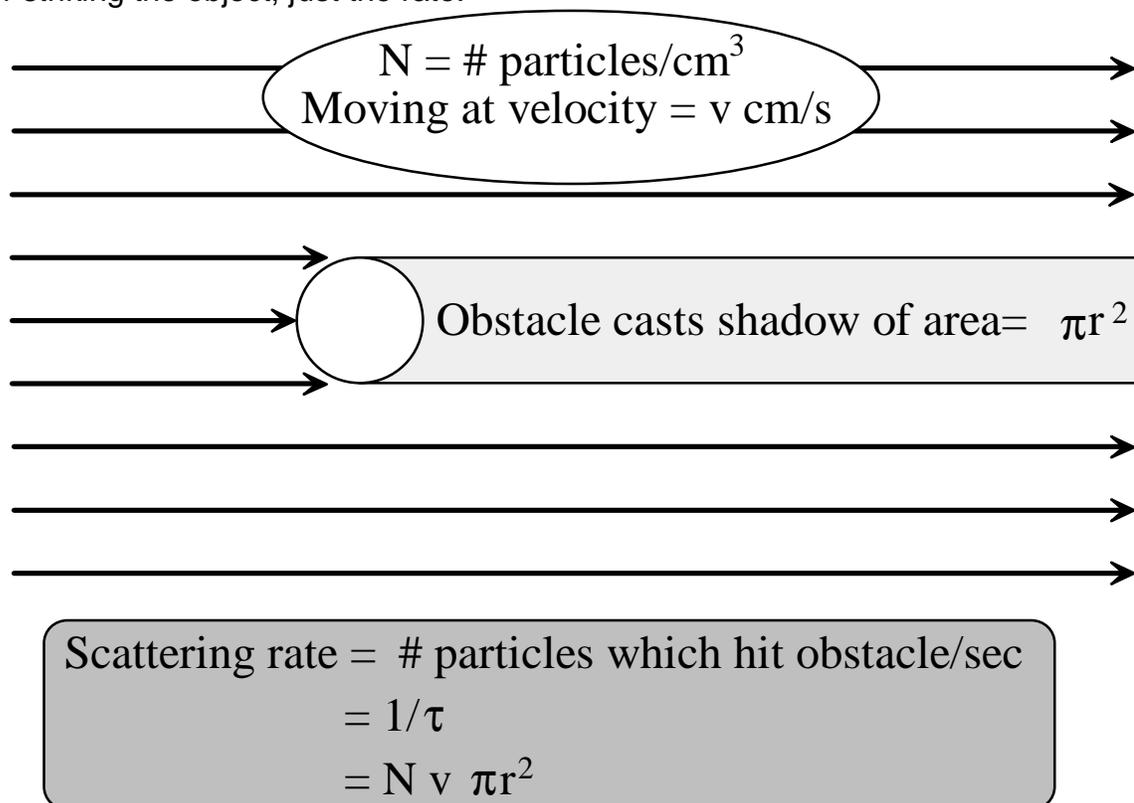$$= 1/\tau$$
$$= N \, v \, \pi r^2$$

Fig. 12: Calculating Scattering Rates is Essentially a Geometry Problem: How Big Does this Particular Kind of Obstacle Appear to be When this Particular Kind of Moving Particle Strikes It?

This is called the collision rate, or equivalently the scattering rate, and the effective size of the obstacle (given by πr^2 here) is called the *cross section*. Note

that the scattering rate depends both on properties of the moving particle (such as their density and their velocity) as well as on properties of the obstacle (in this case, the cross section of the obstacle).

When the moving "particles" are phonons or charge carriers, almost anything can look like an obstacle and impede the flow: charged impurities, neutral impurities, grain boundaries, inclusions, and so on. We use the term *scattering mechanism* to distinguish one type of obstacle from another. Most obstacles cannot be treated as simple hard balls, as suggested in Figure 12. Usually, in fact, the apparent size (i.e. the cross section) of the obstacle depends on whether the particles hitting it are moving fast or slow. Or the obstacle size can depend on whether the phonon, for example, is acoustic or optical.

It is easy to become lost in the mathematics, but all we are really trying to do is to figure out how often this type of particle is colliding with that type of obstacle. If we know this (the scattering rate), we can work out the balancing act for the distribution function (using Boltzmann's equation) and then calculate the currents which result from electrical or thermal gradients.

Now, what are the important scattering mechanisms for phonons? For charge carriers? These points are addressed next.

7.5. Phonon Scattering Mechanisms
7.5.1. No Scattering

Although the concept of a phonon "mean free time" is implicit even in discussion the equilibrium distribution of phonons, the effect of scattering is much more profound on the non-equilibrium distribution function. Indeed, only scattering mechanisms tends to return the distribution function to its equilibrium values. If the scattering rate were truly and exactly zero, then once a phonon-heat current was established (for example) the heat current would continue to flow *even after the temperature gradient was removed*. Without scattering, nothing would stop the current from flowing!

This situation is sometimes said to imply an infinite thermal conductivity, but it might be more accurate to say that the thermal conductivity is simply not defined because the thermal conductivity is, *by definition*, the proportionality constant between heat current and temperature gradient. Persistence of heat current in the absence of a temperature gradient does not occur in common experience, but if it did we could not use the concept of "thermal conductivity" at all.

Nevertheless, this discussion serves to point out that a small scattering rate corresponds to a large thermal conductivity and vice-versa.

7.5.2. Phonon-Phonon Scattering

One of the first questions to consider is the thermal conductivity of the ideal crystal, one with no defects of any kind. But even a single phonon represents a defect, in the sense that the atoms have been disturbed from their ideal positions. Does one phonon represent an obstacle to another phonon? The answer is "yes," but the scattering rate of one phonon due to collision with another is really very small, which is why many ideal, insulating crystals (diamond, sapphire, BeO, etc.) have very large thermal conductivity values.

To first order, in fact, all the phonons just add up without disturbing each other at all. And if all the springs in our original mass-and-spring model were ideal springs

there would be no phonon-phonon scattering. But in real materials the springs never quite ideal and these small deviations from ideal behavior mean that the presence of one phonon does disturb all the other phonons. This is called a phonon-phonon interaction and the resulting phonon-phonon scattering rate increases with increasing temperature simply because there are more phonons around.

In the quantum mechanical picture of phonons, this type of phonon-phonon scattering is described as the absorption or emission of one phonon by another phonon, as suggested in Figure 13.

Scattered Phonon:
Increased Energy and Momentum

Incoming Phonon
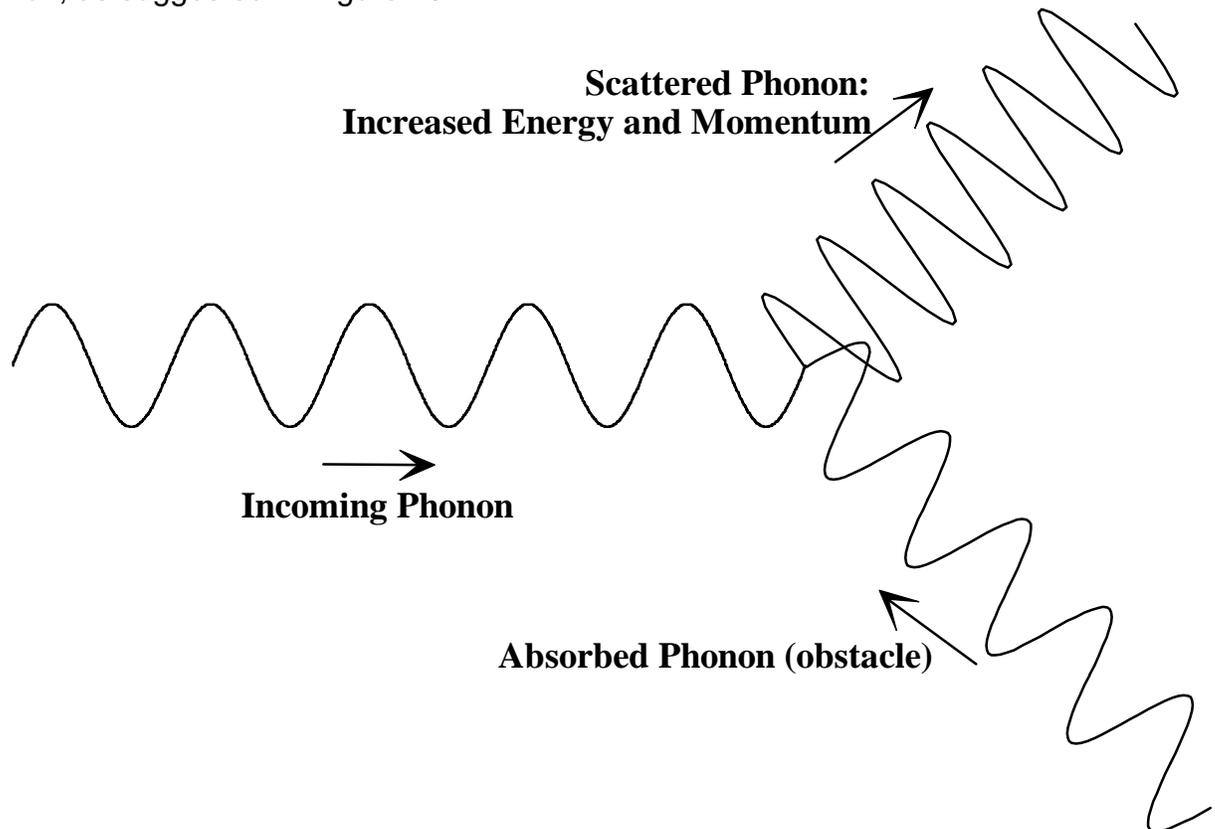
Absorbed Phonon (obstacle)

Fig. 13: Schematic of a Phonon-Phonon Interaction in Which the Incident Phonon Increases Energy, While the "Obstacle" is Represented by an Absorbed Phonon. Phonon Emission is Similar, Except the Incident Phonon Loses Energy While the "Obstacle" is Represented by an Emmited Phonon.

7.5.3.   Point Defect and Alloy Scattering

The next most important source of scattering for phonons is due to point defects. A point defect simply means that one of the atoms making up the crystal is different from all of the others, such as shown in Figure 14.

A point defect is (by definition) very small and has little or no effect on long wavelength, low energy phonons. But short wavelength, high energy phonons are strongly scattered by point defects as suggested in Figure 14. Any type of defect will scatter phonons, but the most important type of point defect in thermoelectric materials is usually an atom with a mass very different from the host.

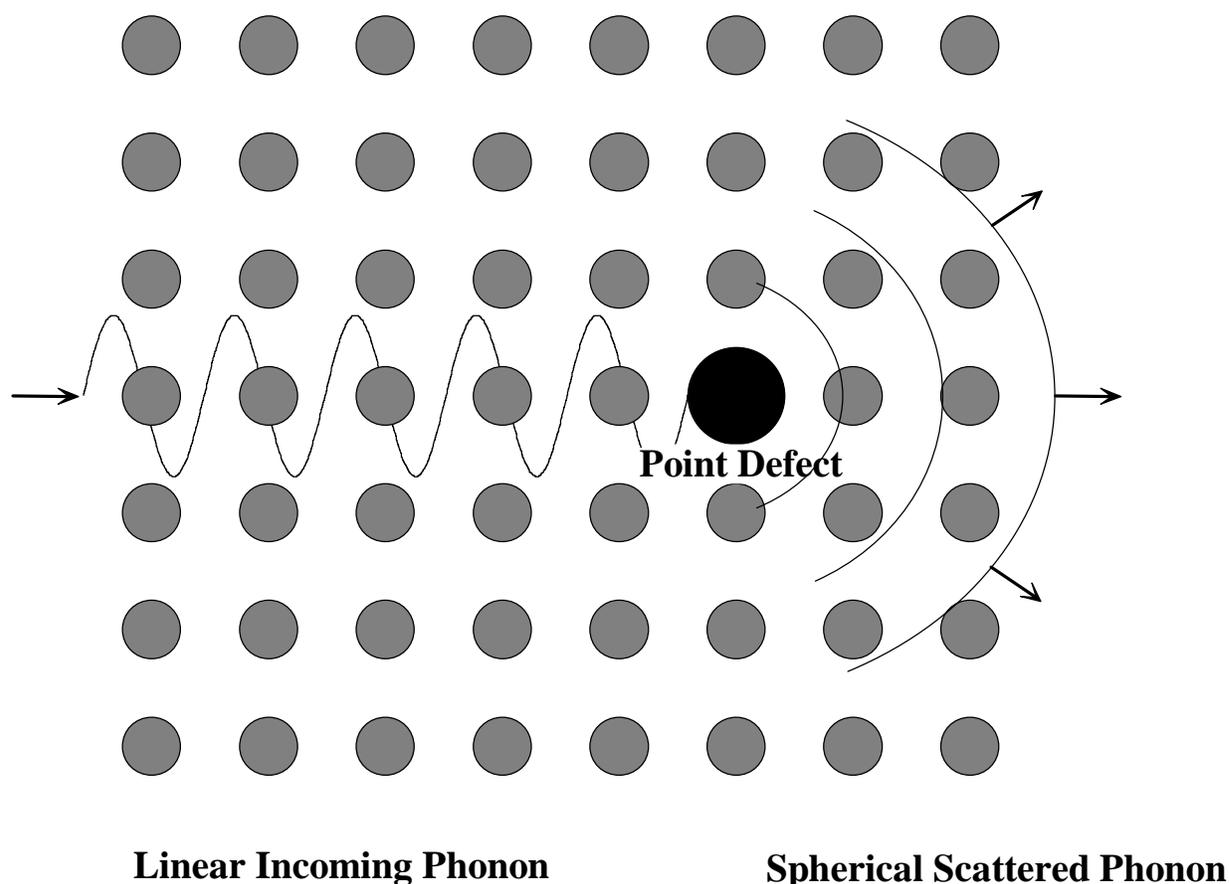**Linear Incoming Phonon**   **Spherical Scattered Phonon**

Fig. 14. A Point Defect Scatters an Incoming Phonon Very Much Like a Rock
Scatters a Water Wave: A Linear Incoming Wave Scatters in all Directions.

When the main difference between the point defect and the host is the mass of
the atom, the scattering is often called *mass fluctuation scattering* or *alloy scattering*.
These terms are generally preferred over the term "point defect" when there are
almost as many "defect" atoms as host "atoms," such as a 50%Si-50%Ge alloy. But
the idea is the same: if the lattice is really uniform, phonons travel with very little
scattering. When the lattice has lots of defects, phonons are strongly scattered.

Alloy scattering is utilized in almost all of the important thermoelectric materials
as a method of lowering the lattice thermal conductivity.

7.5.4.   Phonon-Electron (or Hole) Scattering

When a crystal is doped and charge carriers are created there are at least two
effects which increase the scattering of phonons. First, whatever defect was
introduced to produce carriers (donor or acceptor dopants, vacancies, interstitials,
etc.) represents a point defect and these point defects will scatter phonons as
described above. Generally, however, the number of point defects associated with
dopants that this point defect scattering is much smaller than the point defect
scattering due to, say, alloying.

A much larger effect is the scattering of phonons due to the charge carriers
themselves. To see that charge carriers and phonons should affect each follows
from a fairly simple argument. When we described how to calculate the allowed
energy levels of the electrons we had to take into account the positions of the atoms

in the lattice. The simplest thing to do is to assume the atoms are all in their undisturbed positions and electronic band structure calculations are generally performed using this assumption. But this assumptions means there are no phonons present at all. And indeed, if a single phonon is added to the crystal *the entire band structure is modified* (however slightly).

The shift in the electronic energy levels due to a small deformation of the lattice is called the *deformation potential* and this provides a link between the system of charge carriers and the system of phonons. Through this interaction, a phonon may deposit its energy and momentum into one of the charge carriers. Or, a charge carrier can lose energy and momentum, creating a phonon. In either case, both the phonon and the charge carrier are scattered.

In order to calculate the total scattering rate for any one type of phonon, we just add up the scattering rates between that particular phonon and all of the charge carriers. It turns out that conservation of energy and momentum considerations severely restrict which phonons can interact with which charge carriers. Very low energy, long wavelength phonons can interact with essentially all the charge carriers. But above a certain phonon energy, there are essentially no charge carriers around to interact with. So, the phonon-electron (or hole) scattering mechanism is much more effective at scattering low energy, long wavelength phonons than it is at scattering high energy, short wavelength phonons.

7.5.5. Grain Boundary Scattering and Microstructure

Grain boundaries, voids, inclusions, precipitates and the like are all essentially geometrical obstacles and their scattering rates on phonons can be calculated very much as suggested in Figure 12. There has been a great deal of effort, both theoretical and experimental, on the effect of such microstructural effects on the lattice thermal conductivity and the area continues to be of some interest. It should be pointed out that the sample walls themselves also scatter phonons. Indeed, as the temperature is reduced phonon scattering due to other mechanisms (such as phonon-phonon scattering, for example) can become very small and phonon mean free path values can easily become as large as the sample itself. Under these conditions, the total scattering rate and therefore the thermal conductivity will depend on the sample size!

7.5.6. Typical Total Phonon Scattering Rate

The total scattering rate for a particular type of phonon is the sum of all of the individual scattering rates for that type of phonon. Once the total scattering rate is known, the non-equilibrium phonon distribution function can be determined and the procedure outlined in Table 5 applied to determine the total heat current. The total heat current will typically involve a kind of weighted average of the mean free time, τ, and the heat current will be proportional to the temperature gradient. Again, the proportionality constant is the thermal conductivity due to phonons.

While the usual procedure involves writing down an integral, the procedure of summing all of the contributions to the thermal conductivity can be summarized graphically as shown in Figure 15. Each curve represents the mean free time due to various combinations of scattering mechanisms, in this case for heavily doped SiGe at high temperatures. The thermal conductivity is given by the area under the curves. Note that more scattering mechanisms always gives a lower thermal conductivity.
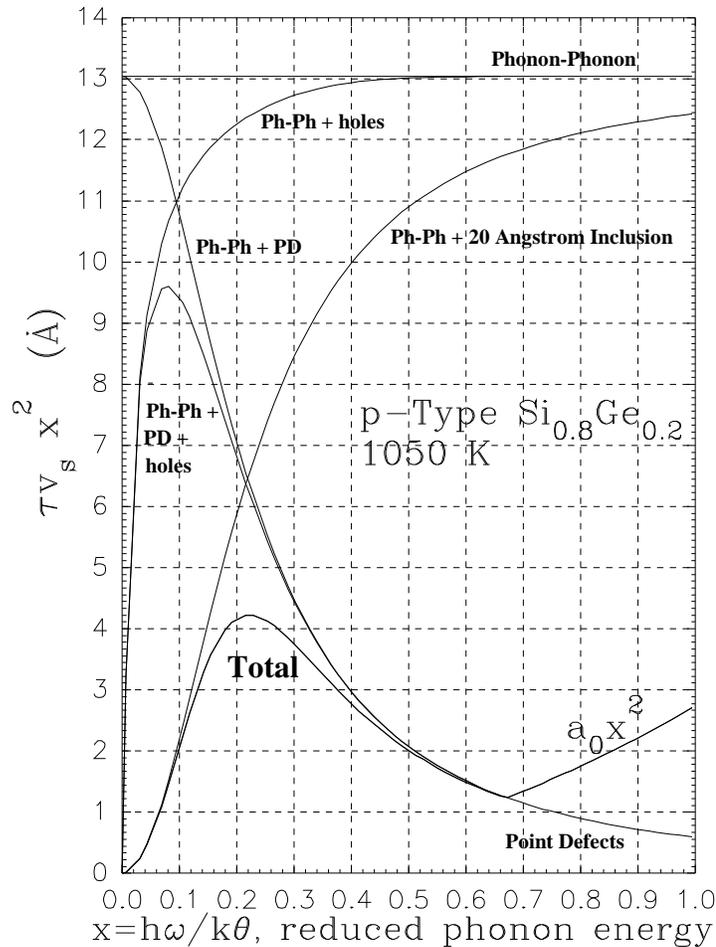
Fig. 15: The Phonon Mean Free Path ($l = \tau v$) for Several Combinations of Scattering Mechanisms, Weighted as Appropriate for Heat Conduction. The Lattice Thermal Conductivity is Given by the Area Under the Curve Appropriate to the Combination of Scattering Mechanisms Under Consideration.

7.6. Charge Carrier Scattering Mechanisms

7.6.1. No Scattering

Just as discussed for phonons above, if there charge carriers were not scattered at all a material could carry a current without any driving force at all. Unlike for phonons, however, there actually are materials in which the charge carrier scattering is truly zero. We call such a material a superconductor and electrical currents induced in such a material will persist indefinitely, even after the action which produced the currents is removed. We say that superconductors have zero resistance, but it might be more accurate to just say that Ohm's law has utterly failed and that the resistivity simply is not defined for such a material.

7.6.2. Electron-Electron Scattering

Electrons do interact with each other, this scattering mechanism is usually neglected altogether in the simplest calculations. The reason is not because electron-electron scattering rates are always small. The reason electron-electron scattering is usually neglected is because this scattering has the relatively unusual property that it does not tend to return the charge carrier system to equilibrium. When an electron collides with another electron, momentum can be exchanged

between the electrons but it cannot be destroyed. So if there was a current before the collision, there will be exactly the same current after the collision. For many purposes, therefore, electron-electron scattering can be neglected. Be aware, however, that a really proper and complete model still must include the effect.

7.6.3. Electron (or Hole)-Phonon Scattering

Above, we discussed the scattering of phonons by electrons. For exactly the same reasons, electrons (and/or holes) are also scattered by phonons. To find the total scattering rate of an electron due to all the phonons, we just add up the scattering of that particular electron due to each of the phonons around.

In this case, there is a simple physical interpretation to the sum of all of the phonons. A single phonon describes displacement of a particular type and wavelength of all of the atoms in the crystal. But the sum of all phonons describes the average displacement of an atom due to thermal agitation. Kind of the average wobble of an atom. Since it is moving back and forth, the atom looks like an obstacle to an electron. And in fact this "obstacle" looks the same size to all electrons.

But since thermal agitation increases with increasing temperature, the scattering rate increases with temperature. For most semiconductors and metals, electron scattering due to phonons is the main scattering mechanism and this is why the resistivity of metals increases with temperature and why the mobility of semiconductors decreases with increasing temperature.

7.6.4. Charged Impurity Scattering

The next most important scattering mechanism for charge carriers is due to charged impurities, usually the donors or acceptors which created the charge carriers themselves. This is a type of point defect scattering, but the charge on the impurity deflects passing carriers very strongly. Charged impurity scattering is basically independent of temperature and often becomes the most important scattering mechanism at low temperatures, where electron-phonon scattering becomes negligible.

7.6.5. Neutral Impurities and Alloy Scattering

Neutral impurities, such as dopants which are not ionized or alloys of materials with the same number of outer shell electrons (such as Si alloyed with Ge) are still defects, even if they are not charged. And they still scatter charge carriers and act to reduce the carrier mobility. This effect is well known in metals: an alloy of Cu and Ag in fact has an electrical resistivity many times the resistivity of pure Cu or pure Ag.

It was mentioned above that most useful thermoelectric materials are alloys because the lattice thermal conductivity is reduced due to alloy scattering. But in fact the electrical mobility (and electrical conductivity) is also generally reduced by alloying. Alloying is successful for thermoelectric materials because the reduction in the lattice thermal conductivity is generally much greater than the reduction in the electrical conductivity. In terms of electrical performance alone, however, the pure material is generally significantly better than the alloy.

7.6.6. Grain Boundaries and Other Scattering

Grain boundaries and other types of crystalline defects do scatter the charge carriers, but non-scattering effects are often much greater. A grain boundary, for example, is a disruption of the regular pattern of bonds in the crystal. Generally there are strains in the bonds or incomplete bonds around the grain boundaries

which can amount to extra (or absent) energy states and extra (or absent) charge. The net result is that an electrical potential barrier is set up along a grain boundary.

The grain boundary potential barrier may not be as large as the barrier at the edge of the sample, but it is still large enough to affect motion of carriers across the boundary. Not all of the carriers will have enough energy to cross the potential barrier and the current flow can be seriously reduced. While scattering is also present, the major effect is that the barrier acts much like a high resistance inclusion. It can be very difficult to untangle the effects of grain boundaries from true scattering mechanism effects.

7.6.7.   Typical Total Charge Carrier Scattering Rate

Many thermoelectric materials can be well described by accounting for just two charge carrier scattering mechanisms, scattering due to phonons and scattering due to charged impurities. The mean free path due to these scattering mechanisms is illustrated in Figure 16. The deviation of the distribution function from the equilibrium distribution function is proportional to the mean free path, so the mean free path essentially determines all of the electrical transport coefficients.
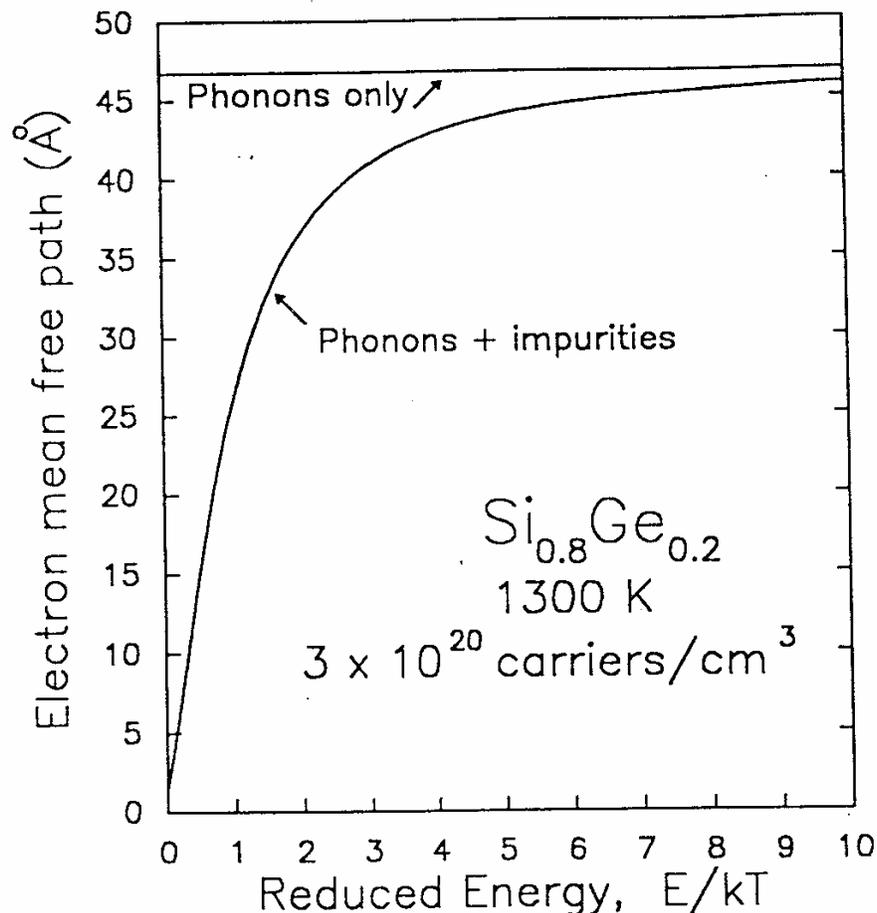

Fig. 16: The Electron Mean Free Path ($l = \tau v$) due to Electron-Phonon Scattering Alone (Upper Curve) and Due to the Combined Effects of Phonon and Impurity Scattering (Lower Curve).

8.   SELECTED THERMOELECTRIC PROPERTY TRENDS

While the entire procedure for calculating thermoelectric properties has in fact been outlined above, a few schematic examples may help to illustrate how the process works in practice. This can be a complex mathematical operation as it typically involves triple integrals to account for the summations over all three dimensions of wavenumbers which are allowed. Instead, the summations over allowed wavenumbers are often converted to a single summation over allowed energy states. An additional factor is introduced to account for the fact that there are typically many charge carriers with the same energy, but different wavenumbers. This factor is called the *density of states*. The density of states, $D(\varepsilon)$, contains a great deal of the difficult three dimensional integration factors and only needs to be calculated once.

We also note that the non-equilibrium distribution function can always be expressed as a sum of the equilibrium distribution function plus a small correction, which we calculate using Boltzmann's equation and the scattering rate. If we are calculating currents, the equilibrium portion of the full distribution function can be safely ignored, because there are no currents in equilibrium.

Let us now examine the calculation of electrical and heat currents associated with a single band of electrons. The general procedure given can, with the simplifications just described, be rewritten as shown in Table 6.

Table 6: Procedure for Calculating the Electrical and Heat Currents Associated with a Single Band of Electrons.

Total Property		Sum over allowed energy states	x	# of allowed wavevectors/energy	x	Contribution of each electron	x	Distribution Function
Electrical Current	$=$	$\varepsilon \geq 0$	x	$D(\varepsilon)$	x	$(-e)\, x\, v(\varepsilon)$	x	$\delta f(\varepsilon)$
Heat Current	$=$	$\varepsilon \geq 0$	x	$D(\varepsilon)$	x	$(\varepsilon-\mu)\, x\, v(\varepsilon)$	x	$\delta f(\varepsilon)$

Band Edge | Band Edge | Band Edge

m | m | m

Equilibrium Distribution Function f

0 | 0 | 0

Deviation from Equilibrium $t\left(-\dfrac{df}{de}\right)$

0 | 0 | 0

Density of States

0 | 0 | 0

Contribution of Each Carrier

$(-e)$ | $(e-m)$ | $(e-m)^2$

0 | 0 | 0

Weighted Contribution from Each Energy

0 | 0 | 0

Transport Coefficient Given by Area Under Curves:

Energy | **Energy** | **Energy**
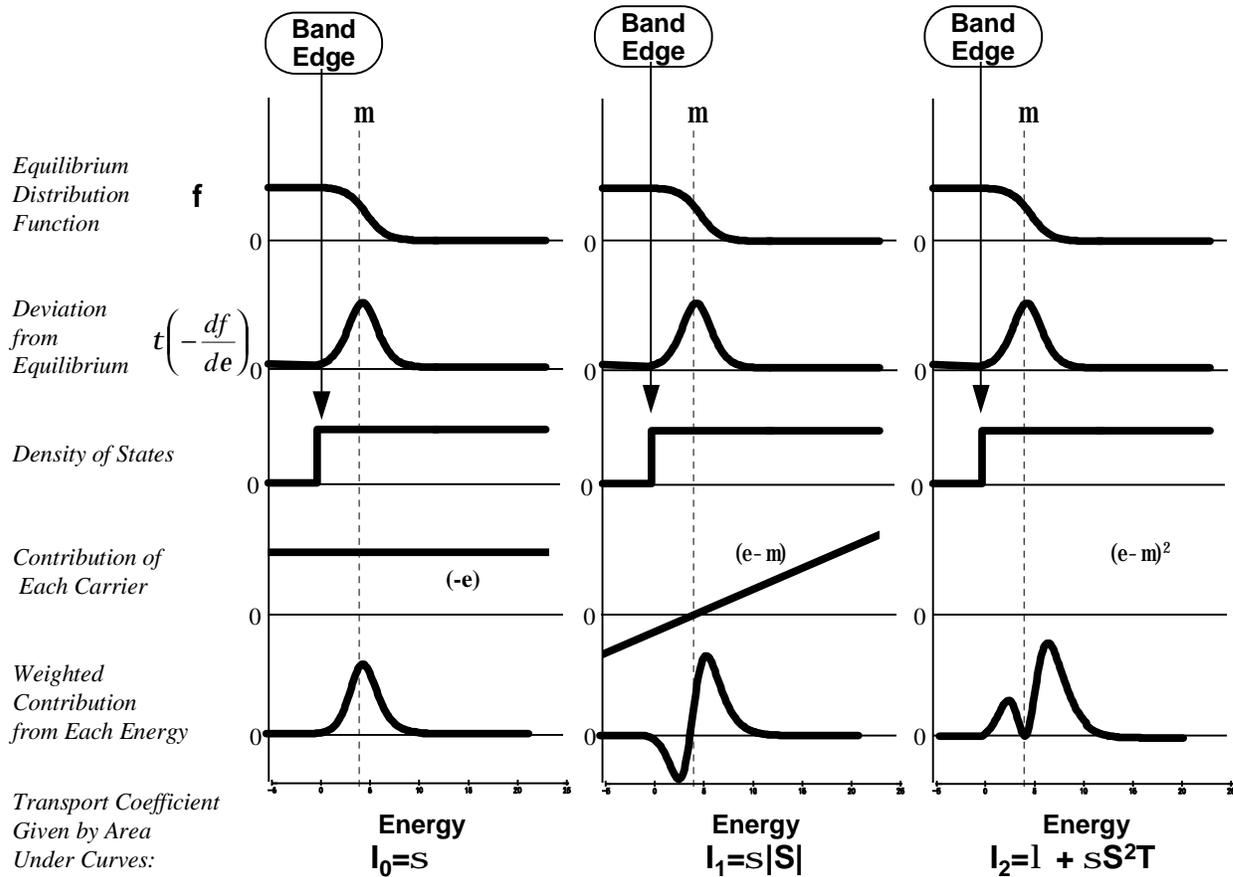
$I_0 = s$ | $I_1 = s|S|$ | $I_2 = l + sS^2T$

Fig. 17: Schematic of Calculation of Transport Coefficients. The Band Edge Represents the Lowest Energy State Allowed for the Particular Band Under Consideration.

Note that each electron carries an electric current given by $(-e)v$, since electrons are negatively charged. The heat current carried by each electron is $(\varepsilon-\mu)v$. ε is the total energy of the electron. μ is called the *chemical potential* and essentially it represents the internal energy associated with a single electron. Heat is the difference between the total energy and the internal energy, which is basically wh y the factor $(\varepsilon-\mu)$ is used for the heat current.

These factors can be illustrated graphically as shown in Figure 17. The main points in this Figure can be extracted directly from the definitions given previous ly, but it is only schematically correct and intended merely as an illustration. Each of the transport coefficients is given by a certain type of weighted average of the scattering time. With one weighting factor, you get the electrical conductivity. Another weighting factor gives a quantity related to the Seebeck coefficient. A third weighting factor gives a quantity related to the thermal conductivity.

8.1. Electrical Conductivity

The electrical conductivity (σ) is the simplest property to calculate. From Figure 17, you can see that a greater chemical potential (which just corresponds to a larger number of carriers) will increase σ. More carriers, better conductivity. Also, a

greater scattering time will increase σ. This is to say that less scattering means greater conductivity.

8.2. Seebeck Coefficient

Before examining the calculation, remember what the Seebeck coefficient means: a material in a temperature gradient will develop a voltage between the hot end of the sample an the cold end of the sample. Why? The charge carriers at the hot end of the sample have, on average, more energy than the charge carriers at the cold end. So, they are moving faster at the hot end than the cold end. Why don't they just tend to diffuse down to the cold end?

The answer is: they *do* diffuse to the cold end. But after only a few extra carriers have collected on the cold end, they set up a voltage which prevents further carriers from building up. At this point the hot end is deficient by a few carriers. The Seebeck coefficient represents the electrical potential required to balance the thermally driven diffusion.

But, not all the charge carriers have the same velocity. In fact, as we have discussed, the charge carriers have an entire distribution of velocities. The Seebeck coefficient represents the *average* balancing act between thermal and electrical forces. Carriers with below average energy tend to under contribute to the Seebeck and carriers with above average energy tend to over contribute to the Seebeck.

The middle panel of Figure 17 illustrates the calculation is somewhat greater detail. The magnitude of the Seebeck coefficient, $|S|$, is related to the area under the bottom curve in the middle panel. Carriers with energy above the chemical potential contribute to making $|S|$ bigger, while carriers with lower energy contribute to making $|S|$ smaller. To make the Seebeck larger, you only need to increase the relative contribution of carriers with $\varepsilon > \mu$ compared to the carriers with $\varepsilon < \mu$.

The first way to increase the Seebeck coefficient is to decrease the chemical potential, μ. Which is just another way of saying, lower the carrier concentration. Conversely, as the carrier concentration and chemical potential are increased, the carriers become (in a sense) more symmetrically divided between states below average and above average in energy. So, a high doping levels the cancellation becomes more complete and the $|S|$ becomes smaller.

Other ways to alter $|S|$ involve modifying the density of states or the scattering rate to shift the balance to higher energy states. This is a little harder to control in practice and the only readily adjustable tool to change the Seebeck coefficient is to alter the doping level.

8.3. Electronic Contribution to the Thermal Conductivity

In addition to the heat current carried by the phonons, there is also a heat current due to the charge carriers called the electronic contribution to the thermal conductivity. The quantity which is actually calculated with the techniques described here is the thermal conductivity plus another term related to the Seebeck and electrical conductivity, as shown in the third panel of Figure 17. Although the calculation is somewhat more complex, Figure 17 suggest the same factors which increase the electrical conductivity (increase μ and/or τ, for example) also increase the electronic contribution to the thermal conductivity.

In fact, the electronic contribution to the thermal conductivity is approximately proportional to the electrical conduction. This relationship between electrical conduction and thermal conduction due to carriers is called the *Wiedemann-Franz law*.

8.4. Optimum doping

Finally, we are ready to consider the full thermoelectric figure of merit. Figure 18 shows idealized trends in the thermoelectric properties as a function of doping level. The Seebeck coefficient and lattice contribution decrease with increasing doping level. The electrical conductivity and lattice contribution increase with doping level. Typically, the optimum doping level is in the range of 10^{19}-10^{20} cm^{-3}.

8.5. Alloying

Several effects take place when forming an alloy between two different semiconductors, such as $A_{1-x}B_x$. Even if the carrier concentration values is the same for all samples in the alloy system, each of the thermoelectric properties will in general vary as the alloy composition is varied. Ideally, the Seebeck changes very little with alloy composition (this is *not true* for metals, however). Because of alloy scattering, however, both the electrical and thermal conductivities will generally be smaller than simple linear average of the two end members of the alloys. These effects are illustrated in Figure 19.

9. SUMMARY

This course has outlined the conventional theory of the thermoelectric properties of solids. The main concepts pertaining to phonons and charge carriers, both in equilibrium and in non-equilibrium have been discussed. The concepts have been emphasized here, rather than the mathematics, with the belief that the mathematics can be learned with practice.
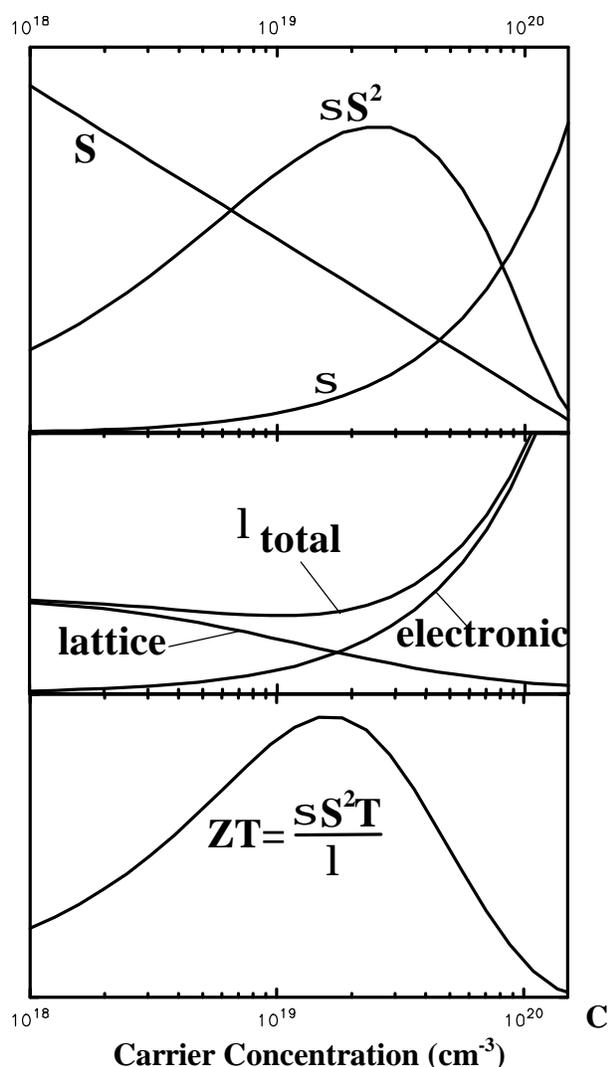
Fig. 18: The Effect of Carrier Concentration on the Various Thermoelectric Properties.
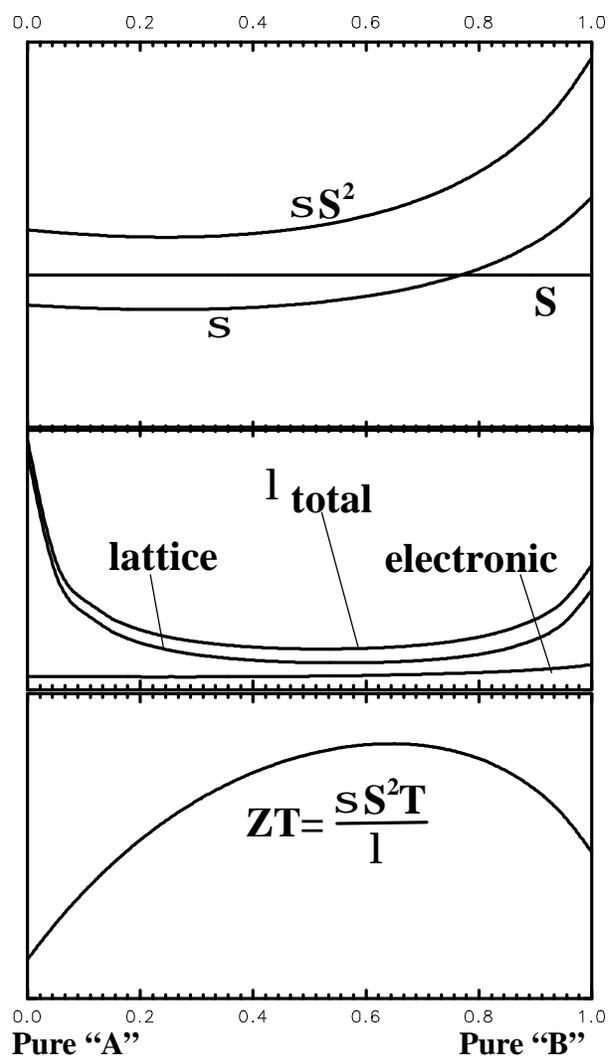
Fig. 19: The Effect of Alloying on the Various Thermoelectric Properties. The Largest Effect is Usually on the Lattice Component of the Thermal Conductivity and for this Reason Alloys are Generally Preferred Over Pure Compounds.

It should be emphasized at this point, however, that by omitting the mathematics the descriptions have become necessarily imprecise. Where several paragraphs, a Table and a Figure have been required in the present discussion, exactly the same thing can be often be stated in a single line with the appropriate equation. It is hoped, however, that by presenting the concepts here in a verbal and visual format, the student will more easily be able to grasp the meaning of the mathematics when it is finally confronted. For the serious student, however, fluency with the appropriate mathematics is essential and further reading of some of the more standard texts is highly recommended.

10. SUGGESTED READING

Ziman, J. M, *Electrons and Phonons*, Oxford Press, Oxford, 1960.
> This classic text offers a very deep and well organized discussion of transport theory. It is not for the timid, however, as a rather high level of mathematical physics is assumed.

Ashcroft, N. W. and Mermin, N. D., *Solid State Physics*, Holt, Rinehart and Winston, New York, 1976.
> An excellent overall introduction to solid state physics for the advanced undergraduate or early graduate student. This is a general text and while transport theory is quite adequately covered, the thermoelectric specialist may want a deeper discussion of thermoelectric-related issues.

Fistul', V. I., *Heavily Doped Semiconductors*, Plenum Press, New York, 1969.
> Uniquely focused on issues peculiar to heavily doped semiconductors (including thermoelectrics) this book is particularly strong on providing a consistent notation for the essential transport integrals.

Rowe, D. M., and Bhandari, C. M., *Modern Thermoelectrics*, Holt Saunders, London, 1983.
> Easily the best and most complete resource specifically on thermoelectricity in many years. Every thermoelectrician should read this book.

Bhandari, C. M., and Rowe, D. M., *Thermal Conduction in Semiconductors*, Wiley, New York, 1988.
> Specifically focused on transport in semiconductors, and not just thermal transport. This book supersedes all of the earlier texts on thermoelectric properties of semiconductors.

Ioffe, A. F., *Semiconductor Thermoelements and Thermoelectric Cooling*, Infosearch, London, 1957.
> Ioffe's classic text is still valuable after all these years. If you think you are doing something new, check here first because probably Ioffe thought about it.

de Groot, S. R., and Mazur, P., *Non-equilibrium Thermodynamics*, Dover, New York, 1984.
> Thermoelectricity is a special case of cross-effects and many other non-equilibrium systems have been studied. This text places thermoelectric phenomenology on a firm footing with regard to thermodynamics in general. Not much immediate impact on device design or even materials development, but required reading for the well educated thermoelectrician.

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1. Dolling, G., *Int. Atomic Energy Agency*, Vienna 1, 37, 1963.
2. Krishnamurthy, S., and Sher, A., *Phys. Rev.,* **B33**, 1026, 1986,