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Citation: Appl. Phys. Lett. 94, 181901 (2009); doi: 10.1063/1.3127224
View online: http://dx.doi.org/10.1063/1.3127224
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v94/i18
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Lower limit to phonon thermal conductivity of disordered, layered solids

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(Received 26 January 2009; accepted 12 April 2009; published online 4 May 2009)

The past decade of work focusing on increasing the thermoelectric figure of merit (ZT) in material systems has made thermoelectric solutions appealing for a wide range of applications. Recent research has shown that the thermal conductivity of materials (which is inversely proportional to ZT) can be reduced below the theoretical minimum of an amorphous solid by controlling various aspects of nanostructures. Nanowires have shown significant thermal conductivity reduction by limiting the phonon mean free path. Thin film interfaces and disordered alloys have also reduced thermal conductivity by introducing other channels of phonon scattering. Recently, Chiritescu et al. measured the thermal conductivity of disordered, layered structures of WSe2 and reported values six times smaller than the theoretical minimum. These structures have the lowest thermal conductivity to mass density ratio ever reported.

These aforementioned studies have shown that the theoretical minimum of a disordered crystal, as originally proposed by Einstein and later modified by Cahill et al. [Cahill–Watson–Pohl (CWP) model] to account for coupled oscillators with the Debye model, overpredicts the measured thermal conductivity in disordered, layered alloys. In this letter, the cause of this overprediction is investigated by considering boundary scattering, which would reduce the thermal conductivity in layered alloys below that of the minimum thermal conductivity predicted by the CWP model. From this, a model for minimum conductivity is developed, which explains the overprediction of the CWP model to recent data.

The phonon thermal conductivity of an isotropic Debye solid is given by

\[ \Lambda = \frac{1}{6 \pi^2} \sum_j \int_0^{\omega_j} \frac{h^4 \omega^3}{k_B T^2} \frac{\exp[h \omega/k_B T]}{(\exp[h \omega/k_B T] - 1)^2} \tau_j \omega_j \, d\omega, \]  

(1)

where the thermal conductivity is summed over the \( j=3 \) modes (one longitudinal and two transverse), the subscript \( j \) refers to the mode, \( h \) is Planck’s constant divided by \( 2 \pi \), \( \omega \) is the phonon angular frequency, \( \omega_j \) is the cutoff frequency, \( T \) is the lattice temperature, \( \tau \) is the scattering time, and \( v \) is the phonon group velocity. The minimum thermal conductivity is derived by assuming that the minimum scattering time is one-half the period of vibration—\( \tau_{\text{min}} = \pi / \omega \)—and the velocity is therefore given by \( v_{\text{min}} = n^{1/3} / \tau_{\text{min}} \), where \( n \) is the atomic density and therefore \( n^{-1/3} \) is the atomic spacing. Therefore, the CWP model for minimum thermal conductivity (which is slightly modified in this work, as discussed below) is given by

\[ \Lambda_{\text{min,CWP}} = \frac{1}{6} n^{1/3} \sum_j \int_0^{\omega_{j,CWP}} \frac{h^4 \omega^3}{k_B T^2} \frac{\exp[h \omega/k_B T]}{(\exp[h \omega/k_B T] - 1)^2} \tau_j \omega_j \, d\omega. \]  

(2)

In Eq. (2), the cutoff frequency for each mode is calculated by \( \omega_{j,CWP} = \sqrt{6 / n \pi^2} \) since a Debye solid is assumed. The power in this model lies in the fact that it contains no free parameters since \( \omega_j \) and \( n \) are known or can be measured for an unknown material. The average crystal velocity is used in calculating the cutoff frequency, not the minimum velocity, since the cutoff frequency is related to the specific heat of the crystal. However, when substituting in for \( \omega_j \) and \( \tau_j \) to determine \( \Lambda_{\text{min}} \), the minimum velocity and scattering time must be used. This approach of using the minimum velocity as the transport velocity as opposed to the sound velocity is a slight modification to the traditionally used CWP model for minimum conductivity. This modification essentially localizes all the modes as opposed to the traditional CWP model that assumes all the modes are propagating throughout the crystal at the speed of sound. In this work, the CWP model refers to this modified CWP model using the minimum velocity as the velocity of localized mode oscillations.

The CWP model considers only the minimum scattering time in the disordered crystal between two oscillators. However, epitaxial deposition and atomic control of layering can create heavily disordered alloys with interfaces occurring on the order of monolayers, causing oscillations of atoms to scatter at layer boundaries. This is the cause of the drastic thermal conductivity reduction of WSe2 crystals below \( \Lambda_{\text{min,CWP}} \). In this case, the expression for minimum thermal conductivity must take into account these scattering events since atomic vibrations and minimum scattering times will be affected by the interfaces in the alloys.

The scattering rates of the various phonon processes for each polarization per unit volume are derived from the energy perturbation matrix and given by

\[ \Lambda_{\text{min,CWP}} = \frac{1}{6} n^{1/3} \sum_j \int_0^{\omega_{j,CWP}} \frac{h^4 \omega^3}{k_B T^2} \frac{\exp[h \omega/k_B T]}{(\exp[h \omega/k_B T] - 1)^2} \tau_j \omega_j \, d\omega. \]  

(2)
where \( a \) is the interatomic spacing, \( N \) is the number of atoms in the crystal, \( \omega' \) is the frequency of the oscillator that is causing the scattering event, \( M \) is the mass of the atom, and \( c \) is the coefficient in the perturbation Hamiltonian related to the scattering event, \( \omega' = \omega \).

Therefore, to evaluate a scattering rate arising from certain scattering events, say, at an interface, \( c \) must be evaluated. Note that Eq. (3) gives the scattering time per polarization, as opposed to the original expression of Klemens, which lumps all phonon polarizations together into an effective scattering time. The original derivations of Klemens are well suited for applications where the dominant longitudinal and transverse phonon velocities are similar, but in materials and at temperatures where the difference between the velocities of the different phonon polarizations are appreciable, the scattering rates must be rederived via Eq. (3) to account for the different polarizations.

Phonon scattering at interfaces can be treated as scattering by an atom of a different binding force, that is, an atom bound to its neighbors by binding forces of different elastic properties from those of normal linkages. The contribution of normal linkages to the unperturbed Hamiltonian of an oscillator is

\[
H_j = \frac{1}{2} M \left( \frac{v_j}{a} \right)^2 (u_j - u_{j-1})^2, \tag{4}
\]

where \( u \) is the atomic displacement given by \( u_j = b_j \exp[i(kx + \omega t)]/N^{1/2} \), where \( b_j \) is the amplitude of the wave, \( k \) is the wavevector, and \( t \) is the time. The amplitude of the wave is described by

\[
b_j = \left( \frac{\hbar}{M\omega N} \right)^{1/2} \exp[-i\omega t]. \tag{5}
\]

The changes in the elastic constants from those of the “homogeneous” solid material to those due to a change in the atomic binding force are described by changes in the phonon velocities \( \delta v \). Following Eq. (4), the perturbation Hamiltonian of an oscillator is \( H'_j = M v_j \delta v_j (u_j - u_{j-1})^2/a^2 \) so that the change in displacement between two neighboring atoms is given by

\[
u_j - u_{j-1} = \left( \frac{\hbar N}{M\omega} \right)^{1/2} \exp[ikx] \left( 1 - \exp[ika] \right). \tag{6}
\]

In the case of scattering processes, the factor of \( \exp[ikx] \) can be omitted since it introduces a phase-factor into the Hamiltonian and does not affect \( c \). In the case of long waves, which, when considering minimum scattering lengths for thermal conductivity, all waves are relatively long when scattering is on the order of the interatomic spacing, \( \exp[ika] \rightarrow 1 \approx ika \), and therefore, the perturbation Hamiltonian reduces to \( H'_j = -M v_j \delta v_j k^2 / \omega \). The perturbation energy matrix is of the form of

\[
H'_j = \left( \frac{\hbar N}{M\omega} \right) c_j, \tag{7}
\]

and from inspection of the perturbation Hamiltonian, \( c_j = \pm M v_j \delta v_j k^2 / N \). Assuming a Debye solid, \( k = \omega/|v_j| \), and from Eq. (3), the phonon scattering rate of a given polarization due to a plane of atoms with a different binding force is given by

\[
\frac{1}{\tau_{j,\text{int}}} = n^{-1} \left( \frac{\delta v_j}{v_j} \right)^2 \omega^4 \frac{\omega^4}{\pi^2 v_j^2}. \tag{8}
\]

Note that this expression differs from the original expression derived by Klemens.

In the case of a disordered solid with minimum oscillation times and phonon velocities, as previously described, the interfacial phonon scattering rate is given by

\[
\frac{1}{\tau_{\text{min},\text{int}}} = \pi^2 \left( \frac{v_{\text{int},\text{total}}^1}{\omega} - 1 \right)^2 \tag{9}
\]

where \( v_{\text{int}} \) is the phonon velocity associated with the interatomic bonds at the interface.

In the case of disordered films adjacent to interfaces, such as amorphous films on substrates or the WSe\(_2\) structures described in Chirulescu et al., the primary phonon scattering due to the interfaces is described by Eq. (8). The limit to this interlayer scattering time is described by the minimum scattering time in Eq. (9), and the interlayer scattering time is given by \( \tau_{\text{min}} = \pi/\omega \). Using Matthiessen’s rule, the minimum scattering time for a solid and an interface is given by

\[
\tau_{\text{min},\text{total}} = \left[ \frac{\omega}{\pi} + \frac{\pi^2 v_{\text{int},\text{total}}^1}{\omega} \left( \frac{v_{\text{int},\text{total}}^1}{\omega} - 1 \right)^2 \right]^{-1}. \tag{10}
\]

Using Eq. (10) in Eq. (1) with \( v_{\text{min}} = \pi^{-1/3}/\tau_{\text{min}} \) gives the minimum conductivity for a structure where scattering occurs at interface due to different binding forces, \( \Lambda_{\text{min},\text{int}} \). The first term on the right hand side of Eq. (10) represents the
within the sheets, but the sheets are bonded by weaker van der Waals forces. The weak forces bonding the two-dimensional sheets would create an interatomic interaction and scattering phenomenon described by Eq. (8). The minimum limit of this scattering is described by Eq. (9). Assuming highly disordered WSe₂ layers in plane, the minimum scattering time of the WSe₂ layered structure is given by Eq. (10). Calculations of \( \Lambda_{\text{min,int}} \) using Eq. (10) set a lower limit for WSe₂ layered alloys, taking into account interfacial phonon scattering, which agrees very well with the measured data. This indicates that the WSe₂ films grown by Chiritescu et al.⁹ have the lowest possible conductivity for WSe₂ layered films.

In summary, a model for the minimum thermal conductivity of disordered, layered solids is presented, which takes into account phonon scattering arising from changes in interatomic forces. This minimum conductivity model elucidates the physical phonon processes that cause thermal conductivity reduction and give an avenue to quantify the effects of different interatomic forces on the minimum limit to conductivity. This model also successfully explains the reduction in measured thermal conductivity of a-Ge and WSe₂ films below that of the CWP minimum conductivity predictions.

P.E.H. is greatly appreciative for funding by the Harry S. Truman Fellowship through the LDRD Program at Sandia National Laboratories. The authors thank Thomas E. Beechem of Sandia National Laboratories for critical reading of this manuscript. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed-Martin Co., for the United States Department of Energy’s National Nuclear Security Administration under Contract No. DE-AC04-94AL85000.

Figure 2 shows the minimum thermal conductivity of 24 and 62 nm WSe₂ films by Chiritescu et al.⁹ The measured thermal conductivity of the WSe₂ film is lower than the predicted minimum with the CWP model. The W and Se atoms are covalently bonded through van der Waals forces. The weak forces bonding the two-dimensional sheets would create an interatomic interaction and scattering phenomenon described by Eq. (8). The minimum limit of this scattering is described by Eq. (9). Assuming highly disordered WSe₂ layers in plane, the minimum scattering time of the WSe₂ layered structure is given by Eq. (10). Calculations of \( \Lambda_{\text{min,int}} \) using Eq. (10) set a lower limit for WSe₂ layered alloys, taking into account interfacial phonon scattering, which agrees very well with the measured data. This indicates that the WSe₂ films grown by Chiritescu et al.⁹ have the lowest possible conductivity for WSe₂ layered films.

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