

BRIEF COMMUNICATION

Atomic Displacement Parameters and the Lattice Thermal Conductivity of Clathrate-like Thermoelectric Compounds

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A new structure–property relationship links atomic displacement parameters (ADP) 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, 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 crystallography data, reported in the literature, are used to apply this analysis to several promising classes of thermoelectric materials. © 1999

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Key Words: atomic displacement parameters; thermal conductivity; thermoelectric; clathrate; skutterudite; thallium; heat capacity; rattler.

I. INTRODUCTION

Atomic displacement parameters (ADPs) measure the mean-square displacement amplitude of an atom about its equilibrium position in a crystal. In the description of a new crystalline compound, crystallographers normally tabulate the room temperature ADP values for each distinct atomic site in the structure (1–4). The various ADP values 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, ADPs are not normally used by solid state physicists or chemists as a guide in the search for new compounds with specific properties. ADPs are still regarded by many scientists as unreliable, since in many of the earliest structure determinations, ADPs often became repositories for much of the error in the structure refinement. In addition, crystallographers have not always reported ADP information using a consistent definition (1), adding further confusion as to the usefulness of ADPs. The purpose of this article is to illustrate that when properly determined, ADPs 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 (5–8). The analysis discussed below is restricted to clathrate-like compounds in which one of the atom types “rattles” about its equilibrium position in the crystal substantially more than the other atoms in the structure.

The compounds investigated here are the filled skutterudites ($R_x\text{Co}_{4-y}\text{Fe}_y\text{Sb}_{12-z}\text{Sm}_z$, where $R = \text{La, Ce, or Tl}$, $0 < x, y, z < 1$) and two new promising thermoelectric compounds Tl_2SnTe_5 and Tl_2GeTe_5 (9). The filled skutterudites have been studied extensively for the past few years and exhibit excellent thermoelectric properties at elevated temperatures (10–16). In this structure, the rattling of the R atom in an oversized atomic cage is believed to be responsible for its low thermal conductivity. Tl_2SnTe_5 and Tl_2GeTe_5 exhibit more complicated tetragonal crystal structures, relative to the cubic-filled skutterudites, but have

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the common features of weakly bound TI atoms that reside at the centers of distorted, oversized cubic sites.

II. EXPERIMENTAL

Synthesis of the compounds is similar to that described in Ref. (14), as are the details of the thermal conductivity measurements. Heat capacity data from 2–300 K were collected using a commercial system from Quantum Design. The ADP values were determined by powder neutron diffraction using ORNL’s high flux isotope reactor, and a neutron powder diffractometer equipped with a closed cycle helium refrigerator. For each sample, the powder pattern was collected at several selected temperatures and refined using GSAS (General Structure Analysis System) software developed by Larson and von Dreele at the Los Alamos National Laboratory. As an additional check of the refinement methods, ADP values were also determined on single crystals of the filled skutterudites using a four-circle neutron diffractometer. Details of the refinement methods are described in Ref. (17). All of the ADP data have been converted to an isotropic, U_{iso} , value that has the dimensions of \AA^2 . U_{iso} measures the mean-square displacement amplitude of the atom averaged over all directions. However, most ADP data reported in the literature are obtained using X-ray diffraction from small single crystals. Therefore, the examples of the structure–property link between ADP and lattice transport and dynamics in clathrate-like compounds shown in Table 1 and Fig. 4, were calculated using reported X-ray ADP data. Obtaining quantitative ADP data using X-rays is, in general, more difficult than with neutrons. Absorption corrections are significant for X-rays and must be made using either an empirical or analytical approach for the ADP values to be quantitative. As shown below, however, the Debye or Einstein temperatures depend on the square root of the ADP value, so that errors in an ADP value of 20–40% result in only a 9–18% variation in the Debye temperature. Both X-ray and neutron ADP data are available for the compounds $\text{LaFe}_4\text{Sb}_{12}$ and Tl_2SnTe_5 , discussed below, and there is good agreement between the neutron and X-ray ADP values.

III. RESULTS AND DISCUSSION

The simplest expression for the lattice thermal conductivity of a solid is given by an expression adapted from the kinetic theory of gases (3):

$$\kappa_{\text{Lattice}} = \frac{1}{3}C_v v_s d \quad [1]$$

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, the mean free path (or relaxation

TABLE 1
Comparison between Thermodynamic Quantities Estimated Using Room Temperature X-Ray Crystallography Data (ADP Columns) and the Same Quantities Measured Either Directly or Inferred from Another Technique

	$\text{LaFe}_4\text{Sb}_{12}$		Tl_2SnTe_5		$\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$	
	ADP ^a	Other	ADP ^b	Other	ADP ^c	Other
Θ_D (K)	299	305 ^d	159	160 ^e	275	—
Θ_E (K)	79	80 ^f	38	30 ^e	51	—
v_s (m/s)	2886	3007 ^d	1448	—	2123	—
d (\AA)	7.9	9	6.45	—	5.38	—
κ_L (W/cmK)	0.014	0.017 ^d	0.0039	0.004 ^e	0.007	0.009 ^g

^aADP data from Ref. (22).

^bADP data from Ref. (23).

^cADP data from Ref. (24).

^dData from Ref. (14).

^ePresent work.

^fData from Ref. (19).

^gThermal conductivity data from Ref. (25) on $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$.

time) and heat capacity depend on frequency, but for the present analysis C_v depends only on temperature, while v_s and d are treated as scalars. It is well known to crystallographers that ADP data can be used to estimate the Debye temperature, Θ_D , C_v , and v_s for any compound (4). U_{iso} versus temperature can be calculated exactly for a cubic monatomic solid within the Debye model (4). Figure 1 illustrates how U_{iso} depends on temperature for Debye temperatures of 100, 200, and 300 K and an atomic mass of 100 amu. 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. A natural extension of this analysis to a multielement compound is accomplished by determining U_{iso} for each element (or crystallographic site) and calculating the average U_{iso} and the average atomic mass. As an example, for the skutterudite $\text{LaFe}_4\text{Sb}_{12}$, the average room temperature U_{iso} value is $(0.014 + 0.0028 \times 4 + 0.0049 \times 12)/17 = 0.0049 \text{ \AA}^2$ and the average mass per atom is 107 amu. This results in a Debye temperature of 285 K (308 K measured (14)). From the Debye model, the average velocity of sound is given by $v_s = \omega_D/K_D = [\Theta_D \cdot k_B \cdot 2\pi/h]/[6\pi^2 n]^{1/3}$, where n is the number of atoms per unit volume. For $\text{LaFe}_4\text{Sb}_{12}$, this gives in $v_s = 2750 \text{ m/s}$ (2923 m/s measured) (14). The heat capacity is easily estimated once the Debye temperature is known and, at room temperature, is usually close to the classical Dulong and Petit value of 24.9 J/(K mole atoms).

The above analysis, using only the room temperature ADP values, can be used to estimate the Debye temperature, velocity of sound, and heat capacity of any compound with a small amount of static disorder. Qualitatively, the effects of static disorder tend to displace the curves shown in Fig. 1, upward by a constant amount. In all of the thermoelectric compounds that we have studied using neutron diffraction, static disorder is only a problem for alloys in which the crystallographic sites are only partially occupied. For the stoichiometric compounds, $\text{LaFe}_4\text{Sb}_{12}$, $\text{CeFe}_4\text{Sb}_{12}$, Tl_2SnTe_5 , and Tl_2GeTe_5 , the temperature-dependent ADP values all extrapolate close to the origin. This is illustrated in Fig. 2 for Tl_2SnTe_5 . The Tl at site (1) in the Tl_2SnTe_5 crystal structure is weakly bound at the center of a distorted cube and clearly rattles more about its equilibrium position than the other atoms in the structure.

To estimate the lattice thermal conductivity using Eq. [1], however, requires a value for d . The phonon mean free path (or scattering rate) in the clathrate-like compounds is determined by the various scattering mechanisms in the crystal, such as acoustic phonons, grain boundaries, electron-phonon interactions, static defects, voids, and rattlers. Phonon scattering in these materials appears to be dominated by the rattlers (18). If the rattlers are truly localized vibrations (or Einstein oscillators), as suggested by Keppens *et al.* (19), then the heat-carrying phonon mean free path should be a function of the distance between the rattlers in the crystal. The simplest estimate of the phonon mean free path is therefore the distance between the rattlers. Physically, this implies that the resonant scattering of the acoustic phonons by the rattlers is so strong that d attains a minimum value given by the average distance between rattlers. The scattering of acoustic phonons by the rattlers will clearly be a maximum when the acoustic phonon and

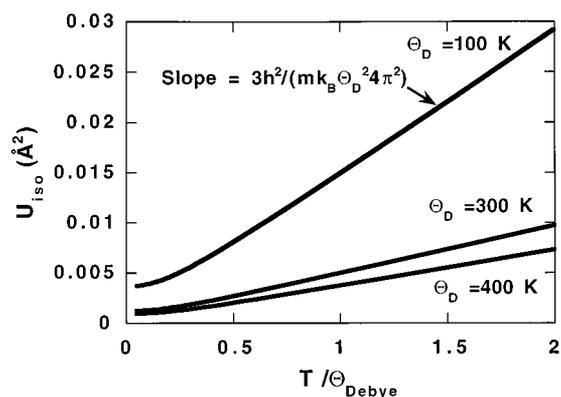


FIG. 1. Mean square displacement, U_{iso} , vs temperature scaled by the Debye temperature, Θ_D , for a monatomic cubic solid. U_{iso} is shown for a solid composed of atoms with a mass of 100 amu for three different Debye temperatures. For temperatures greater than Θ_D , U_{iso} is linear in T with a slope as indicated.

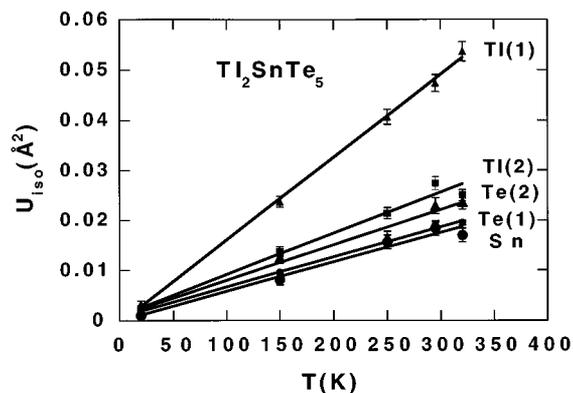


FIG. 2. ADP vs temperature for Tl_2SnTe_5 determined from powder neutron diffraction. Note the larger ADP values for Tl at site 1 in the crystal structure. These Tl rattle in oversized atomic cages.

rattling frequency are equal (20). However, even on resonance, it seems physically unlikely that d could be less than the rattler separation distance. At room temperature, this argument works well for the filled skutterudites such as $\text{LaFe}_4\text{Sb}_{12}$ (14). Using the measured thermal conductivity, heat capacity and an average value for the velocity of sound (14) yield a mean free path of $d = 9 \text{ \AA}$. The nearest neighbor distance of the La atoms in $\text{LaFe}_4\text{Sb}_{12}$ is 7.9 \AA . If the role of other scattering mechanisms can be minimized, this simple model would suggest that the thermal resistivity should vary as $x^{1/3}$, where x is the concentration of rattlers (the average spacing between rattlers varies as $x^{-1/3}$). This behavior was carefully examined in two families of filled skutterudites: $\text{Tl}_x\text{Co}_4\text{Sb}_{12-y}\text{Sn}_y$ and $\text{Tl}_x\text{Co}_{4-y}\text{Fe}_y\text{Sb}_{12}$ ($0 < x, y < 1$). Within the uncertainty of the measured thermal resistance data, an $x^{1/3}$ law provides a surprisingly good description of the data as the concentration of the Tl rattlers is varied between 0 and 1 (Fig. 3). For values of $x > 0.5$, we estimate that at least 80% of the room temperature thermal resistance is due to scattering by the Tl rattlers. We caution, however, that at low Tl concentrations we would expect, on general theoretical grounds, the increase in the thermal resistivity to be linear in the Tl concentration, x . How this behavior saturates at higher concentrations is not understood. The data shown in Fig. 3 simply suggest that replacing d in Eq. [1] by the average rattler separation is plausible. The real test of this hypothesis is whether this analysis results in good estimates of the room temperature lattice thermal conductivity for a variety of clathrate-like compounds. Estimates of the room temperature lattice thermal conductivity, determined using published X-ray data, are compared in Table 1 with the measured values for three classes of promising thermoelectric materials. The estimates are surprisingly close to the measured values.

Data similar to that shown in Fig. 3 have been previously reported for La and Ce rattlers in the filled skutterudite

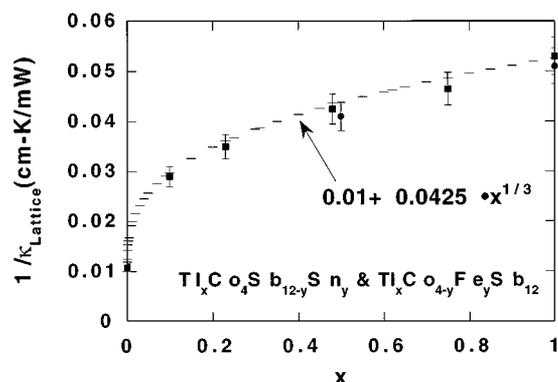


FIG. 3. Variation of the room temperature thermal resistivity vs the fraction of cages filled with the rattler Tl. In the filled skutterudite structure, the average separation distance between Tl rattlers varies as $x^{-1/3}$. For all but the two lowest concentrations of Tl, $x \approx y$. The square (circle) symbols refer to charge compensation with Sn (Fe). The electronic contribution to the thermal conductivity has been subtracted using the Wiedemann–Franz law.

structure. The present data agree reasonably well with the previous La data reported by Nolas *et al.* (18), particularly at the low La concentrations. The peak in the thermal resistivity for Ce-filling fractions near $x = 0.6$ – 0.7 reported by Meisner *et al.* (21) was not observed in the present work.

If the rattler represents a localized vibrational mode that resonantly scatters acoustic phonons, the dynamics of the rattler are more appropriately described by a quantized harmonic oscillator (Einstein oscillator) rather than the Debye model. This implies that all of the rattlers vibrate at about the same frequency and are poorly coupled to the lattice dynamics of the rest of the solid. Of course, there has to be some coupling, otherwise the rattlers could not scatter acoustic phonons! This suggests that a better starting point for understanding the low-energy lattice dynamics of these types of materials is to treat the rattlers as Einstein oscillators and the other atoms as part of a Debye solid. The decomposition of these solids into an Einstein part and a Debye part does not significantly affect the estimate of the room temperature lattice thermal conductivity, discussed above, since at high temperatures the Debye and Einstein models both tend toward the classical value for the heat capacity. The Einstein mode, however, will significantly affect the temperature dependence of the heat capacity at low temperatures and will result in a peak in the phonon density of states. This mode should also be visible in a variety of spectroscopic measurements.

The room temperature ADP values for the rattler can also be used to estimate the Einstein frequency of the rattler. The mean-square displacement amplitude, $\langle u^2 \rangle$ of a quantized harmonic oscillator (2) is given by

$$U_{\text{iso}} = \langle u^2 \rangle = h/(8\pi^2 mv) \cdot \coth(hv/2k_B T) \quad [2]$$

where m is the mass of the rattler and ν is the frequency of the vibration. The temperature dependence of Eq. [2] is qualitatively similar to that shown in Fig. 1 with $\Theta_E = hv/k_B$ replacing Θ_D . At high temperatures, where $hv < 2k_B T$, Eq. [2] reduces to the classical expression $U_{\text{iso}} = k_B T/K$, where K is the force constant of the oscillator; $K = m(2\pi\nu)^2$. As was the case for the Debye model, the room temperature ADP data can be used to estimate the Einstein temperature of the rattler only if the static disorder is small and the Einstein temperature is less than about 300 K. Comparisons between the Einstein temperatures determined using the room temperature ADP data, with the Einstein temperatures determined using other techniques (inelastic neutron scattering, heat capacity, and elastic constant data) are shown in Table 1.

As an example of the surprisingly good results that can be obtained using room temperature X-ray ADP values, the heat capacity of Tl_2SnTe_5 was predicted, with no adjustable parameters, and then measured. An Einstein contribution was used to describe the Tl rattler (the Tl at site 1 in the crystal structure, see Fig. 2) with an Einstein temperature of 38 K and an amplitude of $\frac{1}{8} \cdot 3R$, where R is the gas constant. The $\frac{1}{8}$ is because only 1 out of the 8 atoms per formula units is a rattler. For the rest of the atoms, a Debye heat capacity was used with a Debye temperature of 159 K and an amplitude of $\frac{7}{8} \cdot 3R$. A comparison between the measured and predicted heat capacity is shown in Fig. 4. The agreement is remarkable. At temperatures below 15 K (Fig. 4 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.

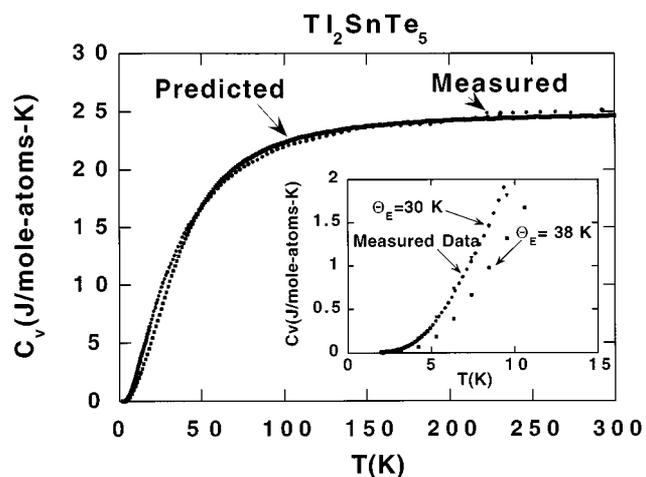


FIG. 4. Predicted and measured heat capacity for Tl_2SnTe_5 . The predicted heat capacity was determined using the published room temperature X-ray crystallography ADP data of Ref. (24). There were no adjustable parameters. The inset shows the predicted and measured heat capacity. At low temperatures, an Einstein temperature of 30 K provides a better description of the data than the predicted value of 38 K.

IV. SUMMARY

In summary, we have shown that room temperature ADP data can be used to identify new compounds with unusually low lattice thermal conductivities. For large classes of clathrate-like compounds, the room temperature ADP data reported as part of crystal structure determinations can be used to estimate the Debye temperature, velocity of sound, mean free path of phonons, lattice thermal conductivity, heat capacity, and the Einstein frequency of the rattler. The Si and Ge clathrate compounds, such as those recently reported by Nolas *et al.* (25), are excellent candidate materials to further test some of these simple ideas.

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