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Reduction of Lattice Thermal Conductivity by Point Defects at Intermediate Temperatures

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The lattice thermal conductivity is reduced by point defects because they scatter phonons. An analytic expression can be derived only in the limit of high temperatures; at lower temperatures one must have recourse to numerical calculations. Because the conductivity is due mainly to phonons of low frequencies when point-defect scattering is strong, the high-temperature approximation can be used at temperatures above half the Debye temperature. Numerical calculations, using the Ge–Si system as an example, show that the error incurred by using the high-temperature approximation is less than 10%.

KEY WORDS: alloys; germanium; intermediate temperatures; phonons; point defects; thermal conductivity.

1. INTRODUCTION

Because point defects scatter phonons with a scattering cross section varying as the fourth power of frequency, while other interaction processes vary more slowly with frequency, the lattice thermal conductivity can be expressed in an algebraic form only in the limit of high temperatures [1], where the spectral contribution to the specific heat attains the simple form of the classical limit. When the highest-frequency phonons are strongly scattered by point defects, these phonons make only a small contribution to the conductivity integral.

If point defects eliminate the contribution from the high frequencies, the classical or high-temperature approximation should still be good at somewhat lower temperatures, when the classical limit no longer holds for

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the highest frequencies but still holds at those lower frequencies which make the major contribution to the thermal conductivity. Hence the high-temperature approximation of Ref. 1 might still be useful even at intermediate temperatures below the Debye temperature, provided point-defect scattering is strong enough. The present work tests this conjecture by numerically comparing the evaluated thermal conductivity integrals with the high-temperature approximation.

The model calculations are done with parameters which are typical for solid solutions such as the well-studied Ge–Si system. The conclusion arrived at is that the high-temperature approximation works well down to half the Debye temperature; this conclusion should be generally valid.

2. LATTICE THERMAL CONDUCTIVITY

In general, for an isotropic Debye solid the lattice thermal conductivity is given by the integral

$$\lambda = \frac{k_B \omega_D{}^3}{2\pi^2 v} \left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} \frac{x^4 e^x}{(e^x - 1)^2} \tau(\omega)\, dx \tag{1}$$

where k_B is the Boltzmann constant, ω_D and θ are the Debye frequency and temperature, respectively, T is the absolute temperature, v is the spherically averaged speed of sound, τ is the overall relaxation time, and $x = \hbar\omega/k_B T$ the reduced frequency. Here $\hbar$ is the Planck constant divided by 2π.

We consider two scattering processes which contribute to the relaxation rate $1/\tau$ and provide the thermal resistance. The first are the anharmonic three-phonon interactions. Their relaxation rate is of the form [1]

$$1/\tau_u = B\omega^2 T \tag{2}$$

The other processes are scattering of phonons by point defects, with a relaxation rate [1]

$$1/\tau' = A\omega^4 \tag{3}$$

The coefficient A depends on the nature of the defect and the concentration. For mass-defect scattering it has the form

$$A = (a^3/4\pi v^3)\, \varepsilon \tag{4}$$

where a^3 is the atomic volume, and

$$\varepsilon = \sum_i f_i (M_i - M)^2 / M^2 \tag{5}$$

and M is the average mass, i.e.,

$$M = \sum_i f_i M_i \tag{6}$$

Here f_i is the fraction of atoms of type i of mass M_i.

The overall relaxation time is the reciprocal of the sum of the relaxation rates given by Eqs. (2) and (3), i.e.,

$$\tau = [BT(T/\theta)^2\, \omega_D{}^2 x^2][1 + (T\omega_D/\theta\omega_0)\, x^2]^{-1} \tag{7}$$

where ω_0 is defined by

$$\omega_0^2 = BT/A \tag{8}$$

so that $\tau'(\omega_0) = \tau_u(\omega_0)$. Note that in the case of no point-defect scattering, $\omega_0 \to \infty$ and, according to Eq. (7), $\tau \to \tau_u$. Then if Eq. (7) is substituted into Eq. (1), one obtains the intrinsic thermal conductivity λ_i. The ratio of λ, the thermal conductivity in the presence of point defects, to λ_i, the intrinsic conductivity, is therefore

$$\frac{\lambda}{\lambda_i} = \frac{\int_0^{\theta/T} e^x(e^x - 1)^{-2}\, x^2[1 + (T\omega_D/\theta\omega_0)^2\, x^2]^{-1}\, dx}{\int_0^{\theta/T} e^x(e^x - 1)^{-2}\, x^2\, dx} \tag{9}$$

Previously [1] Eq. (9) was approximated in the high-temperature limit where $e^x(e^x - 1)^{-2} \simeq 1$. This gave the analytical expression

$$\frac{\lambda}{\lambda_i} = \frac{\omega_0}{\omega_D} \tan^{-1}(\omega_D/\omega_0) \tag{10}$$

The present work tests the limits of validity of Eq. (10) by comparing it to numerical evaluations of Eq. (9).

3. NUMERICAL EVALUATION AND RESULTS

The numerical comparison of Eqs. (9) and (10) was done for the binary alloy system Ge–Si. This system has been well studied, and the necessary parameters are available.

In order to evaluate Eqs. (9) and (10) for different fractions f_{Si} of silicon, a linear interpolation was assumed between Si and Ge of those parameters which depend on the average material, in the manner of Abeles [2]. Debye temperatures θ for Si and Ge are, respectively, 645 and 374 K [3]; atomic masses are 28.1 and 72.6; spherically averaged sound velocities, calculated from elastic moduli, are 6.60×10^5 and 3.98×10^5 cm $\cdot$ s^{-1}; and lattice constants are 5.43 and 5.66 Å [4].

The values of $\lambda_i(T)$ were those recommended by Touloukian et al. [5]; from these the product $T\lambda_i(T)$ near θ was formed, and thus values of B for the elements. For the alloys values of B were obtained by interpolation. The values of $T\lambda_i(T)$ used are $365\ \mathrm{W \cdot cm^{-1}}$ for Si and $191\ \mathrm{W \cdot cm^{-1}}$ for Ge.

With these data, Eqs. (9) and (10) were evaluated, in the former case using Bode's method [6]. The results of the calculations are displayed in Fig. 1 in the following manner. The ratio λ/λ_i was calculated from Eq. (9). The approximate ratio $(\lambda/\lambda_i)_{\mathrm{approx}}$ was obtained from Eq. (10). The fractional difference, expressed as a percentage, i.e.,

$$100[\lambda/\lambda_i - (\lambda/\lambda_i)_{\mathrm{approx}}]/(\lambda/\lambda_i) \qquad (11)$$

is the ordinate. This difference is a function of T/θ. For various values of T/θ (ranging from 3 to 0.2) it is plotted as a function of the silicon content.

One notes several features. First, it is found that the approximation given by Eq. (10) agrees with the numerical calculation to within 2% at $T > \theta$, as one would expect from a high-temperature approximation. Second, the difference is less than 10% for T/θ ranging from 0.5 to 1, so that for most purposes the approximation is still useful. The fractional error is only mildly sensitive to concentration in the middle range of f_{Si}, where ε is large and point-defect scattering strong.

What is surprising at first sight is that the fractional discrepancy decreases at a low solute content. This is a consequence of presenting the results as ratios λ/λ_i. As point-defect scattering decreases, both calculations make λ tend toward λ_i, so that the fractional difference must be small.

The curves are not symmetrical about $f_{\mathrm{Si}} = 0.5$. This is due to the difference in material parameters of the two constituents, especially their difference in Debye temperature θ. It is of interest that the deviation curves show a maximum at $f_{\mathrm{Si}} = 0.35$, which is where the two elements make equal contributions to the average Debye temperature $\sum_i f_i \theta_i$.

The present calculations do not tell us over what range of temperature the high-temperature approximation for λ_i can be used.

In conclusion, the ratio was calculated between the lattice thermal conductivity, including anharmonic processes and point-defect scattering, and the intrinsic conductivity, limited only by anharmonic processes. This was done for the binary alloy system Ge–Si, as a function of the fractional silicon concentration, at a number of fixed temperatures T/θ. The results were then compared to the high-temperature approximation [1]. Very good agreement was found for $T > \theta$, the temperature range for which Eq. (10) had been derived. Reasonable agreement was found for the intermediate temperature range $\theta > T > 0.5\theta$, allowing one to use Eq. (10) to

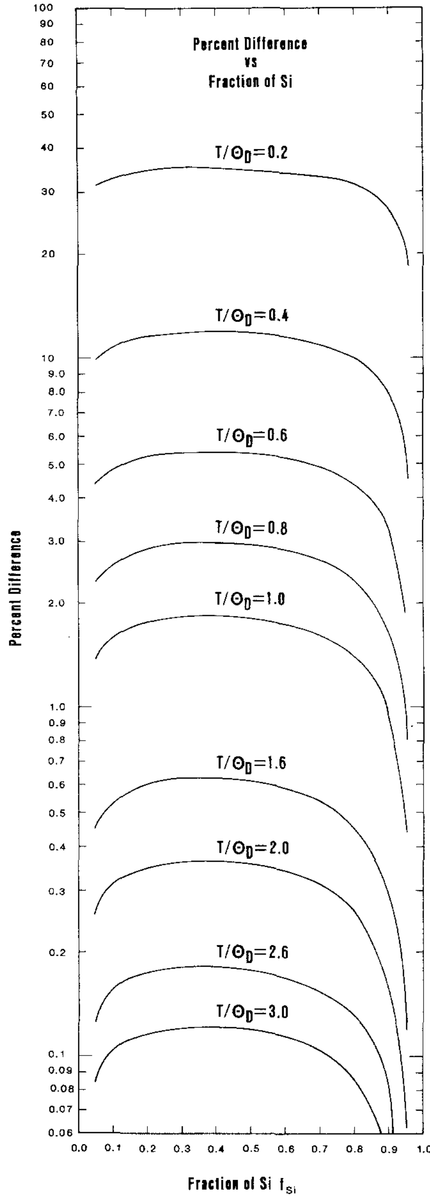

Fig. 1. Percentage difference versus fraction of Si for fixed values of T/θ as indicated. The percentage difference is that between λ/λ_i calculated numerically from Eq. (9) and the approximate value obtained from Eq. (10).

somewhat below the Debye temperature. This illustrates that point-defect scattering extends the limit of validity of the classical high-temperature approximation, because the modes of highest frequency are removed from the conduction process.

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