

Determining the Kapitza resistance and the thermal conductivity of polycrystals: A simple model

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(Received 5 September 1997)

A simple model for the thermal conductivity of polycrystals is presented by incorporating the concept of the Kapitza resistance with an effective medium approach. By applying this model to a few thermoelectric alloys reported in the literature, we show that it quite well describes the often observed grain size-dependent thermal conductivity of polycrystals and also provides a simple and practical method to determine the Kapitza resistance. We estimate the Kapitza resistance in real polycrystals and the effects of microstructural scales, such as spatial variations in the grain size and grain shapes, on the thermal conductivity. [S0163-1829(98)03013-6]

Thermal conductivity of polycrystals is of quite general interest due to its technological importance in many practical applications of polycrystals, for example, $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ and SiGe thermoelectric alloys,¹ and SiC ceramics and recently developed diamond films for thermal management of high-density-high-power microelectronics.² Generally, polycrystals show lower thermal conductivity than their corresponding bulk single crystals because of the existence of grain boundaries and pores in polycrystals. The effect of pores is an old problem which has been attacked by many researchers.³ In most cases the conductivity of polycrystals decreases linearly with the porosity as predicted by effective medium approaches (EMA).⁴ At present, it is also quite generally accepted that the thermal conductivity of polycrystals decreases with grain sizes.⁵⁻⁹ The model usually proposed to understand the grain size-dependent behavior is the relaxation time approaches of boundary scattering¹⁰ based on the Klemens-Callaway theory.¹¹ In this model, by adding a boundary scattering relaxation time into the total relaxation time of various scattering processes, the lattice thermal conductivity of polycrystals has been calculated only numerically as a function of average spherical grain sizes after choosing a number of other adjustable parameters.¹⁰ The (diffuse) grain-boundary scattering can produce thermal resistance at grain boundaries. A very recent molecular dynamics simulation of heat conduction across Si bicrystal¹² has shown the presence of the thermal boundary resistance, i.e., the Kapitza resistance.¹³ Similarly to the thermal interfacial resistance between two different phases in composites,¹⁴ the Kapitza resistance can commonly exist in polycrystals and its overall effect is to reduce the thermal conductivity of polycrystals. This reduction can be very pronounced for fine-grained polycrystals. To our knowledge, a complete understanding of the effect of the Kapitza resistance on the thermal conductivity of polycrystals is still missing. On the other hand, there has been no report on the Kapitza resistance in real polycrystals since there has been no appropriate method to measure the Kapitza resistance across grain boundaries in real polycrystals, whilst complicated dynamical simulations have so far been performed only for idealized Si bicrystal¹² and simple interfaces.¹⁵

In the present paper, by incorporating the concept of the Kapitza resistance with EMA we present a simple model for the lattice thermal conductivity of polycrystals without going into details of various scattering processes. We show that our Kapitza resistance-EMA model provides answers to two problems which are being widely investigated. The first problem is the often observed grain size-dependent thermal conductivity of polycrystals⁵⁻⁹ and the effects of microstructural scale. The second problem is the determination of the *in situ* Kapitza resistance^{12,15} which will be made for real polycrystals. Compared to the Klemens-Callaway type relaxation time approaches^{10,11} which are *microscopically* theoretical models, the present Kapitza resistance-EMA model is a more *macroscopic*, analytical method in which microstructurally stochastic effects, such as spatial variations in the grain size and Kapitza resistance, grain shapes and orientations, can be readily incorporated. The Kapitza resistance may be taken as a connection between the *microscopic* Klemens-Callaway type and the *macroscopic* EMA type theories.

Consider a real polycrystal with grains of various orientations. For convenience, let us consider first an isolated ellipsoidal crystallite with the thermal boundary resistance on its surface, in the polycrystal. Following Nan, Birringer, Clarke, and Gleiter,¹⁴ we can obtain the lattice thermal conductivities K_{ii}^c of the crystallite along its symmetric axes X_i ($i = 1, 2, 3$) as follows:

$$K_{ii}^c = K_{ii}^o / (1 + \gamma_{ii} L_{ii}), \quad (1)$$

$$\gamma_{ii} = \begin{cases} (2 + 1/p)L_{K_{ii}}/a_1, & \text{for } p \geq 1, \\ (1 + 2p)L_{K_{ii}}/a_3, & \text{for } p \leq 1, \end{cases} \quad (2)$$

where a_i are radii of the crystallite along its X_i axes, $p = a_3/a_1$ is its aspect ratio [$p > 1$ and $p < 1$ are for a prolate ($a_1 = a_2 < a_3$) and oblate ($a_1 = a_2 > a_3$) crystallite, respectively], and L_{ii} are the depolarization factors dependent on the crystallite shape. Here we have introduced Kapitza lengths $L_{K_{ii}}$ as defined by

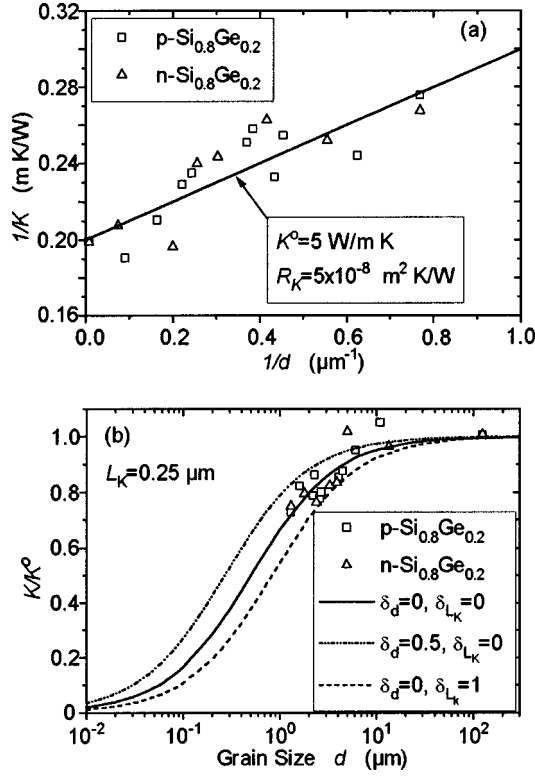


FIG. 1. (a) $1/K$ vs $1/d$ plots [Eq. (6)] of experimental data at room temperature for p - and n -type $\text{Si}_{0.8}\text{Ge}_{0.2}$ alloys (Ref. 8), where the solid line is a best-fit line. (b) The effects of the grain size d and variations in both d and the Kapitza length L_K on the normalized thermal conductivity of the $\text{Si}_{0.8}\text{Ge}_{0.2}$ alloys. For comparison, the experimental data are also shown.

$$L_{K_{ii}} = R_{K_{ii}} K_{ii}^o, \quad (3)$$

where K_{ii}^o and $R_{K_{ii}}$ are, respectively, the bulk lattice thermal conductivities of the crystallite and the Kapitza resistances along its X_i axes. Generally, $0 \leq R_{K_{ii}} \leq \infty$, with $R_{K_{ii}} = 0$ corresponding to a grain boundary with perfectly thermal contact. For $R_{K_{ii}} > 0$, temperature jumps across the boundary.

We now consider the dense polycrystal (of course, the porosity is very easily incorporated) composed of the crystallites with the thermal boundary resistance existing between crystallites of various orientations. From EMA,⁴ the thermal conductivities K_{ii} of the polycrystal can be obtained as

$$\left\langle \frac{K_{ii}^c - K_{ii}}{L_{ii}K_{ii}^c + (1 - L_{ii})K_{ii}} \right\rangle = 0. \quad (4)$$

Further combining Eqs. (1) and (4) gives

$$\left\langle \frac{K_{ii}^o - (1 + \gamma_{ii}L_{ii})K_{ii}}{L_{ii}K_{ii}^o + (1 - L_{ii})(1 + \gamma_{ii}L_{ii})K_{ii}} \right\rangle = 0, \quad (5)$$

where $\langle \rangle$ denotes averaging over various crystallite sizes, shapes, orientations, and the Kapitza resistances. Equation (5) is the desired general formulation of this proposed Kapitza resistance-EMA method that incorporates various stochastic effects. For simplicity, we discuss two common isotropic cases below.

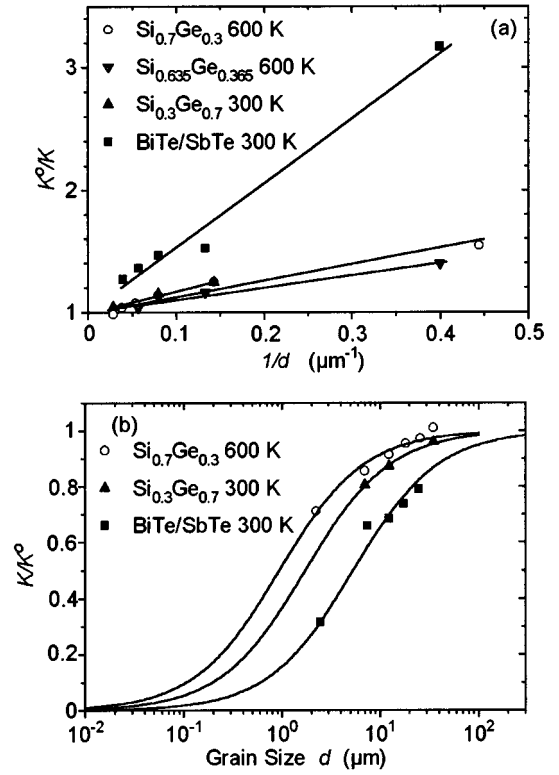


FIG. 2. Comparison of Eq. (6) and experimental data for a few SiGe alloys (Refs. 6 and 7) and $(\text{Bi}_2\text{Te}_3)_{0.25}(\text{Sb}_2\text{Te}_3)_{0.75}$ alloys (Ref. 9).

First, for common polycrystals with isotropic, equisized spherical crystallites, the thermal conductivity K can be obtained directly from Eq. (5) as

$$K/K^o = 1/(1 + 2L_K/d) = 1/(1 + 2R_K K^o/d), \quad (6)$$

where d is the grain diameter. It is important to note from Eq. (6) that the normalized conductivity of such polycrystals is a function of only L_K/d , i.e., there is a general scaling law $K/K^o = F(L_K/d)$. This means that all data will fall upon a supermaster curve in K/K^o vs L_K/d plot, irrespective of composition and temperature, though the thermal conductivity (K and K^o) and the Kapitza length (L_K) depend on composition and temperature.

Secondly, for the case of randomly oriented ellipsoidal crystallites with isotropic R_K and K^o , we obtain

$$K/K^o = [\sqrt{g^2 + 2f(L_{11} + 2L_{33})} + g]/f, \quad (7)$$

$$f = 2(1 + 3L_{11})(1 + \gamma L_{11})(1 + \gamma L_{33}), \quad (8)$$

$$g = 2 - 3L_{33} + \gamma L_{11}(2 - 3L_{11}), \quad (9)$$

$$\gamma = 4p^{1/3}(1 + 1/2p)L_K/d, \quad (10)$$

here $d = 2(a_1^2 a_3)^{1/3}$ is an equivalent spherical diameter.

In order to examine the validity of this proposed model, we compare it with the data available in the literature for lightly doped $\text{Si}_{0.7}\text{Ge}_{0.3}$ and $\text{Si}_{0.3}\text{Ge}_{0.7}$,⁶ n -type heavily doped $\text{Si}_{0.635}\text{Ge}_{0.365}$,⁷ n - and p -type heavily doped $\text{Si}_{0.8}\text{Ge}_{0.2}$,⁸ and p -type $(\text{Bi}_2\text{Te}_3)_{0.25}(\text{Sb}_2\text{Te}_3)_{0.75}$ alloys.⁹ These alloys are technologically important thermoelectric materials,¹ where the effect of the grain size on thermoelectric properties is

TABLE I. Bulk lattice thermal conductivity K^o , Kapitza resistance R_K , and Kapitza length L_K , determined at room temperature (300 K) for a few thermoelectric alloys.

Polycrystals	K^o (W/m K)	R_K ($\text{m}^2 \text{K/W}$)	L_K (μm)
$p\text{-Si}_{0.8}\text{Ge}_{0.2}$	5.0	4.98×10^{-8}	0.249
$n\text{-Si}_{0.8}\text{Ge}_{0.2}$	4.96	4.9×10^{-8}	0.243
$\text{Si}_{0.7}\text{Ge}_{0.3}$	6.56	9.5×10^{-8}	0.623
$n\text{-Si}_{0.635}\text{Ge}_{0.365}$	4.33	1.15×10^{-7}	0.498
$\text{Si}_{0.3}\text{Ge}_{0.7}$	7.84	1.1×10^{-7}	0.862
$p\text{-Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$	0.19	1.4×10^{-5}	2.66

a very important but not yet well-established issue.^{6-9,16,17} The comparison of the calculated and experimental data for these alloys is shown in Figs. 1 and 2. Despite some scatter in these data because of different processing routes⁸ and inaccurate values taken for average grain sizes,^{6,7,9} the comparison shows that our model is in good agreement with these reported data.

From the best-fit lines of the experimental data in $1/K$ vs $1/d$ plots predicted by Eq. (6), we can determine the values of R_K and K^o for these alloys, which are shown in Table I and Fig. 3. Of interest to note is that both n - and p -type $\text{Si}_{0.8}\text{Ge}_{0.2}$ have almost the same values of K^o as reported in Ref. 8 and the same R_K . Estimated K^o values for these SiGe alloys are in agreement with their bulk data.⁶⁻⁸ Much lower K^o value and higher R_K value for $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ alloys are attributed to the effect of porosity.⁹

It is interesting to see that R_K increases by only a small amount with temperature from 300 to 900 K for n -type $\text{Si}_{0.635}\text{Ge}_{0.365}$, which may be attributed to some damage and/or disorder at grain boundaries at high temperature, but that the values of R_K at 300 K and 600 K are almost the same for $\text{Si}_{0.7}\text{Ge}_{0.3}$ [Fig. 3(a)]. This behavior that R_K is not very sensitive to temperature seems to agree with the dynamical simulations and experimental data for simple interfaces, which showed that R_K is almost independent of temperature over a wide range around room temperature.¹⁵ A very striking finding is the composition dependence of R_K for the SiGe alloys as shown in Fig. 3(b). Although these reported SiGe alloys⁶⁻⁸ experienced different processing and doping routes, the trend is clear — the composition dependence of the estimated R_K is similar to that of the thermal resistivity of the SiGe alloys.¹⁸ Comparison of Fig. 3(b) indicates that the polycrystals of the single elements have lower R_K (and thus higher thermal conductivity¹⁸) than their mixed alloys.

Returning to the grain-size dependence of K [Figs. 1(b) and 2(b)], we can see that L_K in $K/K^o = F(L_K/d)$ is an important characteristic length. As $d = 2L_K$, K decreases down to $K^o/2$. Only as $d \gg L_K$, K approaches K^o . In contrast, as $d \ll L_K$, K reaches its so-called “minimum value.”¹⁹ For example, $K = 0.1$ W/m K as $d = 10$ nm for the $\text{Si}_{0.8}\text{Ge}_{0.2}$ alloys. If it is assumed that a large L_K value remains *unchanged* in the small grain size range, Eq. (6) predicts a lower “minimum value” for K than the relaxation time approaches.¹⁶

Further from Eq. (5) it is easy to show the effect of spatial variations in both d and L_K . For convenience, however, simply by replacing L_K and $1/d$ in Eq. (6) with their averaging

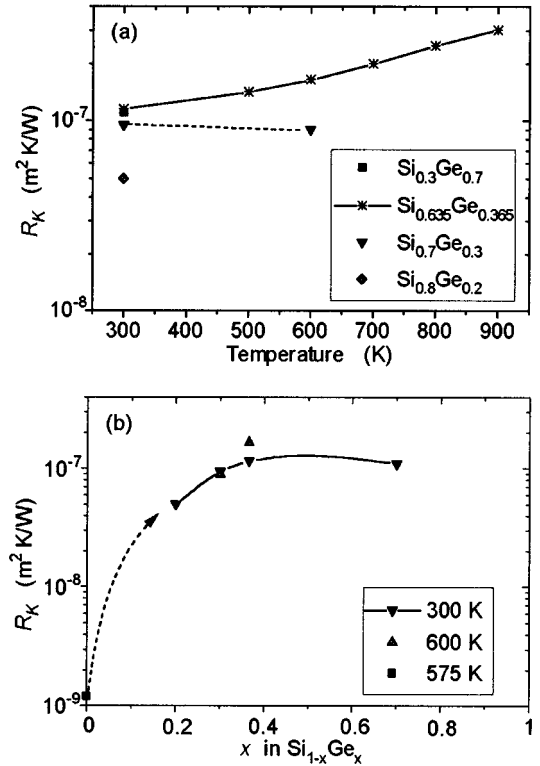


FIG. 3. Determined Kapitza resistance R_K for these SiGe alloys as a function of (a) temperature and (b) composition. For comparison, the value of R_K at 575 K for Si bicrystal calculated by dynamical simulations (Ref. 12) is also shown in (b).

$\langle L_K \rangle$ and $\langle 1/d \rangle$, and using a log-normal distribution function for both lengths, Eq. (6) can be rewritten as

$$K/K^o = 1/[1 + (2L_K/d)\exp(\delta_{L_K}^2/2 - 2.5\delta_d^2)], \quad (11)$$

where δ_d and δ_{L_K} denote their standard deviations. Equation (11) and a numerical example in Fig. 1(b) show that the variations in d result in increasing K/K^o and by contrast the variations in L_K cause a decrease of K/K^o .

Let us turn now to the effect of the grain shape [Eqs. (7)–(10)]. There are no available experimental data on the grain shape effect for comparison at this time. For illustration, we show a numerical example of the model for the $\text{Si}_{0.8}\text{Ge}_{0.2}$ alloys in Fig. 4. It is interesting to see from Fig. 4 that K/K^o always decreases with the grain shape anisotropy in the case of large grain sizes ($d > 2L_K$) and that oblate grains result in a more pronounced decrease of K/K^o than spherical and prolate grains. As $d < 2L_K$, K/K^o increases with the aspect ratio p . The predictions on the grain shape effect remain to be experimentally verified.

We would finally like to address three points. First, as we have already stated, our Kapitza resistance-EMA model is a *macroscopic* approach which successfully accounts for the microstructurally stochastic effects, whilst the Klemens-Callaway-type relaxation time model^{10,11} which has been successful in describing microscopic scattering mechanisms is a *microscopic* one. It could be argued that the reported data on the grain size-dependent thermal conductivity can also be fitted well by the Klemens-Callaway-type model which includes the boundary scattering relaxation time

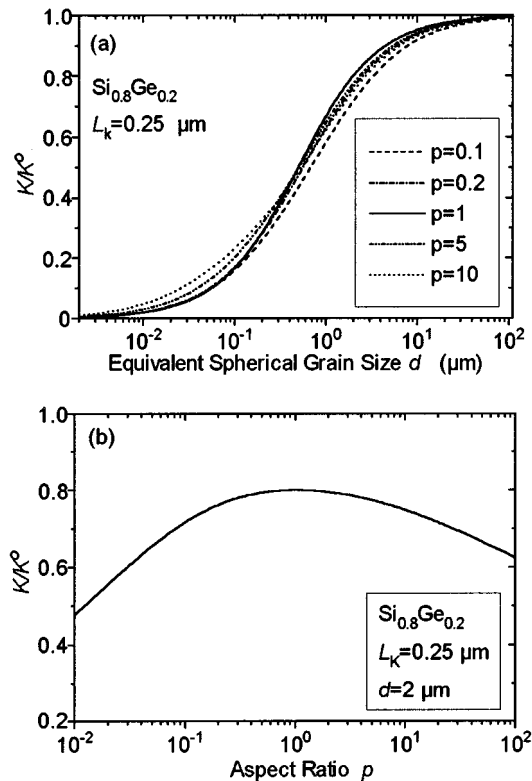


FIG. 4. Predictions for the effect of the grain shape on the normalized thermal conductivity of $\text{Si}_{0.8}\text{Ge}_{0.2}$.

$\tau_b = \alpha d/v$ (v , the average phonon velocity, and α , a constant of order unity). However, the correspondence between experiment and the predictions of the Klemens-Callaway-type model is not unique since different numerical values for those adjustable parameters in the microscopic model can be chosen and the fits can always be obtained with a sufficient number of free parameters. On the other hand, the Klemens-Callaway-type model does not yield the information about the Kapitza resistance at grain boundaries. It is important to emphasize that our macroscopic model does not contain adjustable parameters beyond the Kapitza length L_K , which

permits the direct determinations of the *in situ* Kapitza resistance values in real polycrystals. Second, although there have been a very large number of measurements on polycrystals in the literature, available data which contain variations in the thermal conductivity with the grain sizes and thus can be used for comparison are rather limited. Nevertheless, several examples presented in this work have provided good support for the present model. Third, so far there have been no reports on the values of the Kapitza resistance in real polycrystals. The comparison between the above estimates for real alloys that we have made and the existing calculation only on idealized Si bicrystal¹² [Fig. 3(b)] shows that the polycrystals of the single elements have lower Kapitza resistance (and thus higher thermal conductivity¹⁸) than their mixed alloys. This comparison also indicates that our estimates are reasonable. The accurate determination of the Kapitza resistance values requires accurate measured values for the thermal conductivities and the grain sizes, and, on the other hand, neglecting porosity can give rise to overestimate of the Kapitza resistance in polycrystals. The quantitative correlation of the estimated Kapitza resistance for real polycrystals with the microscopic phonon reflection at the grain boundaries remains to be explored.

In conclusion, the comparison of the calculated and experimental data for thermoelectric alloys available in the literature has demonstrated that the grain size-dependent thermal conductivity of polycrystals is quite well described by the Kapitza resistance-EMA model. The present model accounts for the Kapitza resistance, grain size, grain shape, and orientation as well as their spatial variations, which provides a guideline for tailoring the thermal conductivity of polycrystals such as thermoelectric ceramics. Furthermore, the simple formula of this model presents a very simple and practical method to determine the *in situ* Kapitza resistance in real polycrystals.

The authors thank Professor H. Gleiter for his support. Financial help from the Alexander von Humboldt Foundation and the State Education Commission of China through the Trans-Century Training Program Foundation for the Talents is gratefully acknowledged (C.W.N.).

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