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Application of the CALPHAD method to predict the thermal conductivity in dielectric and semiconductor crystals

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ABSTRACT

A novel method, based on the Debye model of the density of the lattice vibration energy [1,2], is used to predict the thermal conductivity of insulator materials from room temperature up to the melting point. The model links the density of the lattice vibration energy and the mean free path of the phonons to the high temperature limit of the Debye temperature, $\overline{\theta_D}(\infty)$, and to the Grüneisen parameter, $\gamma(\infty)$. The phonon contribution to the thermal conductivity can be predicted from the knowledge of $\overline{\theta_D}(\infty)$ and $\gamma(\infty)$. The contribution of the present work is a new CALPHAD (CALculation of PHAse Diagrams) Method, based on physical models, where the heat capacity, the thermal expansion and the adiabatic bulk modulus are optimized simultaneously in order to calculate $\overline{\theta_D}(\infty)$ and $\gamma(\infty)$. In addition, a simple method to predict $\overline{\theta_D}(\infty)$ and $\gamma(\infty)$, and thus the thermal conductivity without any experimental data, is also presented. Results are given for the thermal conductivities of some typical insulator materials such as salts (halides), oxides and semiconductors. It is found that the agreement between the calculations and the available experimental data is excellent.

1. Introduction

The thermal conductivity is one of the most important physical parameters of a solid. There are many situations in design or in process modelling where the thermal conductivity plays an important role, above all for the prediction of heat and mass transfer phenomena. The thermal conductivity controls the temperature gradients occurring in materials. These temperature gradients lead to internal stresses and thus, for transformations depending on the cooling rate and on the temperature, the thermal conductivity is directly related to the grain size and to the residual tensile strength. Hence, the thermal conductivity is an essential property for the prediction of the temperature dependence of the microstructure and thermo-mechanical properties, and for understanding heat treatment and solidification. The thermal conductivity is not easily measured, particularly for dielectric crystals with low thermal conductivity. Therefore, the thermal conductivity data of many dielectrics and semi-conductors, often close to ambient temperature conditions, are commonly scarce and incomplete. For most common materials, however, reliable experimental data are readily available in the literature. Hence it would be desirable to be able to predict the thermal conductivity of a wide range of materials by the means of a proven methodology, based on a plausible physical model. More recently, first principle calculations, based on ab initio molecular dynamics in which the forces are computed from the density functional theory, have been applied to predict the thermal conductivity of simple oxides [3–6] (MgO, SiO_2, ZrO_2 and $MgSiO_3$) and semiconductors elements (Si and Ge) [7,8]. The predictions agree with the experimental data within 15% to 40%. The phonons mean free path has a magnitude of few nanometers requiring a large simulation box size for the calculation of the thermal conductivity. Several nanoseconds (>10 ns) are also necessary to simulate the thermal conductivity of solids. Atomistic first principle calculations of the thermal conductivity are thus extremely time consuming.

A number of empirical relationships and models have been developed to predict the thermal conductivity of insulating materials. Unfortunately, many of these methods are restricted to homogeneous series of materials and require many adjustable parameters which have not been correlated with the readily available physical properties. In addition, the higher the temperature, the less precise and predictive are the empirical relationships. From a theoretical point of view, the thermal conductivity of dielectric crystals is governed by the phonon–phonon scattering, but even at present an exact analytical expression is lacking. Since the work of Debye [9] and Pierls [10], many analytical models for the thermal conductivity have been developed based on the single mode relaxation time approximation in the Boltzmann transport equation with different degrees of complexity

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[11,12]. In these models, some forms of the temperature and frequency dependencies of the relaxation times are assumed and must be fitted to experimental data. On account of the complex structure of the Brillouin zone and the strong temperature dependence of the phonon distribution function, the relaxation time can have a complicated dependence on the phonon frequency and temperature.

Slack et al. [1,2] showed that, for many dielectrics, the "unklapped process" (U-process) model combined with the Klemens–Callaway approximation of relaxation times could lead to a quite good prediction of the thermal conductivity and of its temperature dependence. The Klemens–Callaway's relation links the relaxation time to the high temperature limit of the Debye temperature $\Theta_D(\infty)$, and to the Grüneisen parameter, $\gamma(\infty)$. Consequently, the relaxation times, and thus the thermal conductivity, can be predicted with a quite good accuracy if the parameters $\Theta_D(\infty)$ and $\gamma(\infty)$ are precisely known.

In this article, a new CALPHAD Method, leading to an accurate determination of both parameters $\Theta_D(\infty)$ and $\gamma(\infty)$, is proposed to predict with a high level of accuracy the intrinsic thermal conductivity of phonons in dielectric and semiconductor materials. Not only does the model presented in this paper have a theoretical basis but also the parameters are correlated with readily available physical properties.

Sample calculations for various types of materials are presented. We will show that the new method presented in this work allows prediction of the thermal conductivity as a function of temperature with a good accuracy.

2. Modeling the thermal conductivity of insulators

The macroscopic thermal conductivity is defined from Fourier's Law for heat flow under thermal gradient. The steady state heat flow $\vec{q}$ is obtained by keeping the system and heat reservoirs in contact, thus:

$$\vec{q} = - \vec{\nabla} T \tag{1}$$

where is the thermal conductivity tensor, and $\vec{q}$ is the heat flux produced by the temperature gradient $\vec{\nabla} T$. Fourier's Law of heat flow can be derived from linear response theory [13]. For isotropic systems, the conventional thermal conductivity is given by the average quantity in the different directions:

$$\langle \lambda \rangle_{iso} = Tr(\lambda)/3 \tag{2}$$

Thermal conductivity for many salts is, to a good approximation, isotropic, particularly for halides. For insulators, the contribution to the thermal conduction comes from atomic vibrations, the so-called lattice thermal conductivity, and radiative heat transfer if the medium is translucide, the so-called radiative thermal conductivity. In both the high and low temperature cases the lattice thermal conductivity is given by [14–16]:

$$\langle \lambda \rangle_{iso}(T) = \frac{1}{2\pi^2} \int_0^{\omega_D} \frac{\tau(\omega)}{v} C_{v,ph}(\omega)\omega^2 d\omega \tag{3}$$

where v is the phonon velocity, a is the volume of a single atom (molecule), k_B is the Boltzmann constant and $\hbar$ is the reduced Planck constant. $\omega_D = (6\pi^2)^{1/3}\ v/a$ is the Debye frequency, C_{vph} (ω) is the specific heat at constant volume per normal mode at ω, and $\tau(\omega)$ is the effective phonon relaxation time. A comprehensive model for lattice thermal conductivity of a solid requires not only the knowledge of the crystal structure and phonon spectrum but also an understanding of various types of phonons scattering rates and their temperature and frequency dependencies. At high temperature, $(T \geq \theta_D/3$, where $\theta_D$is the Debye temperature) Roufousse and Klemens [17,18] suggested that the relaxation time does not include the effect of three-phonon momentum conservation. In the case of a non-momentum conservation process (the so-called "Umklapp" or "U-processes") only the interactions among the phonons themselves via anharmonic processes are significant and the phonon free path length decreases with temperature and is inversely proportional to the density of phonons. Under these conditions, and assuming that only the acoustic phonon modes participate in the heat conduction process, several expressions of the relaxation time were suggested in the literature. There are several expressions for the relaxation time due to the U-processes in the literature; however, it was shown [12,15,19] that at high temperature the relaxation can be approximated by a function proportional to $\sim(\omega T)^{-2}$. For a system with one atom per primitive cell, Slack [19] suggests that the relaxation time can be approximated as:

$$\tau(\omega) = [\omega^2 \xi(T)]^{-1} \tag{4}$$

where $\xi(T) = 18\pi^3 k_B T \gamma^2(T)/\sqrt{2} m a^2(T) \omega_D^3(T)$, with $\gamma = -(\partial \ln\theta_D / \partial \ln V)_V$which is the Grüneisen parameter, and m is the average atomic (or molecular) weight. With these considerations, and assuming that at high temperature the phonon contribution to the heat capacity is approximated by the Dulong-Petit limit ($3k_B$), and that the Debye frequency and Grüneisen parameter are equal to their high temperature limit (respectively, $\omega_D^3(\infty)$ and $\gamma(\infty)$), the integration of Eq. (3) leads to:

$$\langle \lambda \rangle_{iso}(T) = \frac{f m a(T) \omega_D^3(\infty)}{\gamma^2(\infty) T} \tag{5}$$

where f is a constant, and for a expressed in Å and m in atomic mass unit (for which$f = 4.342 \times 10^{-17}$). However Julian et al. [19,20] showed that the previous relation must be corrected to take into account the phonon–phonon and the phonon-defect interaction~~s~~ effects. They determined the following expression for the parameter f:

$$f = \frac{1.856 \times 10^{-17} \gamma(\infty)^2}{0.228 - 0.514\gamma(\infty) + \gamma^2(\infty)} \tag{6}$$

Thereafter, Slack [21,22] extended the model to more complex structures using a simple counting scheme. For crystals with n atoms per primitive unit cell he suggested that:

$$\langle \lambda \rangle_{iso}(T) = \frac{f m a(T) \omega_D^3(\infty) n^{1/3}}{\gamma^2(\infty) T} \tag{7}$$

In this model, the Debye frequency is directly determined by integration of the acoustic portion of the phonon density of state. Thus, the knowledge of either the phonon density of states or the phonon dispersion relation is required in order to determine the Debye frequency. Unfortunately, these data are not available theoretically and they are difficult to determine from the theory. From a practical point of view it is better to use the Debye temperature, $\theta_D = \hbar\omega_D/k_B$, instead of the Debye frequency. Anderson [23] showed that the classical Debye temperature $\overline{\theta_D}$ (determined from the heat capacity, the sound velocity and the elastic constants) can be linked to the acoustic mode Debye temperature as follows: $\theta_D = n^{-1/3}\overline{\theta_D}$, and thus the thermal conductivity of an insulator with a complex crystalline structure is defined as:

$$\langle \lambda \rangle_{iso}(T) = f \left(\frac{k_B}{\hbar}\right)^3 \frac{m a(T) \overline{\theta_D^3}(\infty)}{n^{2/3} \gamma^2(\infty) T} \tag{8}$$

The thermodynamic Grüneisen parameter γ_{th} is defined by [26]

$$\gamma_{th}(T) = \alpha_V(T) V_m(T) B_S(T) C_p(T)^{-1} \tag{9}$$

where $\alpha = V^{-1}(\partial V/\partial T)_P$ is the volumetric thermal expansion, $V_m(T)$ is the molar volume, $C_p(T) = (\partial H/\partial T)_P$ the molar heat