

Use of Atomic Displacement Parameters in Thermoelectric Materials Research

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I. Introduction

Progress in thermoelectrics requires new materials, and finding new materials requires new ideas and new guidelines for materials selection. Most of the present chapter is devoted to explaining how a particular piece of crystallographic information—atomic displacement parameters (ADPs)—can be used to identify materials with an extremely low lattice thermal conductivity. Before launching into an exposition of this new guideline, however, we briefly review the existing guidelines as there are few places in which they are discussed all together.

Modern thermoelectrics research dates from Ioffe's observation (Ioffe, 1957) that *heavily doped semiconductors* ($n = 10^{18} - 10^{20} \text{ cm}^{-3}$) *make the best thermoelectrics*. This observation follows from the expression for the thermoelectric figure of merit, $Z = S^2\sigma/\kappa$ ($S \equiv$ Seebeck coefficient, $\sigma \equiv$ electrical conductivity, $\kappa \equiv$ thermal conductivity) and the behavior of real-world materials as the carrier concentration is varied. Metals have a high σ but a low S ; insulators have a high S but a low σ . It turns out that a carrier density of about 10^{19} cm^{-3} maximizes the quantity $S^2\sigma$ (known as the *power factor*), and such a carrier density is characteristic of a heavily doped semiconductor.

The next guideline is the “ $10 k_B T$ rule” and concerns the size of the semiconducting energy gap. This rule states *that good thermoelectrics should have energy gaps that are $10 k_B T_{op}$* , where T_{op} is the operating temperature. The reasoning behind this rule is as follows. Small gaps are generally good for thermoelectric performance because they lead to higher carrier mobilities. However, if the gap is too small then the thermal excitation of minority carriers will adversely affect the figure of merit, since electrons and holes carry heat in opposite directions. An in-depth examination of this situation has been given by Mahan et al 1989.; they find the $10k_B T$ rule holds for direct and indirect gaps, and for both phonon and impurity scattering. The rule is also in reasonable accord with experimental data on good thermoelectrics.

The theory of thermoelectrics shows that $Z \propto \mu(m^*)^{3/2}$ ($\mu \equiv$ carrier mobility, and $m^* \equiv$ density of states effective mass) (Goldsmid, 1986). Therefore it is desirable to maximize both m^* and μ . Two important guidelines for materials result from the above proportionality. The first follows from the observation that m^* can be increased without affecting μ much if the semiconductor has several equivalent bands; therefore, *good thermoelectrics are likely to be multivalley semiconductors, and crystal structures with high symmetry are required to produce several equivalent bands* (Mahan,1998; Goldsmid, 1986). The second concerns the electronegativity difference between the elements making up the thermoelectric material (Slack, 1995). The electronegativity difference is a measure of the covalency of the bonding in a material. Large electronegativity differences indicate ionic bonding, large charge transfer, and strong scattering of electrons by optical phonons. This strong scattering leads to low carrier mobilities, and is one reason why oxides generally make poor thermoelectric materials. High

electron mobilities, on the other hand, are found in materials composed of elements with very similar values of electronegativity. *Good thermoelectrics, then, are composed from elements having small differences in electronegativity.*

Finding materials with favorable electronic properties is only half the story. The other half concerns finding materials with exceptionally low values of lattice thermal conductivity. A simple but useful expression for the lattice component of thermal conductivity is given by $\kappa_{\text{Lattice}} = 1/3 C_V v_s d$, where C_V is the heat capacity per unit volume, v_s is the velocity of sound, and d is the mean free path of the heat carrying phonons. Many of the guidelines for finding materials with a low lattice thermal conductivity can be understood from the above expression.

A key guideline is to *look for materials in which the average atomic weight is high*. The origin of this rule is simple: heavy atoms lead to small sound velocities and a correspondingly low thermal conductivity (Ashcroft and Mermin, 1976).

Next, it is important to remember that *mass fluctuation scattering can be used to reduce the lattice thermal conductivity*. The idea behind this rule is that isovalent substitutions will scatter heat carrying phonons strongly because the wavelength of these phonons is about the same as the distance between the scattering centers. Electrons, on the other hand, have a longer wavelength and will be scattered less. The value of ZT will therefore increase.

Another guideline is that *crystal structures with many atoms per unit cell tend to have low lattice thermal conductivities*. This rule is not as well grounded theoretically (or experimentally) as the first two, but nevertheless seems to be validated by experience. One explanation for this trend is that the number of defects per unit cell tends to grow rapidly as the size of the cell increases. The amount of disorder, then, tends to be relatively greater for materials with many atoms per unit cell. Another explanation may lie in the breakdown of the concept of a phonon as the number of atoms in the unit cell grows large. Remembering that there are $3n$ phonon modes, where n is the number of atoms in the unit cell, it is reasonable to assume that as n grows large these modes will begin to overlap and will no longer be distinguishable. It has been argued by Allen and Feldman (1993) that thermal transport in this situation is beginning to resemble thermal transport in a glass.

Another rule is that *crystal structures in which the ions are highly coordinated tend to have lower thermal conductivities than crystal structures in which the ions have low coordination*. This is an empirical relationship proposed by Spitzer, 1970 based on a compilation of thermal conductivity data on more than 200 semiconductors. We are not aware of any generally accepted explanation for this behavior, although it is interesting that highly coordinated ions are also involved in the reduction in thermal conductivity associated with the “rattling” cations discussed next.

Very recently, a guideline originally proposed by Slack, 1995, involves *finding materials in which one or more atoms per unit cell are loosely bound and “rattle” in an oversized cage*. The cage is invariably constructed from many atoms that highly coordinate the rattler. Such rattlers resonantly scatter phonons, and can reduce the mean free path of the heat carrying phonons to dimensions comparable to an interatomic spacing. The effect on the thermal conductivity is dramatic, as recent work on filled skutterudites (Sales et al., 1996; Sales et al., 2000) and germanium clathrates (Cohn et al. 1999) has shown.

Finally, it is important to recognize that although these guidelines describe most of the better thermoelectrics, there are some relatively good materials that do not obey the rules. A good example is NaCoO_2 . This material is made up of light atoms with large electronegativity

differences, yet at room temperature the power factor of this compound is greater than that of Bi_2Te_3 (Terasaki et al., 1997).

The rest of this chapter is devoted to exploring the connection between a particular piece of crystallographic information, atomic displacement parameters, and lattice thermal conductivity. In the description of a new crystalline compound, crystallographers normally tabulate the room temperature atomic displacement parameter (ADP) values for each distinct atomic site in the structure. These values measure the mean square displacement of an atom type about its equilibrium position and thus comprise some of the first information that is known about a new crystalline compound. The value of the mean square atomic displacement can be due to the vibration of the atom or to static disorder. The effects that this parameter can have on various physical properties, however, have not been widely recognized. In particular, ADP values are not normally used by solid state physicists or chemists as a guide in the search for new compounds with specific properties. ADPs are regarded by many scientists as unreliable since in many of the earliest structure determinations, the ADP values would often act as repositories for much of the error in the structure refinement. In addition, crystallographers have not always reported ADP information using a consistent definition, adding further confusion as to the usefulness of ADPs (Trueblood et al. 1996). The purpose of this chapter is to illustrate that when properly determined, the ADP values can be used as a guide in the search for crystalline materials with unusually low lattice thermal conductivities. These materials are of particular interest in the design of thermoelectric compounds with improved efficiencies.

II. Elementary theory of atomic displacement parameters

Atomic displacement parameters (ADP) measure the mean-square displacement amplitudes of an atom about its equilibrium position in a crystal. In general there is no reason to assume that the displacements are the same in all directions, or that they bear any particular relation to the crystallographic axes. For this reason crystallographers typically report ADP information as a 3x3 matrix, U_{ij} , that allows for anisotropic displacements. In the description of a new crystalline compound, crystallographers normally tabulate the room temperature ADP matrix for each distinct atomic site in the structure (Trueblood et al. 1996; Dunitz et al. 1988; Willis and Pryor, 1975, Kittel 1968). The various ADP values thus comprise some of the first information that is known about a new crystalline compound. Often, an isotropic ADP value, U_{iso} , is given for each site. U_{iso} corresponds to the mean square displacement averaged over all directions and is given by one third of the trace of the diagonalized U_{ij} matrix. U_{iso} is a scalar which makes it easy to qualitatively compare the relative displacements of different atom-types in the structure. Sometimes U_{iso} is the only ADP information given if the full U_{ij} matrix cannot be extracted from the x-ray or neutron diffraction data set or if there are no significant anisotropic displacements. The U_{ij} data are often expressed in crystal structure figures by drawing ellipsoids around each atom. The surface of each ellipsoid corresponds to surfaces of constant probability. Normally the 50 percent ellipsoid is drawn corresponding to a 50 per cent probability of finding the atom inside the ellipsoid. The 50 per cent probability ellipsoids can be drawn for each atom in the unit cell by a computer program such as ORTEP (Oak Ridge Thermal Ellipsoid Plots, Johnson, 1965). An example of an ORTEP drawing of the semiconducting clathrate $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ is shown

in Fig 1(Chakoumakos 2000). The value of the mean square atomic displacement can be due to the vibration of the atom and/or to static disorder.

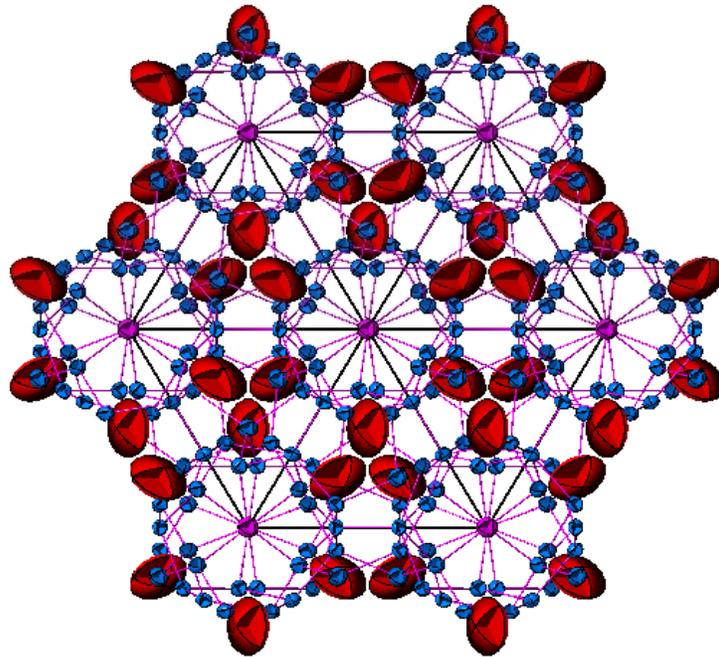


Fig 1. Structure of $Sr_8Ga_{16}Ge_{30}$ as determined using powder neutron diffraction (Chakoumakos et al. 2000). The large ellipsoids correspond to the motion of Sr atoms at the center of a large cage consisting of 24 atoms of Ge or Ga (randomly distributed). The view shown is along the (111) axis of the crystal.

In a neutron or x-ray diffraction experiment, thermal vibrations of the atoms reduce the intensity of the Bragg reflections but do not effect the width. The scattered intensity, I , of a typical Bragg peak is qualitatively given by :

$$I = I_0 \exp [-1/3 \langle u^2 \rangle (\Delta k)^2] \quad (1)$$

where I_0 is the scattered intensity from a rigid lattice (no vibrating atoms), $\langle u^2 \rangle$ is the mean square displacement of an atom about its equilibrium position, and Δk is the magnitude of the scattering vector (which increases as the sine of the scattering angle) (Kittel, 1968). In the

physics literature the exponential factor is often referred to as the Debye-Waller factor. Atoms in a crystal vibrate more at higher temperatures which implies that $\langle u^2 \rangle$ increases monotonically with temperature.

The intensity of X-rays (or neutrons) scattered by a crystal is the sum of the Bragg scattering and the thermal diffuse scattering (TDS). TDS corresponds to scattering in which one or more phonons are excited. As the temperature is raised, the overall intensity from Bragg scattering decreases with a corresponding increase in TDS.

ADP values can be reliably determined using powder neutron diffraction and single crystal x-ray or neutron diffraction. The analysis of neutron data is usually easier for two reasons. First, the neutron wavelength used is typically the order of 1-2 Å which is much larger than the interaction distance between the neutron and the atomic nucleus. The nuclear scattering cross section is, therefore, a scalar with no angular dependence. X-rays scatter from the electron clouds around the nucleus and the resulting atomic form factor does have an angular dependence. This means that the intensity I_0 (Eq. 1) depends on angle. Since the ADP information is in the angular dependence of the scattered intensity ($\langle u^2 \rangle (\Delta k)^2$) (see Eq. 1), it is sometimes difficult to separate ADP information from atomic-form-factor effects. Second, for most compounds, the absorption correction for neutrons is small, but for x-rays absorption must be carefully determined to obtain good ADP values, particularly for compounds with heavy elements.

In the present article ADP data are all interpreted within a harmonic approximation for the atomic potential well. For the analysis of low temperature ADP data, this approximation is adequate. However, there are several examples in the literature (Kisi and Yuxiang, 1998) where high temperature ADP data have been used to determine the anharmonic component to the vibration. This discussion is outside the scope of this article but the interested reader can refer to Willis and Pryor, (1975), and Kuhs (1988).

III. Interpreting ADP Data

Interpreting the meaning of the ADP information requires a model. There are two simple models of the vibrational properties of a solid that can be used to extract useful information from the ADP data: the Debye model and the Einstein model. As will be shown below, both of these models are useful in understanding the thermal transport and thermodynamic properties of clathrate-like thermoelectric compounds.

1. Einstein Model

For clathrate-type compounds, in which one of the atoms is poorly bonded and rattles in an oversized cage, the simplest model for the "rattler" is that of a harmonic oscillator (also called an Einstein oscillator). In this model it is assumed that all of the rattlers vibrate independent of each other and at the same frequency (a local mode). How far this model can be applied to the averaged motion of an averaged atom in a crystal structure is an open question. Clearly the ADP values provide no information about correlations with the motion of other atoms (i.e., lattice dynamics). This local approach, however appears to work well in interpreting the ADP information from the rattler (Sales et al., 1999, Sales et al, 2000).

The mean square displacement amplitude, $\langle u^2 \rangle$, of a quantized harmonic oscillator is given by:

$$U_{\text{iso}} = \langle u^2 \rangle = \frac{h^2}{8\pi^2 m \nu} \cdot \coth(h\nu/2k_B T) \quad (2)$$

where ν is the frequency of vibration, m is the reduced mass, and h and k_B are the Planck and Boltzmann constants, respectively (Dunitz et al., 1988). At high temperatures, where $h\nu \ll 2k_B T$, Eq.(2) reduces to the classical expression:

$$U_{\text{iso}} = k_B T / K = h^2 T / (4\pi^2 m k_B \Theta_E^2) \quad (3)$$

where K is the spring constant of the oscillator and the Einstein temperature of the oscillator is defined as $\Theta_E = h\nu/k_B$. Equation 2 is plotted in Fig. 2 for several values of Θ_E . From the high temperature slope of U_{iso} , the Einstein temperature of the rattler can be estimated. Notice that if the temperature at which the ADP information is known (usually room temperature) is greater than or the order of Θ_E , then the room temperature ADP data and the origin ($T=0$, $U_{\text{iso}} = 0$) can be used to estimate the slope, and hence Θ_E . This is significant since for a new compound usually only room temperature ADP data are available. The above analysis, however, assumes that the value of U_{iso} is all due to dynamic motion of the atom which neglects the possibility of static disorder. Static disorder is normally only a problem in solid solutions or in compounds that contain large concentrations of defects. Static disorder tends to displace the curves shown in Fig. 2 upward by a constant amount. If the static disorder is large, the ADP data from one temperature cannot be used to estimate the Einstein (or Debye temperature, see below).

2. Debye Model

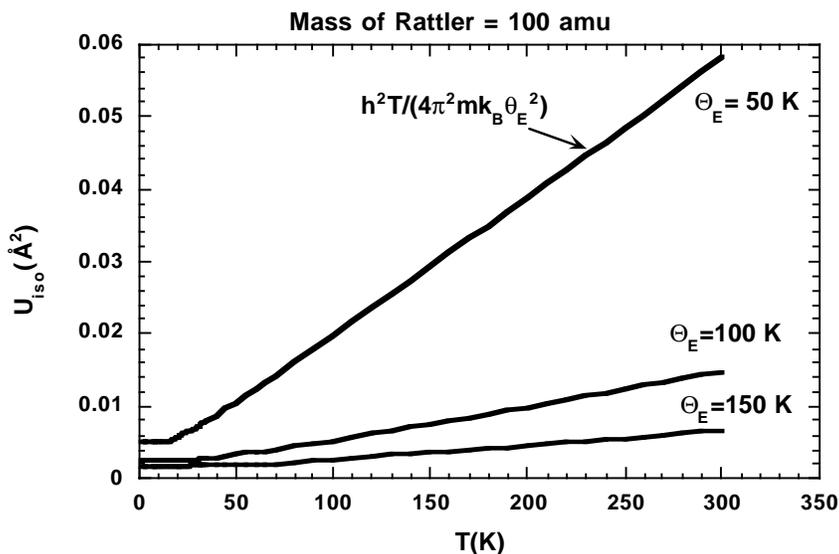


Fig. 2. Calculated mean square displacement amplitude (U_{iso}) of a quantum harmonic oscillator with a mass of 100 amu and the Einstein temperatures (Θ_E) shown. At high temperatures, these curves are linear in temperature with a slope as shown.

In a real crystal, the vibrations of different atoms are correlated and are described by specific wavelike modes (phonons) which represent the fundamental excitations of the crystalline lattice. In general the various phonon modes fall into 3 acoustic branches and $3N-3$ optical branches, where N is the number of atoms in the primitive unit cell (see for example Kittel, 1968, or Willis and Pryor 1975). In principle, these modes can be determined using inelastic neutron scattering or can be calculated using lattice dynamical models. Neither the experimental or theoretical approaches are easy, and as a result the lattice dynamics are only understood in detail for a few simple materials.

The Debye model is the simplest attempt to account for the correlated motion of atoms in a crystal. In the Debye model all of the phonons (normal modes) are assumed to have the same velocity v , which implies a linear relationship between the frequency ω and the wavevector K of each mode since $v = \omega/K$, $K = 2\pi/\lambda$ where λ is the wavelength of the normal mode. The total number of modes is limited to $3N_{\text{solid}}$, corresponding to the correct number of normal modes. This implies an upper limit for ω and K normally denoted as ω_D and K_D . The maximum wavenumber, K_D , is simply related to the number of atoms per unit volume, n , and is given by :

$$K_D = (6\pi^2 n)^{1/3} \quad (4)$$

The Debye temperature, Θ_D , is defined as $\hbar\omega_D/2\pi k_B$. If the Debye temperature is known, the average velocity of sound is also known and vice-versa since

$$v = \omega_D / K_D = \Theta_D 2\pi k_B / [h (6\pi^2 n)^{1/3}] \quad (5)$$

Direct measurements of the transverse, v_t , and longitudinal, v_s velocities of sound can also be used to estimate a Debye temperature or the Debye velocity of sound given in Eq. (5). For isotropic polycrystalline samples, a frequently used expression (Anderson, 1963) is :

$$v = (1/3 [2/v_t^3 + 1/v_s^3])^{-1/3} \quad (6)$$

Expressions relating elastic constant data to the Debye velocity of sound also are described in the literature (Anderson, 1963). The Debye model of lattice vibrations is in general much too simple, but at low temperatures (typically $T < \Theta_D/50$) where only long wavelength phonons are excited, the Debye model is exact.

For a monatomic cubic crystal, U_{iso} vs T can be solved exactly within the Debye approximation (Willis and Pryor, 1965) and is given by :

$$U_{\text{iso}} = \langle u^2 \rangle = [3\hbar^2 T / (4\pi^2 m k_B \Theta_D^2)] [\Phi(\Theta_D/T) + 0.25 \Theta_D/T] \quad (7)$$

and

$$\Phi(x) = 1/x \int_0^x \frac{y dy}{(e^y - 1)} \quad (8)$$

At high temperatures ($T > \Theta_D$) U_{iso} is linear in T and is given by :

$$U_{\text{iso}} = [3h^2/(mk_B 4\pi^2 \Theta_D^2)] T \quad (9)$$

and at low temperatures U_{iso} approaches the zero point value of $3h^2/(16\pi^2 mk_B \Theta_D)$. Fig. 3 illustrates how U_{iso} depends on temperature for Debye temperatures of 100, 200, and 300 K, and an atomic mass of 100 amu. The smaller the mean atomic mass or the lower the Debye temperature the larger the zero point vibration. The Debye temperature can be determined from the high temperature slope ($T > \Theta_D$) of the ADP data, as indicated in the figure. The high temperature slope extrapolates to the origin (no zero-point energy offset). If just the room temperature value for U_{iso} is used to extrapolate a slope to the origin, the error in the calculated Debye temperature is less than 10% if the actual Debye temperature is less than 600 K. If the Debye temperature is greater than 600 K, Eq. (7) can be used to self consistently determine the Debye temperature. This is illustrated in Fig. 4. For example if a material has a Debye temperature of 1200 K, using the room temperature ADP data will result in an error of 38% and give an apparent Debye temperature that is too low ($1200/1.38 = 870$ K).

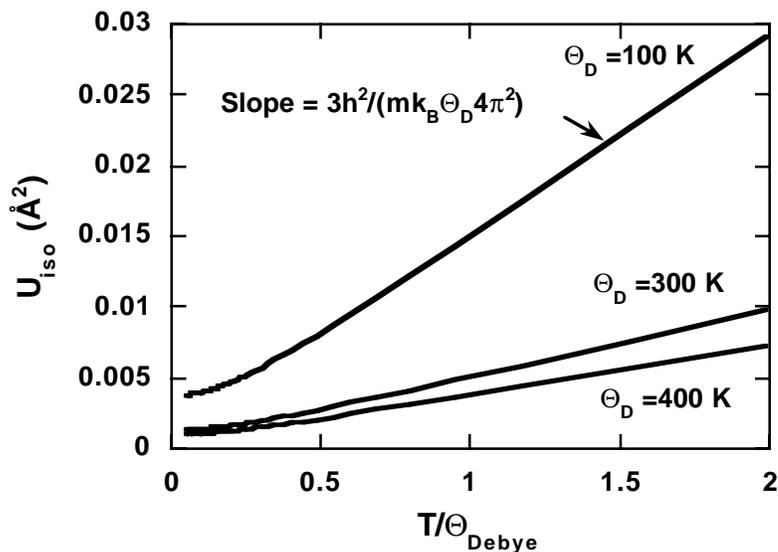


Fig. 3. Mean square displacement, U_{iso} vs. temperature scaled by the Debye temperature, Θ_D , for a monatomic cubic solid. U_{iso} is shown for a solid composed of atoms with a mass of 100 amu for three different Debye temperatures. For temperatures greater than Θ_D , U_{iso} is linear in T with a slope as indicated.

A natural extension of this analysis to a multi-element compound is accomplished by determining U_{iso} for each element (or crystallographic site) and calculating the average U_{iso} and the average atomic mass. Although the extension of Eq. 7 to a multielement compound is plausible, it should be emphasized that the main justification for this extension is that it seems to

work fairly well for many materials. As an example, for the skutterudite $\text{LaFe}_4\text{Sb}_{12}$, single crystal x-ray diffraction data (Braun and Jeitschko, 1980) results in an average room temperature U_{iso} value of $(0.0165+0.0031*4+0.004*12)/17=0.0045 \text{ \AA}^2$, and an average mass per atom of 107 amu. This room temperature ADP data predicts a Debye temperature of 299 K which can be compared to 308 K estimated from room temperature velocity of sound measurements (Sales et al. 1997). Room temperature ADP data can be used to estimate the Debye temperature and average sound velocity of *any* compound *if* the amount of static disorder is small.

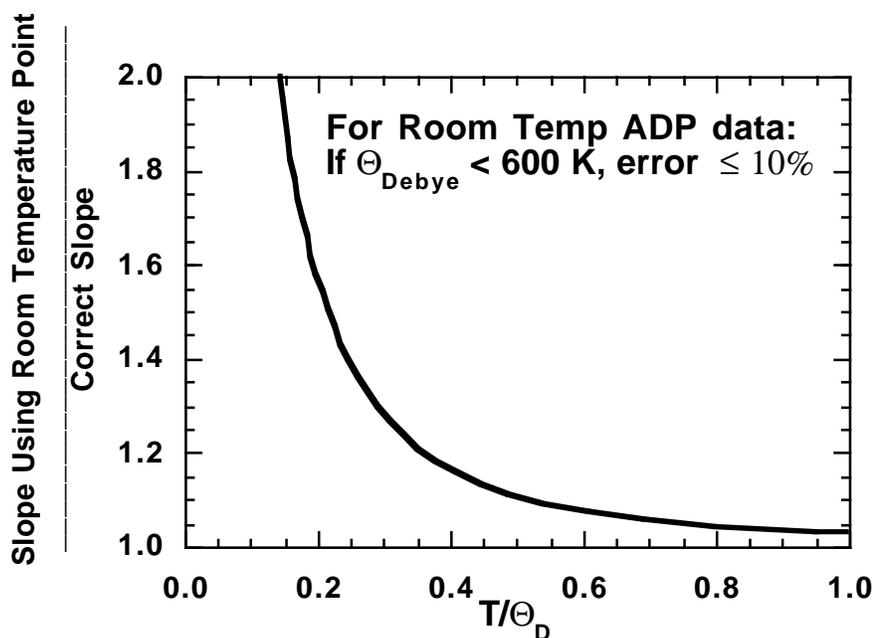


Fig. 4. Plot of error that results when room temperature ADP values are used to estimate the Debye temperature of a solid, when the actual Debye temperature is greater than room temperature. (see text for details).

3. Static Disorder

The effect of static disorder on U_{iso} is qualitatively shown in Fig. 5. The curves shown in Figs 2 and 3 are displaced upward by a constant amount. In all of the thermoelectric compounds that we have studied using neutron diffraction, static disorder has only been significant for alloys in which the crystallographic sites are only partially occupied. For the stoichiometric compounds such as $\text{LaFe}_4\text{Sb}_{12}$, $\text{CeFe}_4\text{Sb}_{12}$, $\text{YbFe}_4\text{Sb}_{12}$, Tl_2SnTe_5 , and Tl_2GeTe_5 , the temperature dependent ADP values all extrapolate close to the origin. This is illustrated in Figs. 6-8. In some stoichiometric compounds (e.g., $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$) a large amount of static disorder appears to be associated with the ability of one or more of the atom types to be displaced away from the center

of the atomic coordination cage. These compounds will be discussed in more detail in the Examples section of this chapter.

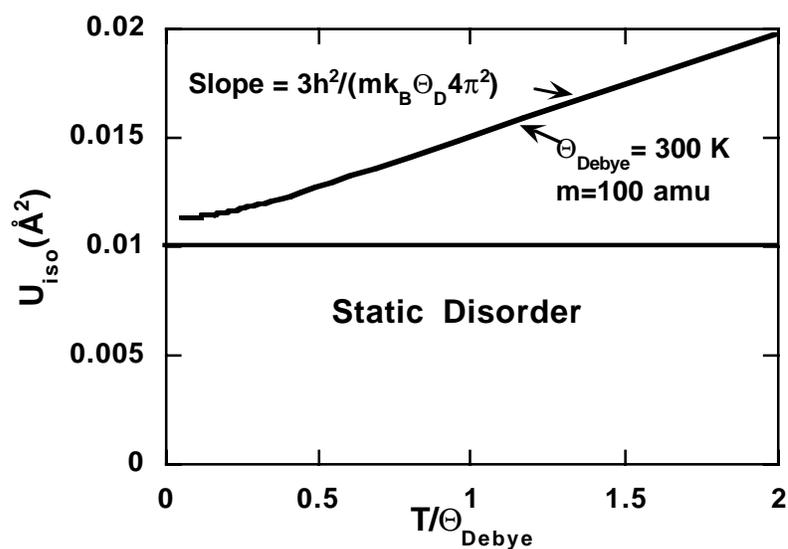


Fig.5. Qualitative effects of static disorder on U_{iso} vs T .

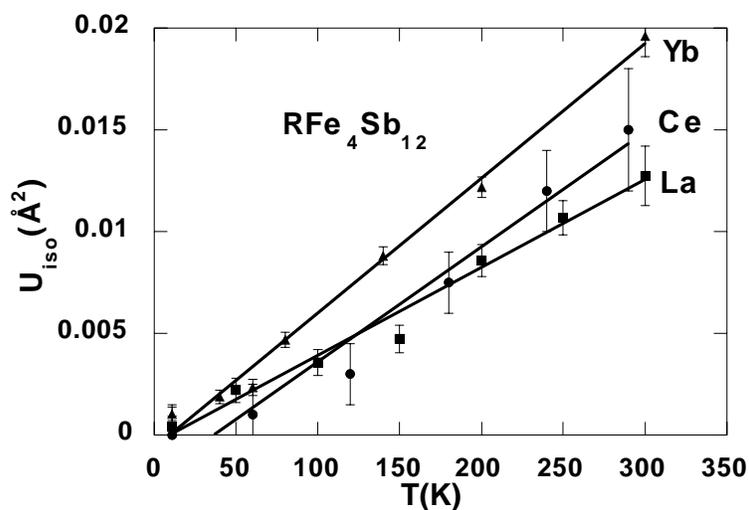


Fig. 6. Atomic displacement parameters versus temperature for $\text{LaFe}_4\text{Sb}_{12}$, $\text{CeFe}_4\text{Sb}_{12}$ and $\text{YbFe}_4\text{Sb}_{12}$. For clarity only the rare earth ADP values are shown. The lines shown are least squares fits to the data (Sales et al. 1998)

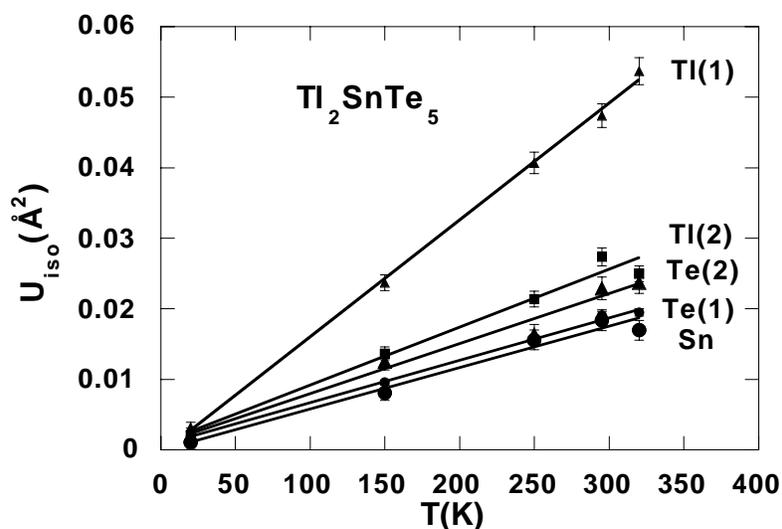


Fig. 7. Atomic displacement parameters vs. temperature for Tl_2SnTe_5 as determined from powder neutron diffraction. Note the larger ADP values for the Tl at site 1. These Tl rattle in an oversized atomic cage. The lines shown are a least squares fit to the data. (Sales et al. 1999)

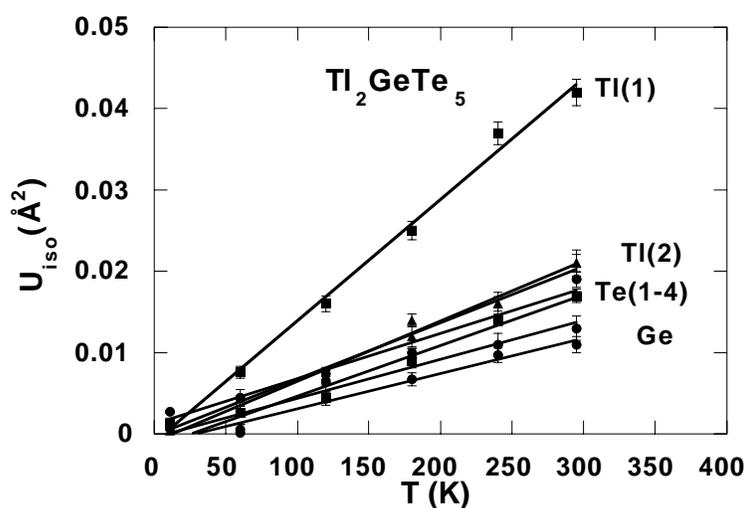


Fig. 8 Atomic displacement parameters versus temperature for Tl_2GeTe_5 . Note the larger ADP values for the Tl atoms at site 1. The lines shown are a least squares fit to the data. (Sales et al. 1998)

4. Einstein and Debye Temperatures from Room Temperature ADP Data

For compounds where static disorder can be neglected and the Debye (Einstein) temperatures are less than 600 K (300 K), the analysis discussed above can be scaled into two simple expressions for Θ_D and Θ_E :

$$\Theta_D(\text{K}) = 208 / (U_{\text{iso}}^{\text{av}} (\text{\AA}^2)/0.01 \cdot m_{\text{av}}/100)^{1/2} \quad (10)$$

and

$$\Theta_E(\text{K}) = 120 / (U_{\text{iso}}^{\text{rattler}}/0.01 \cdot m_{\text{rattler}}/100)^{1/2} \quad (11)$$

where $U_{\text{iso}}^{\text{av}}$ (\AA^2) is the weighted average of room temperature values of U_{iso} for each atom-type in the compound given in units of \AA^2 , and m_{av} is the average mass of an atom in the compound given in amu. Similarly, the Einstein temperature of the rattler is given by Eq. 11 with $U_{\text{iso}}^{\text{rattler}}$ given in \AA^2 and the rattler mass given in amu. As will be shown below, Eqs. 10 and 11 are useful in the rapid screening of new compounds using data extracted from one of the many crystallographic data bases. For example the Inorganic Crystal Structure Database (ICSD, produced by FIZ Karlsruhe) currently has over 50,500 entries and for most of the compounds the structure is all that is known (i.e., no transport data have been measured).

IV. Clathrate-Like Thermoelectric Compounds

Room temperature ADP information can be used to estimate the Debye temperature and an average velocity of sound for *any* compound using Eqs. 10 and 5. This result is well known to crystallographers. The only restriction is that the compound should have a small amount of static disorder so that the ADP values correspond to dynamic motion rather than a static displacement of the atoms.

There is a large class of promising thermoelectric compounds which contain open cages or voids in their crystal structures into which guest atoms can be added. If the guest atom is small relative to the size of the cage, the atom will be weakly bonded to the atoms comprising the cage. These guest atoms are referred to as “rattlers” since at a given temperature these atoms tend to vibrate about their equilibrium positions substantially more than the other atom-types in the structure. Filling the open cages with rattlers rapidly reduces the lattice thermal conductivity (see section V), which is desirable for a good thermoelectric material. Slack (1995) has proposed that the ideal thermoelectric material with the good electrical properties of a crystal but the poor heat conduction of a glass may be produced in these types of compounds.

A clathrate compound is an inclusion complex in which molecules or atoms of one substance are completely enclosed within another compound. Ice that has trapped an inert gas such as argon, can form a new crystalline structure called an ice clathrate in which the argon resides at the center of a large cage of water molecules. In analogy with these clathrate compounds, thermoelectric compounds with weakly bound atoms (rattlers) will be referred to as “clathrate-like” compounds because as a first approximation, the rattler atoms and the cage

framework atoms will be treated as separate phases. Examples of clathrate-like compounds are the filled skutterudites (e.g., $\text{LaFe}_4\text{Sb}_{12}$), some ternary tellurides (e.g., Tl_2SnTe_5), semiconducting compounds with the ice clathrate structure (e.g., $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$), and the rare earth hexaborides (e.g., LaB_6). In all of these compounds, one of the atom types has a room temperature ADP value that is at least three to ten times larger than that of the other atom types in the structure with comparable masses. For example in the filled skutterudite $\text{LaFe}_4\text{Sb}_{12}$, the La ADP value is 0.0165 \AA^2 while the Sb ADP value is only 0.004 \AA^2 (Braun and Jeitschko, 1980).

As a first approximation, clathrate-like compounds are separated into two phases consisting of framework atoms and rattling atoms. Since the rattling atoms are only weakly coupled to the framework atoms, they are more appropriately treated as individual quantum harmonic oscillators (Einstein oscillators). The remaining framework atoms are treated within the Debye model. In this approximation the entire solid is composed of an Einstein mode in a Debye host solid. In a real solid, the Einstein mode will interact with the acoustic phonons of the Debye host, (see Fig. 9) but it is suggested that an Einstein mode in a Debye host is a much better starting point for understanding clathrate-like compounds than just a Debye solid. The ultimate justification for this approximation, however, is that it results in predictions that are in good agreement with experiment.

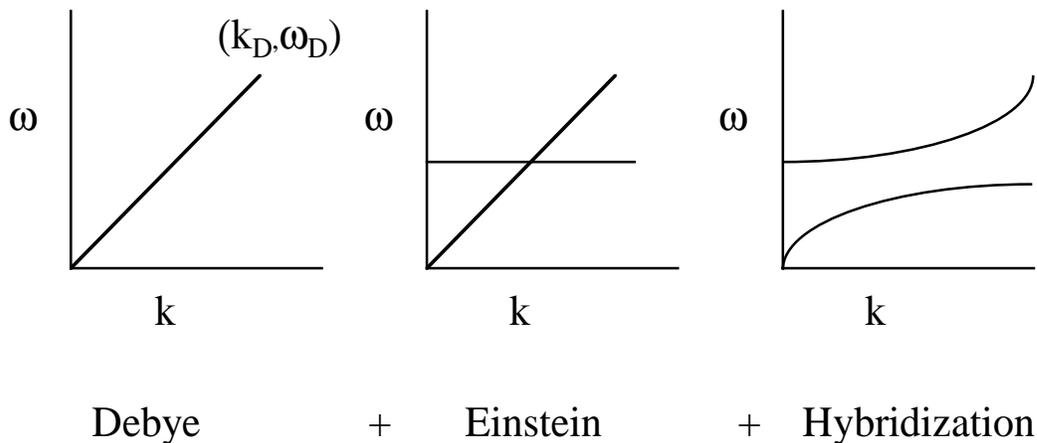


Fig. 9. Schematic illustration of the dispersion behavior of a Debye solid and a Debye solid with a localized Einstein mode. The qualitative effects on the dispersion curves of the interaction between the Einstein mode and the acoustic phonons of the solid are also sketched

For a clathrate-like solid, an Einstein temperature for the rattler can be determined from the ADP data. If static disorder can be neglected, the Einstein temperature can be estimated from the room temperature ADP value using Eq. 11. If static disorder cannot be neglected, the slope of the rattler ADP data versus temperature can be used to estimate an Einstein temperature (the slope will be given by $\hbar^2/(4\pi^2mk_B \Theta_E^2)$, as in Eq. 3).

Within this same approximation, the heat capacity of a clathrate-like compound will have a Debye contribution from the framework atoms and an Einstein contribution from the rattlers. At high temperatures both the Einstein and Debye models for the heat capacity, C_V

(at constant volume) approach the classical Dulong and Petit value of $3R$ or 24.93 J/deg-mole –of atoms. At low temperatures, however, the Debye heat capacity decreases as T^3 , while the Einstein heat capacity has an exponential decrease with temperature. The total molar heat capacity of a clathrate-like compound should approximately be given by :

$$C_v^{\text{Clathrate}}(T) = f C_{\text{Debye}}(T) + (1-f) C_{\text{Einstein}}(T) \quad (12)$$

where, f is the fraction of framework atoms and $(1-f)$ is the fraction of rattling atoms, and

$$C_{\text{Debye}}(T) = 9N_A k_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} dx \frac{x^4 e^x}{(e^x - 1)^2} \quad (13)$$

and

$$C_{\text{Einstein}}(T) = 3N_A k_B \left(\frac{\Theta_E}{T} \right)^2 \frac{e^{\Theta_E/T}}{\left(e^{\Theta_E/T} - 1 \right)^2} \quad (14)$$

As an example of this analysis, the ADP data from a partially filled skutterudite, $\text{Tl}_{0.22}\text{Co}_4\text{Sb}_{12}$ compound is shown in Fig. 10 (Sales et al., 2000). In this compound, 22% of the available voids in the skutterudite structure are filled with thallium atoms. This is the maximum fraction of the voids that can be filled without compensating for the Tl charge by substitution on the Co or Sb sites. The slope of the Tl ADP data yields an Einstein temperature for the Tl atoms of 53 K. Heat capacity measurements on $\text{Tl}_{0.22}\text{Co}_4\text{Sb}_{12}$ and $\text{Co}_4\text{Sb}_{12}$ were made using a commercial instrument from Quantum Design. The heat capacity difference between these two compounds gives the contribution due to the Tl atoms. The Tl contribution is accurately described by an Einstein heat capacity with an Einstein temperature of $55 \pm 2 \text{ K}$ (Fig. 11) and an amplitude of $0.22 \text{ } 3R$. These results are in excellent agreement with Eq. 12 and the value of 53 K predicted by an analysis of the ADP data in Fig 10.

Tl_2SnTe_5 is a tetragonal compound with a thermoelectric figure of merit, ZT , of about 0.6 at 300 K (Sharp et al. 1999). The ADP's for this compound from powder neutron diffraction data (Fig 7) and from single crystal x-ray diffraction data (Agafonov et al., 1991) indicate that the Tl atoms at the center of a distorted cube of Te atoms have an usually large displacement relative to the other atom-types in the structure. Both the x-ray and neutron data ADP data give an Einstein temperature for these Tl atoms of $37 \pm 1 \text{ K}$. The estimated Debye temperatures for the framework atoms (all other atom-types in the structure) are 169 K from single crystal, room temperature x-ray data (Agafonov et al. 1991) and 125 K from powder neutron data. This difference in estimated Debye temperatures from x-ray and neutron measurements is the largest percentage difference (30%) among the various thermoelectric compounds that we have investigated. Normally there is less than a 10% difference in the Debye temperatures calculated from x-ray single crystal versus neutron ADP data. If just the single crystal x-ray ADP data is used, the temperature of the specific heat should be approximately given by Eq(12) with $f= 7/8$ (since only one out of eight atoms in Tl_2SnTe_5 is treated as a rattler), and a Debye temperature of 169 K and an Einstein temperature of 38 K. There are no adjustable parameters. A comparison between the measured and predicted heat capacity is shown in Fig. 12. The agreement is surprisingly good.

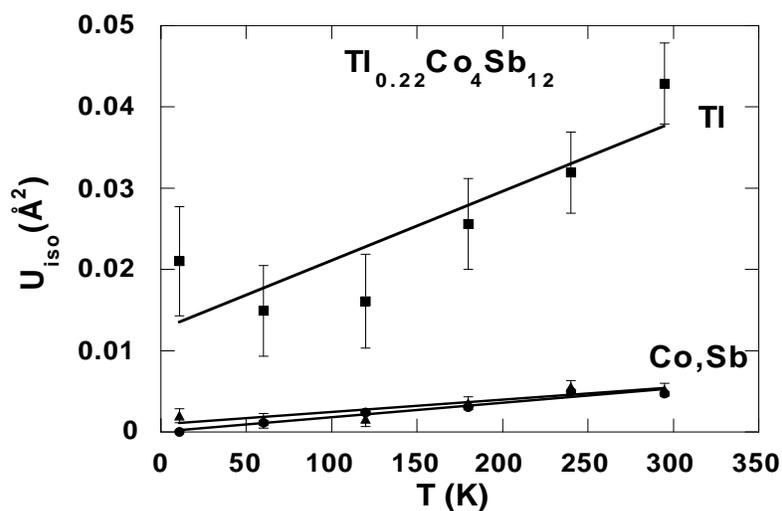


Fig 10. Isotropic atomic displacement parameters versus temperature for a $Tl_{0.22}Co_4Sb_{12}$ alloy. An Einstein temperature for the Tl atoms of 52 K was estimated from the slope of the Tl ADP data. (Sales et al., 2000)

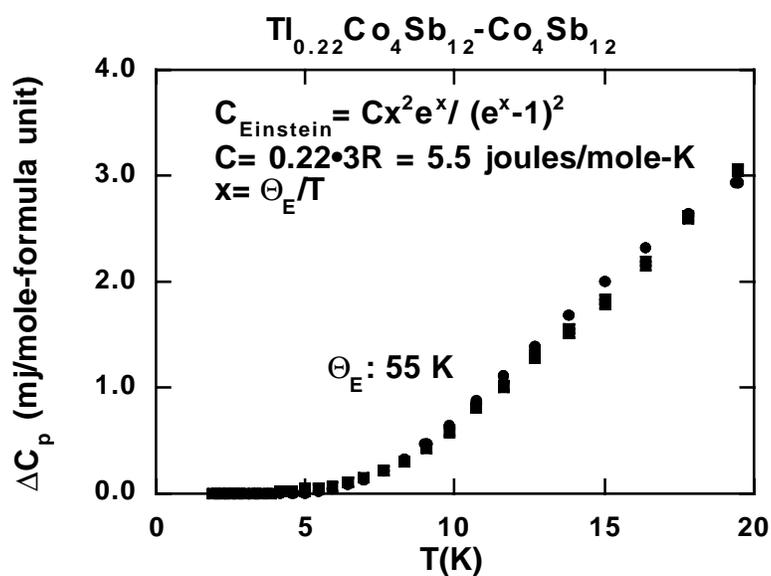


Fig. 11. Difference in heat capacity between Tl-doped Co_4Sb_{12} and Co_4Sb_{12} . The Tl contribution to the heat capacity is accurately described by an Einstein contribution with an Einstein temperature of 55 K. Squares are measured data, circles are calculated.

At temperatures below 15 K (Fig. 12 inset), however, the data indicate that an Einstein temperature of about 30 K provides a better description of the heat capacity data than does the value of 38 K determined from the room temperature ADP data.

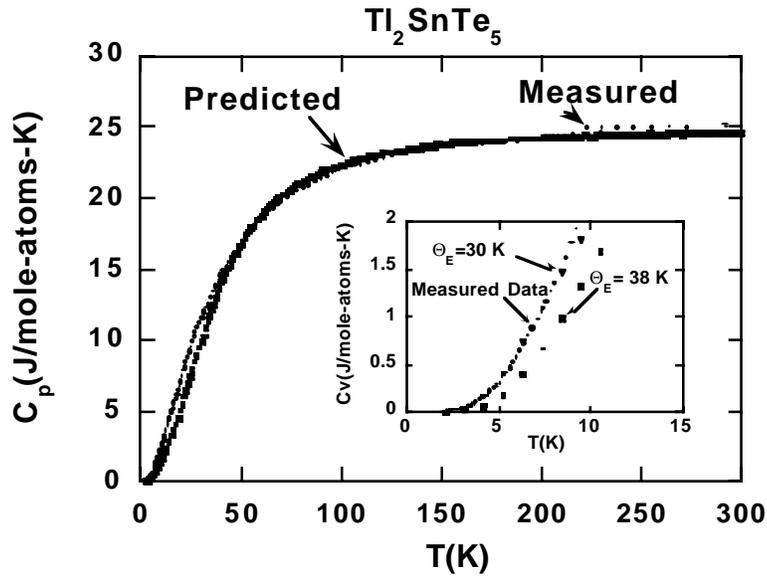


Fig 12. Calculated and measured heat capacity for Tl_2SnTe_5 . The calculated heat capacity was determined from the published room temperature X-ray crystallography data of Agafonov et al. 1991. There were no adjustable parameters. The inset shows the calculated and measured heat capacity. At low temperatures, an Einstein temperature of 30 K provides a better description of the data than does the value of 38 K calculated from the room temperature X-ray data.

V. Estimation of the Lattice Thermal Conductivity from ADP Data

1. Elementary theory of lattice heat conduction

The simplest expression for the lattice thermal conductivity of a solid is given by an expression adapted from the kinetic theory of gases (see for example Kittel, 1968)

$$\kappa_{\text{Lattice}} = 1/3 C_V v_s d \quad (15)$$

where C_V is the heat capacity per unit volume, v_s is the velocity of sound and d is the mean free path of the heat carrying phonons. In a more realistic treatment of lattice thermal conductivity, which is discussed in the next section, the mean free path (or relaxation time) and heat capacity depend on frequency and temperature, but for the present analysis C_V depends only on temperature, while v_s and d are treated as scalars.

In section II, it was shown how room temperature ADP data can be used to estimate the Debye temperature and the Debye velocity of sound. This analysis, which can be applied to all compounds, provides an estimate of the room temperature values of C_v and v_s that appear in Eq. 15. To estimate the lattice thermal conductivity using Eq. 15, however, requires a value for d . There have been several phenomenological expressions derived in the literature that relate the lattice thermal conductivity to the Debye temperature and the Gruneisen parameter, γ (or to the melting temperature and the Gruneisen parameter). Many of these are discussed by Goldsmid 1986, pp 73-76. Most of the formulas are related to one another through various thermodynamic relations. A typical phenomenological expression for the lattice thermal conductivity near room temperature is:

$$\lambda_L = 8 \times 10^{-8} \left(\frac{k_B}{h} \right)^3 M V^{1/3} \Theta_D^3 / (\gamma^2 T) \quad (16)$$

where M is the average mass of an atom (gm), V is the average atomic volume (cm^3) and a typical value for the Gruneisen parameter is 1.8. Since all of the quantities in (16) can be obtained from the crystallography data, equations such as Eq. (16) can provide a first estimate of the thermal conductivity of *any material*. The estimates may be off, however, by as much a factor of 5-10. For example if the thermal conductivity of the filled and unfilled skutterudites are analysed using Eq.(16), both the filled and unfilled materials have about the same average mass, atomic volume and Debye temperatures so that the room temperature lattice thermal conductivity of $\text{Co}_4\text{Sb}_{12}$ should be about the same as $\text{LaFe}_4\text{Sb}_{12}$. The room temperature lattice thermal conductivity of $\text{LaFe}_4\text{Sb}_{12}$, however, is 5 to 6 times lower than that of $\text{Co}_4\text{Sb}_{12}$.

In general there is no easy way to estimate the value of d at room temperature using just crystallography data. Hence, for most compounds there is no obvious way to estimate the lattice thermal conductivity to better than about a factor of 5.

For clathrate-like compounds, it has been experimentally observed by several groups (Nolas et al. 1998, Meisner et al., 1998, Sales et al. 2000) that as relatively small concentrations of rattlers (La, Ce, or Tl) are added to the skutterudite structure ($\text{Co}_4\text{Sb}_{12}$) there is an extremely rapid decrease in the lattice thermal conductivity. The mean free path, d , of the heat carrying phonons in these compounds is determined by the various scattering mechanisms in the crystal such as acoustic phonons, grain boundaries, electron-phonon scattering, static defects, voids and “rattlers”. Resonant scattering by quasi-localized “rattlers” appears to be the dominant scattering mechanism responsible for the rapid decrease in the thermal conductivity as small amounts of Tl, La or Ce are placed in the voids. This mechanism is believed to be similar to the resonant scattering described by Pohl for insulating crystals (Pohl, 1962) and by Zakrzewski and White (1992) in insulating organic clathrates. It has been demonstrated that mass fluctuation scattering is much too weak to explain the rapid decrease in thermal conductivity (Nolas et al. 1998). The thermal resistivity of the lattice ($1/\text{thermal conductivity}$) at room temperature is shown in Fig. 13 as Tl is added to the voids in $\text{Co}_4\text{Sb}_{12}$. Thermal resistivity is shown rather than thermal conductivity because as a first approximation, the scattering rates for different scattering processes should add (Mathiessen’s rule). There is an rapid initial increase in the thermal

resistance, followed by a gradual saturation of the thermal resistance as higher concentrations of Tl are added to the voids. Within experimental error, there is no clear maximum in the thermal resistance data as a function of Tl concentration, and the maximum thermal resistance occurs near complete filling for both the Fe and Sn compensated compounds. The maximum attributed to mass fluctuation scattering by Meisner et al., 1998 as a function of Ce filling is not observed in the present experiments.

If the Tl atoms are treated as localized Einstein oscillators, as suggested by Keppens et al. 1998, then the heat carrying phonon mean free path, d , should be a function of the distance between the Tl atoms in the crystal. The simplest estimate of the phonon mean free path is therefore the average distance between the Tl atoms. This implies that the phonon scattering from the Tl is so strong that d attains a minimum distance given by the average Tl-Tl separation. The scattering of acoustic phonons by the Tl should be a maximum when the acoustic phonon and rattling frequency are equal (Pohl, 1962); however, even at resonance it seems physically unlikely that d could be less than the Tl-Tl separation distance. This simple argument suggests that if the role of other scattering mechanisms is minimal, that the thermal resistivity should vary as $x^{1/3}$, where x is the Tl concentration (the average spacing between Tl atoms varies as $x^{-1/3}$). The additional thermal resistance generated as Tl is added to $\text{Co}_4\text{Sb}_{12}$ reasonably follows an $x^{1/3}$ behavior (Fig 13), even though part of the thermal resistance is due to electron-phonon scattering and other scattering mechanisms (Sales et al. 2000).

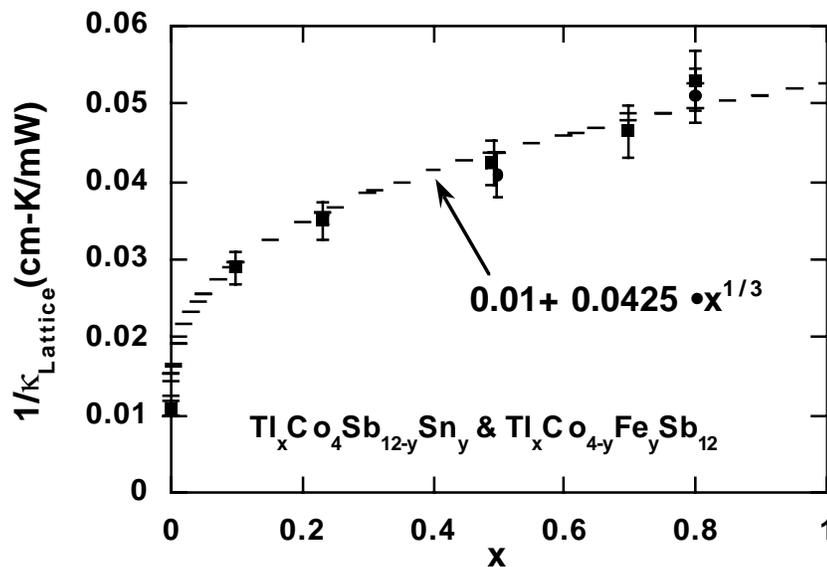


Fig 13. Variation of the room temperature lattice thermal resistivity vs the fraction of the voids filled with the rattler Tl. The average separation distance between Tl rattlers varies as $x^{1/3}$. The square (circles) refer to charge compensation with Sn (Fe). For all but the two lowest Tl concentrations, $x \approx y$.

A plausible approximation for d in clathrate-like compounds is therefore the average separation distance between the rattlers, which *is* known from the crystallography data. At room temperature, this argument works well for the TI-filled skutterudites (Fig 13.) It also works for the filled skutterudites such as $\text{LaFe}_4\text{Sb}_{12}$. Using the measured thermal conductivity, heat capacity and an average value for the velocity of sound yields a mean free path of $d = 9 \text{ \AA}$ (Sales et al. 1997). The nearest-neighbor distance of the La atoms in $\text{LaFe}_4\text{Sb}_{12}$ is 7.9 \AA . The real test of this hypothesis is whether this analysis gives good estimates of the room temperature lattice thermal conductivity for a variety of clathrate-like compounds. As will be shown in Sec VI, for many clathrate-like systems replacing d in Eq. 15 by the average distance between the rattlers predicts a room temperature lattice thermal conductivity in suprisingly good agreement with experiment. This means that for clathrate-like compounds *room temperature crystallography data can be used to provide a reasonable estimate of the lattice thermal conductivity*. This is significant since a low lattice thermal conductivity is a requirement for a good thermoelectric material.

2. Lattice heat conduction: a more realistic model

A more realistic model of lattice heat conduction of a solid, within the Debye approximation, has been described by Callaway, 1959 and Klemens, 1958. The lattice thermal conductivity, κ_{Lattice} , is given by:

$$\mathcal{K}_{\text{Lattice}} = 1/3 \int_0^{\omega_D} v^2 \tau(\omega, T) \frac{dC}{d\omega} d\omega \quad (17)$$

with

$$\tau^{-1}(\omega, T) = \sum_i \tau_i^{-1}(\omega, T) \quad (18)$$

where, ω_D is the Debye frequency, v is the Debye velocity of sound, τ_i is the relaxation time for the i th phonon scattering mechanism, T is the temperature in Kelvin, and $dC/d\omega$ is the specific heat per angular frequency. Within the Debye model, the specific heat per angular frequency is obtained from Eq. 13 by a change of variables, replacing x by $\hbar\omega/2\pi k_B T$. Notice that since v is a constant in the Debye model, the phonon mean free path is just:

$$d(\omega, T) = v \tau(\omega, T) \quad (19)$$

In a crystal various processes can scatter phonons. For the present purposes we will follow the approach described by Pohl 1962, and Walker and Pohl 1963 and consider the the minimum number of scattering mechanisms that can account for the experimental data. For a solid with no resonant scattering (no rattlers) the normal scattering mechanisms are grain boundary scattering, τ_B^{-1} , isotope or mass fluctuation scattering, τ_{iso}^{-1} (Klemens 1958) and phonon-phonon scattering (umklapp and normal), $\tau_{\text{U,N}}^{-1}$ (Walker and Pohl 1963) . These various scattering terms are given by:

$$\tau_B^{-1} = v/L \quad (20)$$

$$\tau_{\text{iso}}^{-1} = V_0 \Gamma \omega^4 / 4\pi = C \omega^4 \quad (21)$$

$$\text{with} \quad \Gamma = \sum_i f_i \left(1 - \frac{m_i}{m}\right)^2 \quad (22)$$

$$\text{and} \quad \tau_{\text{U,N}}^{-1} = B\omega^2 T e^{-b/T} \quad (23)$$

with V_0 is the atomic volume, L is the average grain size, m_i is the mass of the i th atom, m is the average atomic mass, and f_i is the relative concentration of the i th species. Equation 23 is a phenomenological expression that accounts for both umklapp and normal phonon-phonon scattering (Walker and Pohl, 1963). These three scattering processes (Eqs. 20-23) can account for the temperature dependence of the the thermal conductivity of compounds with no rattlers, such as $\text{Co}_4\text{Sb}_{12}$. The resonant scattering by the rattlers can be phenomenologically described by a function that is proportional to the concentration of rattlers, and is peaked at the Einstein frequency of the rattler:

$$\tau_{\text{resonant}}^{-1}(\omega) = A_0 f(\omega - \omega_E) = A_0 T^2 \frac{\omega^2}{(\omega^2 - \omega_E^2)^2} \quad (24)$$

where A_0 is proportional to the rattler concentration and the particular form of the function f is taken from Walker and Pohl (1963).

With regard to the clathrate-like compounds, simple calculations using only the Eqs. 17-24 *do not* reproduce the behavior shown in Fig 13. The calculated thermal resistance increases linearly with the rattler concentration A_0 and does not saturate as is indicated in Fig 13. One of the key ideas to understanding the data displayed in Fig 13 is the concept of a minimum thermal conductivity or a maximum thermal resistance first proposed by Slack in 1979. In any solid, Slack proposed that it does not make sense to consider a mean free path for the heat carrying phonons that is less than an interatomic spacing ($d \approx 3 \text{ \AA}$). This hypothesis, which is born out by experiment (Cahill et al. 1992), suggests that for a crystalline compound the minimum thermal conductivity corresponds to a glass with the same composition for which $d \approx 3 \text{ \AA} = 3 \times 10^{-8} \text{ cm}$. This means that there is a cutoff for the maximum scattering rate given by $\tau_{\text{max}}^{-1} = v/3 \times 10^{-8} \text{ s}^{-1}$, where the velocity of sound is given in cm/s. For materials with thermal conductivities that approach within an order of magnitude or so of the minimum value, Eq 18 is replaced by:

$$d(\omega, T) = \left[\sum_i v \tau_i^{-1}(\omega, T) \right]^{-1} + d_{\text{min}} \quad (25)$$

where $d_{\text{min}} \approx 3 \text{ \AA}$.

To see if this approach produces reasonable results, the temperature dependence of thermal conductivity of the unfilled skutterudite $\text{Co}_4\text{Sb}_{12}$ (no rattlers) was fit using Eqs 17 and 25. The measured Debye temperature (307 K), velocity of sound ($2.93 \times 10^5 \text{ cm/s}$) and grain size (10^{-3} cm) were used as input parameters. The three constants (C, B and b) in Eqs. 21 and 23 were adjusted

to give a fit to the experimental data (Fig 14). The values used were $C=1.58 \times 10^{-42} \text{ sec}^3$, $B=3.87 \times 10^{-18} \text{ sec/K}$, and $b=150 \text{ K}$ (These values are in the same range as found by Walker and Pohl, 1963)

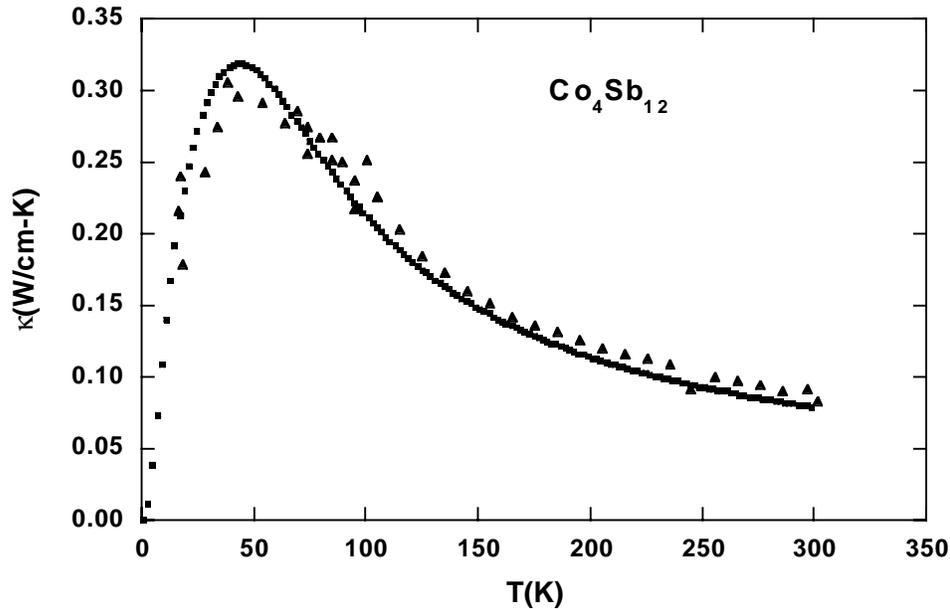


Fig 14. Fit to the lattice thermal conductivity of a polycrystalline CoSb_3 sample with an average grain size of 0.001 cm using Eqs. 17, 20-23 and 25. See text for details.

The resonant phonon scattering due to the addition of Tl rattlers was then modeled using the same parameters used to fit the $\text{Co}_4\text{Sb}_{12}$ data plus a resonant term (Eq. 24) with $A_0 = A 7.42 \times 10^{32} \text{ sec}^{-3}\text{K}^{-2}$ where A is dimensionless and is proportional to the concentration of Tl rattlers. An Einstein frequency was taken from the experimental data (Fig. 11) and corresponded to an Einstein temperature of 55 K. The effect on the thermal conductivity of increasing the strength of the resonant scattering is shown in Fig. 15. In this simple model there is expected to be a dip in the thermal conductivity at a temperature between 10 and 20 K for an Einstein temperature of 55 K. Careful thermal conductivity measurements in this temperature range have not been made for the Tl filled skutterudites. A dip has been recently seen, however, in a related compound, $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ (Cohn et al. 1998). The motivation, however, for calculating the lattice thermal conductivity as a function of Tl concentration was to see if the behavior in Fig 13 could be understood. The room temperature thermal resistance from the calculated data shown in Fig 15 is plotted in Fig 16 vs the amplitude of the resonant scattering (the parameter A). A least squares fit of a power law to the data yield an exponent of 0.35. This exponent is relatively constant for large variations in A and is surprisingly close to the value of 1/3 obtained by simply using the average distance between rattlers for d (Sec. V.1). The calculated and measured thermal resistivity data can be compared directly if the proportionality constant between A and the Tl concentration x is determined. The room temperature thermal resistance of the $\text{Tl}_{0.8}\text{Co}_4\text{SnSb}_{11}$

sample is about 50 cm-K/W. This value is obtained in the model calculation with a value of $A \approx 20$. A comparison between the calculated and measured thermal resistance is shown in Fig. 17. The agreement is good.

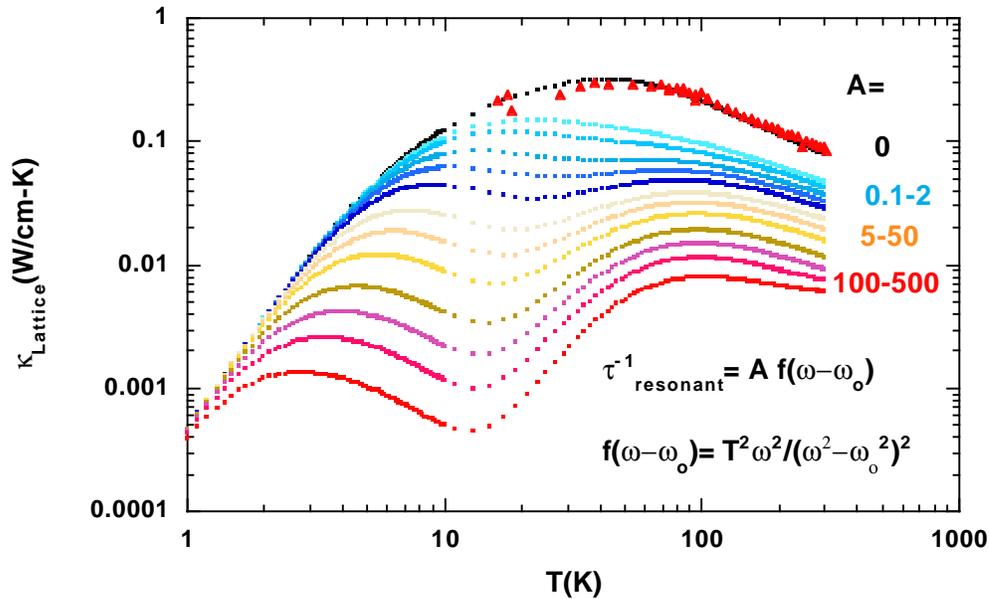


Fig. 15. Log of lattice thermal conductivity vs. log T calculated using Eqs 17, and 20-25. The strength of the resonant scattering and the concentration of rattlers is proportional to the parameter A (Eq 24.) The other parameters are the same as used to fit the $\text{Co}_4\text{Sb}_{12}$ data (The triangles on the $A=0$ curve are the same $\text{Co}_4\text{Sb}_{12}$ data shown in Fig 14.). See text for details.

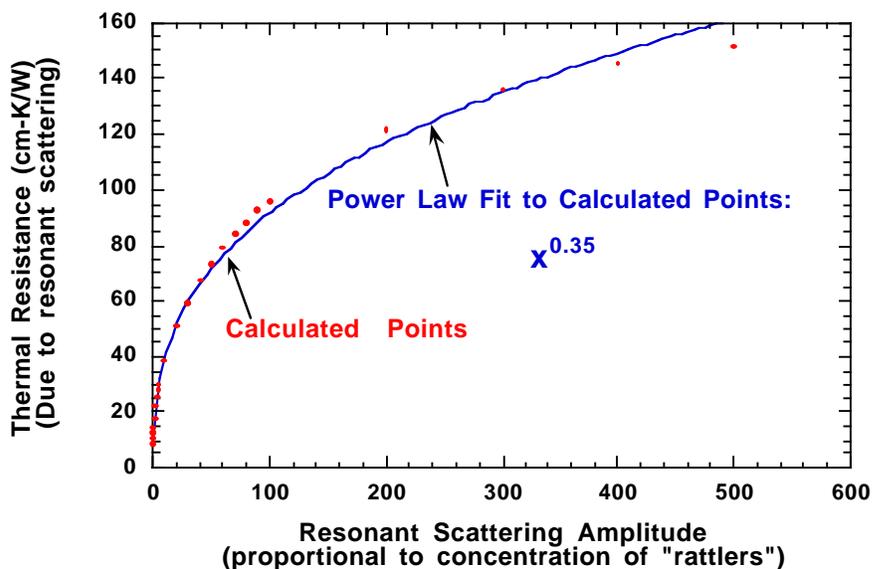


Fig 16. Calculated thermal resistance at room temperature vs the resonant scattering amplitude, A . The room temperature thermal resistance is from the calculated data shown in Fig 15. A is proportional to the concentration of rattlers, x .

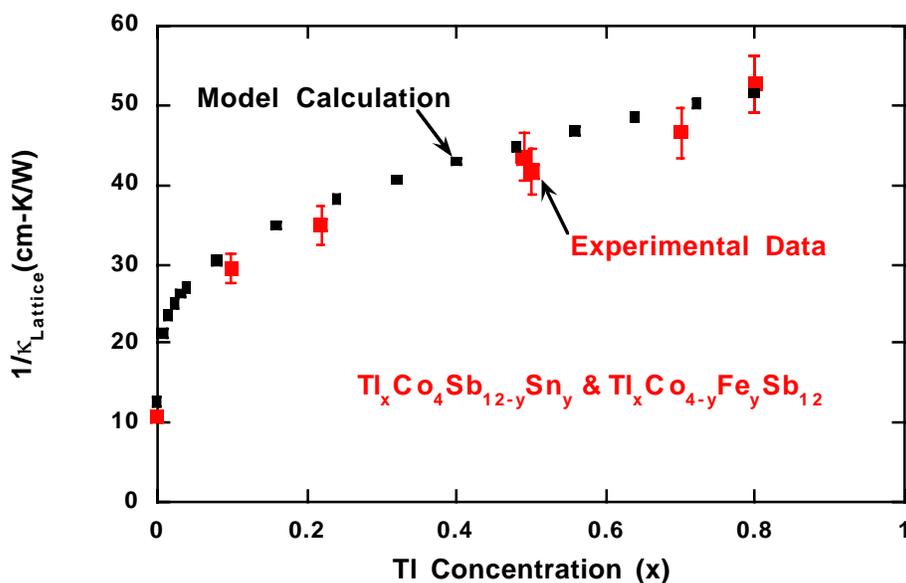


Fig. 17. Thermal resistivity vs TI concentration, a comparison between the model calculation and the experimental data. The thermal resistance of the $Tl_{0.8}Co_4SnSb_{11}$ sample was used to determine the proportionality constant between the resonant scattering amplitude, A , and the TI concentration x .

VI. Examples

In this section, ADP data will be used to extract as much information as possible about the properties of several different families of clathrate-like compounds. Because the vast majority of crystallography data reported in the literature are taken with x-rays, where possible x-ray ADP data will be used in the analysis. The predicted results from the analysis of the ADP data will be compared to the results from a variety of different measurements.

1. Filled Skutterudites: $\text{LaFe}_4\text{Sb}_{12}$, and $\text{YbFe}_4\text{Sb}_{12}$

Single crystal x-ray data are available for $\text{LaFe}_4\text{Sb}_{12}$ (Braun and Jeitschko, 1980) and $\text{YbFe}_4\text{Sb}_{12}$ (Leithe-Jasper et al. 1999). The room temperature x-ray data from each compound were analyzed using Eqs. 10 and 11. The estimated Debye temperatures were 299 K for $\text{LaFe}_4\text{Sb}_{12}$ and 238 K for $\text{YbFe}_4\text{Sb}_{12}$. The corresponding Einstein temperatures were 79 K for La and 62 K for Yb. Room temperature velocity of sound data (Sales et al., 1997) and low temperature heat capacity data (Gajewski et al., 1998) give Debye temperatures for $\text{LaFe}_4\text{Sb}_{12}$ of 300 ± 10 K. Low temperature heat capacity data on $\text{YbFe}_4\text{Sb}_{12}$ (Dilley et al., 1998) yielded a Debye temperature of 190 K, although the a magnetic contribution to the heat capacity data at low temperatures make this value uncertain. The estimated room temperature lattice thermal conductivity from the room temperature x-ray ADP data using Eq. 15 with d replaced by the rattler separation distance (about 7.9 Å for La or Yb) is 0.014 W/cm-K for $\text{LaFe}_4\text{Sb}_{12}$ and 0.011 W/cm-K for $\text{YbFe}_4\text{Sb}_{12}$. These values can be compared to the measured values of 0.017 W/cm-K for $\text{LaFe}_4\text{Sb}_{12}$ (Sales et al. 1997) and 0.014 W/cm-K for $\text{YbFe}_4\text{Sb}_{12}$ (Dilley et al., 2000).

The Einstein temperature for the La in $\text{LaFe}_4\text{Sb}_{12}$ should result in a peak in the La phonon density of states near 79 K. The La phonon density of states was recently measured using inelastic neutron scattering. (Keppens et al. 1998). A clear peak in the La phonon density of states was observed at 80 K along with a weaker and broader peak near 175 K (Fig. 18). Both peaks can be understood within the framework of a detailed investigation of the lattice dynamics of $\text{LaFe}_4\text{Sb}_{12}$ (Feldman et al. 2000, Feldman and Singh, 1996). Qualitatively the two peaks result from a hybridization process similar to that sketched in Fig. 9. A recent summary of ADP information from a variety of filled skutterudite phases has been reported by Kaiser and Jeitschko, 1999 and Chakoumakos et al. 1999.

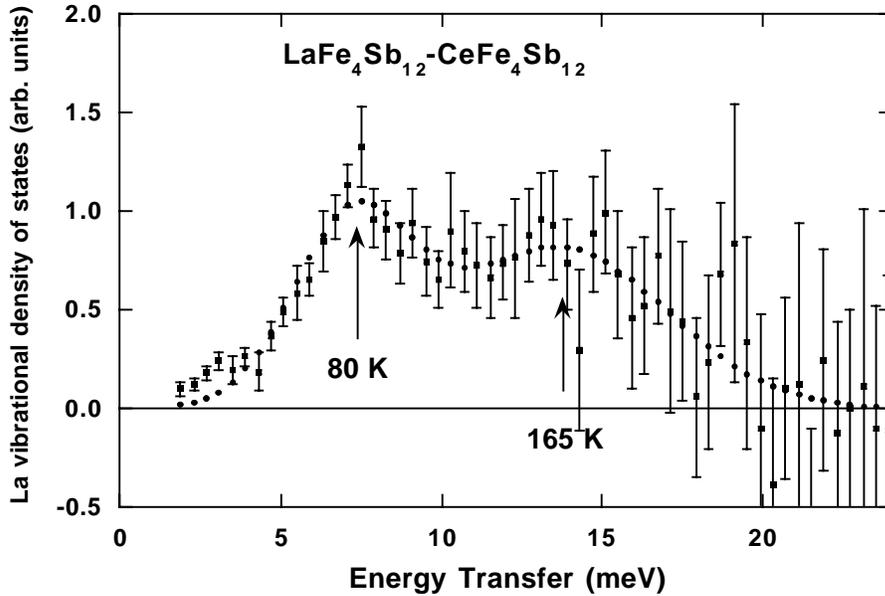


Fig. 18. Difference in the inelastic neutron scattering data between $\text{LaFe}_4\text{Sb}_{12}$ and $\text{CeFe}_4\text{Sb}_{12}$ versus energy loss. The incident neutron energy was 30 meV and the energy resolution was 2 meV. $\text{CeFe}_4\text{Sb}_{12}$ was used as a reference because the neutron scattering cross section of Ce is much smaller than that of La. The difference spectra therefore reflects the vibrational density of states (DOS) associated with the La atoms. The peaks at 7 and 15 meV correspond to temperatures of 80 and 175 K (Keppens et al., 1998).

2. Tl_2SnTe_5

The structure of Tl_2SnTe_5 was first reported by Agafonov et al. in 1991. This compound has a room temperature value for ZT of 0.6 (Sharp et al. 1999). The compound is tetragonal with columns of Tl ions along the crystallographic c axis. There are two distinct Tl sites in the structure and at one of the sites the Tl atoms sits near the center of a large, oversized distorted cube. The Tl ADP parameter at this site is considerably larger than for the other atoms in the structure and the Tl at this site will be treated as a rattler. From the room temperature x-ray ADP data (Agafonov et al. 1991) the Einstein temperature of the Tl rattler was estimated to be 38 K and the Debye temperature of the other atoms in the compound was 169 K. As was shown in Sec. IV, these values can be used to estimate the temperature dependence of the heat capacity, and the calculated heat capacity is in good agreement with the measured values (Fig. 12). The estimate of the room temperature lattice thermal conductivity from the ADP data is 0.0039 W/cm-K. The measured lattice thermal conductivity for Tl_2SnTe_5 is shown in Fig. 19 and at room temperature is close to 0.004 W/cm-K.

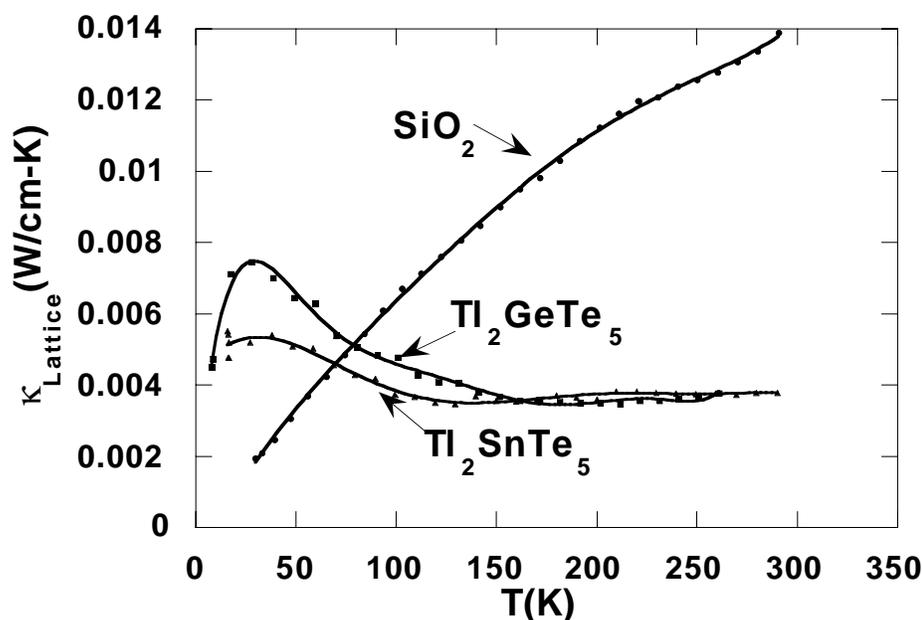


Fig 19. Lattice thermal conductivity versus temperature for vitreous silica, Tl_2SnTe_5 and Tl_2GeTe_5 . The Wiedemann-Franz law has been used to estimate and subtract the electronic portion of the thermal conductivity. The lines through the data are guides to the eye.

3. LaB_6

LaB_6 is not a good thermoelectric material but it is a clathrate-like compound. LaB_6 crystallizes in a simple body-centered cubic structure with La at the cube center and B_6 octahedral clusters at each cube corner (Fig. 20). LaB_6 is a good metal ($\rho_{300\text{ K}} = 5 \mu\Omega\text{-cm}$) that is used as an electron source in most high-performance electron microscopes. Because of its technological importance, much is known about the properties of LaB_6 . When normalized by mass, the lanthanum ions “rattle” significantly more about their equilibrium positions than do the borons. Using published ADP data (Korsukova et al. 1986) on LaB_6 , the Einstein temperature of the La was calculated to be 140 K and the Debye temperature for the boron sublattice to be about 1500 ± 200 K. The extrapolation graph shown in Fig. 4 was used because of the high Debye temperature of the boron sublattice. The temperature dependence of the heat capacity was calculated using an Einstein contribution weighted by 1/7 and a Debye contribution weighted by 6/7. The Debye temperature was adjusted to 1200 K (rather than 1500 K) to provide a better fit to the data. The agreement between the calculated heat capacity and the measured values is shown in Fig. 21. The unusual bump in the heat capacity data at about 70 K is accurately accounted for by this simple analysis using only room temperature ADP data and a 20% adjustment of the Debye temperature for the boron sublattice. Large single crystals of $La^{11}B_6$ allowed Smith et al. (1985) to map the phonon dispersion curves using neutron scattering.

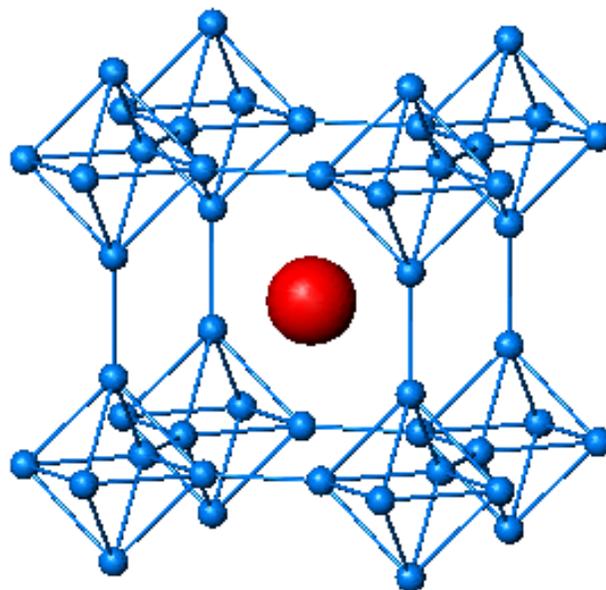


Fig. 20 Model of LaB_6 crystal structure. La atoms (large ball) sit at the center of a cube with B_6 “molecules” at each cube corner. As a first approximation, the La atoms can be treated as Einstein oscillators in a Debye solid composed of B atoms.

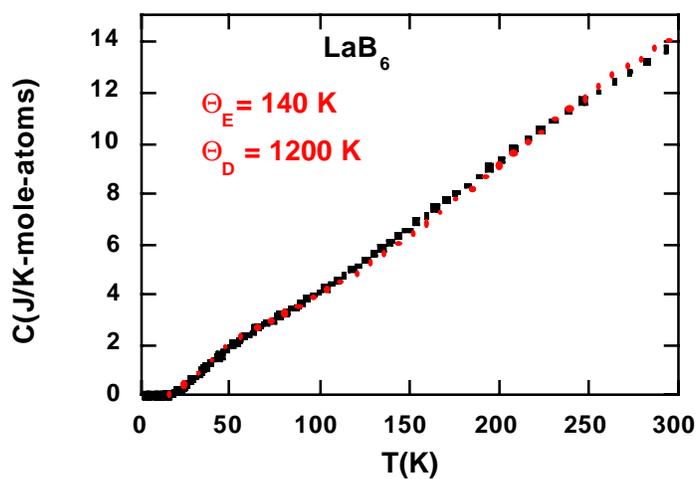


Fig 21. Calculated and measured heat capacity of LaB_6 . Room temperature x-ray ADP data from Korsukova et al. 1986 were used to determine the Einstein temperature for the La and a Debye temperature for the B. (See text for details)

unusually energy-independent phonon mode was found over most of the Brillouin zone at energies corresponding to an Einstein temperature of 150 K; a value close to the 140 K value estimated from the ADP data. This mode was attributed by Smith to the independent vibration of the La atoms in LaB_6 .

4. Semiconducting clathrates : $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ and $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$

These compounds are cubic and have the same structure as the type I ice clathrates (Eisenmann et al. , 1986). The thermoelectric properties of $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ and similar compounds were first reported by Nolas et al. 1998 and Cohn et al. 1999. The structure can be thought of as a tetrahedral framework of Ga and Ge atoms. The framework atoms form large cages of 20 or 24 atoms that surround the Sr or Ba atoms in the structure. The alkaline earth atoms in the larger cage have unusually large ADP values. Room temperature x-ray ADP data for the Ba clathrate (Eisenmann et al. 1986) coupled with Eqs. 10 and 11 estimates an Einstein temperature of 51 K for the Ba atoms, and a Debye temperature of 274 K for the rest of the atoms in the structure. This results in a Debye sound velocity of 2.6×10^5 cm/s, and a predicted room temperature lattice thermal conductivity of about 0.008 W/cm-K. (Eq. 15, with d given by the nearest neighbor distance between the Ba rattlers.) The measured lattice thermal conductivity (Fig 22) is about 0.016 W/cm-K. Although the measured lattice thermal conductivity is about twice the predicted value, this is still better agreement than most other simple methods of estimating lattice thermal conductivity. In general it should be expected that the estimate will be lower than the measured value since it is assumed in this simple analysis that the rattlers scatter phonons at the maximum possible rate (corresponding to d given by the rattler separation distance).

There are no published single crystal x-ray ADP data for the Sr clathrate, so the neutron data reported by Chakoumakos et al. 2000, will be used. ADP data for this compound are available from room temperature down to 11 K (Fig 23). The ADP values of Sr atoms in the large cage (Sr2 in the figure) are huge relative to the other atoms in the structure. The temperature dependence of the Sr2 ADP data is unusually weak, however, suggesting a large amount of static disorder. Such a large amount of static disorder in a nominally stoichiometric compound is unusual as can be seen from comparing the ADP data in figures 6-8 with the data shown in Fig 23. If just the room temperature ADP data are used, the Sr rattlers appear to have an Einstein temperature of 44 K and a Debye temperature for all the atoms of 180 K (without the rattler, this value would be 246 K). For this compound, however, static disorder cannot be ignored—at least for the Sr2 site. Taking the slopes of the ADP data results in a Einstein temperature of 85 K for the Sr rattler, and a Debye temperature of about 270 K and a mean sound velocity of 2.6×10^5 cm/s. The estimated room temperature lattice thermal conductivity is 0.008 W/cm-K. If only the room temperature ADP data were used, the estimated lattice thermal conductivity would be lowered to about 0.006 W/cm-K. The measured value of the room temperature lattice thermal conductivity of $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ is about 0.010 W/cm-K (Fig 22, also see Nolas et al. 1998, Cohn et al. 1999). The large amount of static disorder at the Sr2 site is due to the tendency of the Sr atoms at this site to move or tunnel off center to one of four nearby sites located about 0.75 Å from the center of the cage. The combination of tunneling, in addition to rattling, is apparently responsible for the qualitative difference between the thermal conductivity of the Sr and Ba clathrates. The rattling of the Ba results in a low thermal conductivity but the temperature dependence is crystal-like, while the rattling and tunneling of the Sr results in a true glasslike thermal conductivity (Fig 22, see also Cohn et al. 1999, and Keppens et al. 2000).

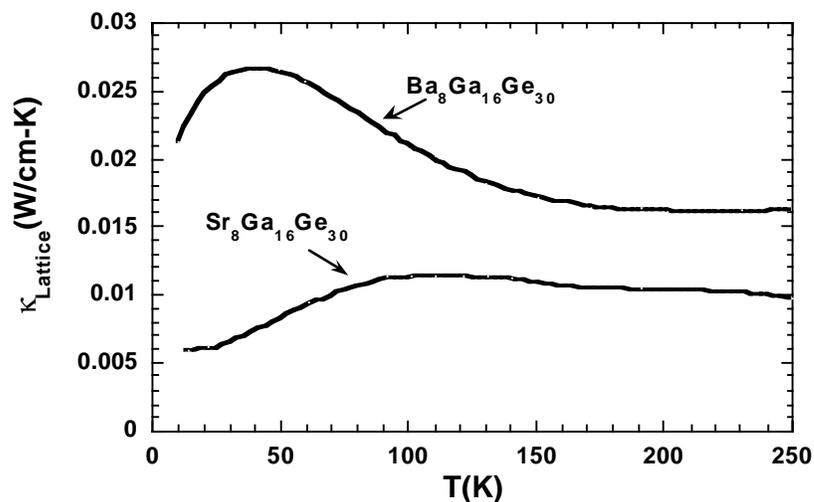


Fig 22. Lattice thermal conductivity versus temperature for $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ and $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ crystals. The thermal conductivity of the Ba clathrate, although small, has a crystalline temperature dependence whereas the temperature dependence of the Sr clathrate is glasslike.

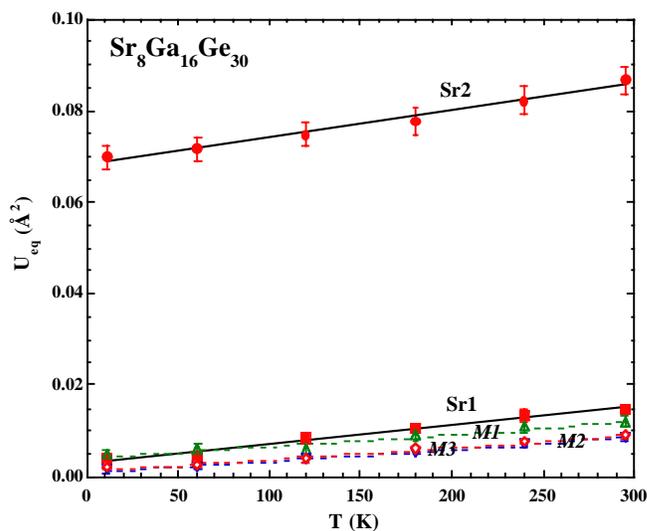


Fig 23. Temperature dependence of the isotropic atomic displacement parameters for $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$. Note the large and weak temperature dependence of the ADP values for Sr at site 2 in the structure. See text for details. (Chakoumakos et al., 2000).

5. CeRuGe₃

To further test some of the simple ideas discussed in this chapter, room temperature ADP information was used to identify a compound that should have a very low lattice thermal conductivity. Unusually large ADP values for one of the Ce sites were reported by Ghosh et al 1995 for the cubic compound CeRuGe₃ (space group Pm3n, $a = 9.0061 \text{ \AA}$). The results of the refinement, which was done using both x-rays and neutrons suggests that one Ce site contains Ce³⁺ ions and the other Ce⁴⁺ ions. A detailed study of the electron density around the various crystallographic sites concluded that the Ce⁴⁺ ions can tunnel or move away from the site center (much like the Sr ions discussed above). Analysis of the room temperature ADP data from this compound gives an Einstein temperature for the Ce⁴⁺ of 23 K and a Debye temperature of 128 K (or 155 K for all of the atoms except the Ce rattlers) and an average sound velocity of $1.37 \times 10^5 \text{ cm/s}$. The distance between the Ce rattlers is 7.9 \AA , and the lattice thermal conductivity at room temperature is estimated to be 0.008 W/cm-K . The measured lattice thermal conductivity (Fig 24) is about 0.005 W/cm-K after the electronic contribution has been subtracted using the Wiedemann-Franz law. CeRuGe₃ has a low lattice thermal conductivity, but also has a low Seebeck coefficient and hence is not a promising thermoelectric material.

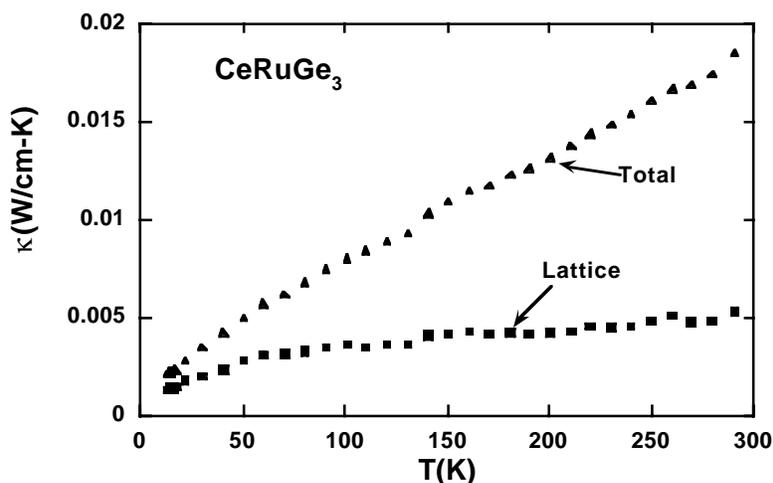


Fig 24. Thermal conductivity vs temperature for CeRuGe₃. The electronic thermal conductivity was subtracted from the total using the Wiedemann-Franz law.

VII. Summary

A new structure-property relationship is discussed that links atomic displacement parameters and the lattice thermal conductivity of clathrate-like compounds. For many clathrate-like compounds, in which one of the atom types is weakly bound and “rattles” within its atomic cage, it is demonstrated that room temperature ADP information can be used to estimate the room temperature lattice thermal conductivity, the vibration frequency of the “rattler” and the temperature dependence of the heat capacity. X-ray and neutron diffraction crystallography data,

reported in the literature, are used to apply this analysis to several promising classes of thermoelectric materials.

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