Theory of Thermal Conduction in Thin Ceramic Films[1]

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The theory of heat conduction in ceramics by phonons, and at high temperatures also by infrared radiation, is reviewed. The phonon mean free path is limited by three-phonon interactions and by scattering of various imperfections. Point defects scatter high-frequency phonons; extended imperfections, such as inclusions, pores, and grain boundaries, affect mainly low-frequency phonons. Thermal radiation is also scattered by imperfections, but of a larger size, such as splat boundaries and large pores. Porosity also reduces the effective index of refraction. For films there are also external boundaries, cracks, and splat boundaries, depending on the method of deposition. Examples discussed are cubic zirconia, titanium oxide, and uranium oxide. Graphite and graphene sheets, with two-dimensional phonon gas, are discussed briefly.

KEY WORDS: graphene; lattice defects; oxides; phonons; pores; thermal radiation.

1. INTRODUCTION

Thermal conduction in ceramics is by means of lattice waves. At high temperatures there may be an additional contribution due to radiation, particularly in large samples. Thin films are influenced by additional factors, such as the film thickness, the presence of additional imperfections, and possible variations of structure with depth. Oriented imperfections will affect the conduction differently in the cases of parallel and perpendicular heat flow.

The thermal conductivity of bulk samples at ordinary and at high temperatures are reviewed briefly, and the additional scattering processes encountered in thin films are considered. At low temperatures, size effects,

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including those due to film thickness, become very important. Size effects can also be significant at ordinary temperatures, even if the film thickness or grain size is larger than the average phonon mean free path. The effects of point defects are important, and nonstoichiometric oxides are emphasized. Finally, the two-dimensional phonon gas is considered, and heat conduction in a graphene sheet, the thinnest film, will be related to the properties of graphite and carbon nanotubes.

2. BULK THERMAL CONDUCTIVITY

2.1. Lattice Waves

The lattice waves in solids cover a substantial frequency range. Their thermal conductivity λ can be expressed as an integral over their frequency ω by

$$\lambda = \tfrac{1}{3} \int C(\omega)\, v(\omega)\, l(\omega)\, d\omega \qquad (1)$$

where $C(\omega)\, d\omega$ is the contribution of waves in the frequency interval $d\omega$ about ω to the vibrational specific heat per unit volume, $v(\omega)$ is the group velocity, and $l(\omega)$ is the attenuation length or phonon mean free path. While the specific heat and group velocity are not sensitive to crystal imperfections, the mean free path is, and it governs both the temperature dependence and the specimen variability of the thermal conductivity. The role of phonon interaction processes in ceramics is reviewed briefly. While phonon heat conduction is emphasized, it must be remembered that thermal radiation or photons can be significant at high temperatures. Because the photons have a longer wavelength, imperfections will act differently for them. Small defects are relatively less important for scattering them, while pores reduce the effective dielectric constant and thus the radiative heat transfer [1].

Only waves of a high group velocity make a substantial contribution to thermal conduction. The possible role of optical modes, which are the relative motions of atoms within a molecular group, have been discussed elsewhere [2]. The modes of the acoustic branches, which have a high group velocity, have a frequency range from zero to ω_m, where in a Debye approximation

$$\omega_m^3 = \frac{6\pi^2 v^3}{a_m^3} \qquad (2)$$

and where a_m^3 is the volume of one molecular group of the solid, and v is the low-frequency limit of the phonon velocity. The contribution of the acoustic lattice waves to the specific heat per unit volume from the frequency interval $d\omega$ is $C(\omega)\,d\omega$, where for $\omega \leqslant \omega_m$,

$$C(\omega) = \frac{9k}{a_m^3 \omega_m^3}\,\omega^2 \qquad (3)$$

and where k is the Boltzmann constant.

While $C(\omega)$ and $v(\omega)$ are not sensitive to crystal imperfections, the phonon mean free path $l(\omega)$ is temperature dependent and is reduced due to the scattering of phonons by solutes and other imperfections. This sensitivity holds for bulk specimens and, to an even greater degree, for thin films. The external boundaries scatter phonons, and thin films usually contain a larger concentration of various defects.

The intrinsic mean free path, limited by anharmonic energy interchange between groups of three waves, is a function of both absolute temperature T and frequency ω and can be shown to be, in the limit of high temperatures, of the form

$$\frac{1}{l_i(\omega,\,T)} = BT\omega^2 \approx 2\gamma^2\,\frac{kT}{\mu a^3}\,\frac{\omega^2}{v\omega_m} \qquad (4)$$

Here a^3 is the volume per atom and μ the shear modulus, while γ is the Grüneisen parameter, a measure of the anharmonicity. Substituting l_i into Eq. (1), we see that the factor $C(\omega)\,l_i(\omega)$ in the integrand is independent of ω, and equal frequency intervals make equal contributions to the intrinsic conductivity λ_i. Thus, low frequencies play a larger role in the thermal conductivity than they do in the specific heat [3]. One obtains

$$\lambda_i = \frac{1}{3}\int_0^{\omega_m} C(\omega)\,l_i(\omega,\,T)\,v\,d\omega = \frac{3ka_m^3\omega_m}{Bv^2T} \qquad (5)$$

From Eq. (5) one can estimate B and thus the magnitude of l_i if measurements of the intrinsic thermal conductivity are obtainable. There are a few cases where this is not so, including the important case of cubic zirconia, which exists only in the stabilized form and contains numerous point defects (solute cations and oxygen vacancies), which depress the thermal conductivity. In such cases one must estimate l_i and λ_i from Eq. (4) and then estimate the mean free path, or scattering probability per unit path length, of the various defects in the specimen, to obtain its lattice thermal conductivity.

2.2. Scattering of Phonons by Defects

Various defects scatter lattice waves and reduce the phonon mean free path. The reciprocals are additive, so that for each frequency ω

$$\frac{1}{l(\omega, T)} = \frac{1}{l_i(\omega, T)} + \sum_d \frac{1}{l_d(\omega)} \qquad (6)$$

where the summation is over all types of defects present, each with a different variation of $l_d(\omega)$ with frequency ω, but not varying with temperature unless the nature or the concentration of defects changes with temperature, a possibility which should be kept in mind but which is not discussed here. In general, the scattering probability increases with increasing frequency, and most rapidly for defects which are of a small size. One can classify defects into point defects, thin sheets, large imperfections, and boundaries.

Point defects are small compared to the wavelengths of interest or of atomic dimension; their reciprocal attenuation length is of the form $1/l_p(\omega) = A\omega^4$, where A depends on the nature of the defect and is proportional to the defect concentration c at low concentrations. They affect $l(\omega)$ mainly at the highest frequencies. They include interstitials, solute atoms, and vacancies. Thin sheets, with a thickness less than the phonon wavelengths, scatter as ω^2, but scattering increases with frequency less rapidly at high frequencies. They include thin platelets and two-dimensional aggregates of foreign atoms or vacancies. Large imperfections scatter independently of frequency with a scattering cross section comparable to their geometrical size or with only a weak frequency dependence. They include colloids and larger inclusions, and pores. Boundaries, both external and internal boundaries between different materials, also scatter independently of frequency with an attenuation length L given by the average distance between them. However, boundaries parallel to the temperature gradient are effective only if they scatter diffusively. The degree of nonspecularity depends on their roughness and can vary with frequency. Thus, the effective value of L may be frequency dependent in some cases. In general, however, large imperfections and boundaries are most important at low frequencies.

For present purposes the defects of greatest interest are point defects and extended defects or boundaries, each in combination with intrinsic three-phonon interactions. For point defects one can define a frequency ω_0 such that $l_i(\omega_0) = l_p(\omega_0)$. Then, writing A in the form appropriate to a substitutional impurity of mass $M + \Delta M$ in place of M (see Ref. 4),

$$\frac{1}{l_p} = \frac{a^3\omega^4}{4\pi v^4} c \left(\frac{\Delta M}{M}\right)^2 \qquad (7)$$

where a^3 is the volume per atom, c is the point defect concentration per atom, and

$$\omega_0^2 = \frac{BT}{A} = \omega_m^2 \frac{4\gamma^2 kT}{3\pi\mu a_m^3} c^{-1} \left(\frac{\Delta M}{M}\right)^{-2} \tag{8}$$

Note that ω_0 increases with temperature and decreases with the strength of point defect scattering. Using the expressions for l_i and l_p in the conductivity integral, one obtains for the reduction in conductivity due to point defects that [5]

$$\lambda = \lambda_i - \delta\lambda_p = \lambda_i \left(\frac{\omega_0}{\omega_m}\right) \arctan \left(\frac{\omega_m}{\omega_0}\right) \tag{9}$$

Equation (9) also applies if $\omega_0 > \omega_m$.

Similarly, if one considers intrinsic scattering, in combination with that by extended imperfections or boundaries with a mean free path L, and defines a frequency ω_B as that for which $l_i(\omega_B) = L$, then [6]

$$\omega_B^2 = \omega_m^2 \frac{\mu a^3}{2\gamma^2 kT} \frac{v}{\omega_m L} \tag{10}$$

and

$$\lambda = \lambda_i - \delta\lambda_B = \lambda_i \left[1 - \left(\frac{\omega_B}{\omega_m}\right) \arctan \left(\frac{\omega_m}{\omega_B}\right)\right] \tag{11}$$

In most cases $\omega_B \ll \omega_m$, so that the arctan function is $\pi/2$. Also, $\omega_0 \gg \omega_m$, so that $\delta\lambda_p$ and $\delta\lambda_B$ are independent of each other, since the reductions occur in widely separated ranges of frequency. Thus, point defects and extended imperfections make independent reductions in conductivity, rather than independent contributions to the thermal resistivity, as is sometimes assumed. However, when the temperature is low and both point defect and boundary scattering are very strong, ω_0 and ω_B approach each other. In such cases λ becomes independent of temperature, varying as $L^{1/4}c^{-3/4}$, a result first given by Pomeranchuk [7].

3. RADIATIVE COMPONENT

The effective thermal conductivity between two black parallel slabs, separated by a distance D and filled with a nonabsorbing dielectric medium of refractive index n, is

$$\lambda_{rad} = 4n^2\sigma DT^3 \tag{12}$$

where T is the absolute temperature,

$$\sigma = \frac{2\pi^5 k^4}{15h^3 c^2} = 5.67 \times 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4} \tag{13}$$

is the Stefan–Boltzmann constant, and c is the velocity of light in vacuum. The maximum value of the radiative component of thermal conductivity, in $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, is thus

$$\lambda_{\max} = 2.27 \times 10^{-7} n^2 D T^3 \tag{14}$$

where D is in meters. The heat transfer is independent of D, but the factor D in the conductivity arises because the temperature gradient varies as $1/D$ for a given temperature drop.

The radiative component can be reduced by absorption and by scattering within the material, by a reduction of n due to pores, and by reduced emissivity of the interfaces.

For a given porosity, small pores, of the order of a micron, are more effective in scattering, while large pores, several microns in diameter, scatter less but reduce the dielectric constant n^2 and, hence, the radiative component [1]. Very small (submicron) pores or inclusions scatter only weakly.

The radiative component of thin films is not well understood. For thermal barrier coatings the interest is in heat flow normal to the film plane at high temperatures (1000 to 1300 K). Measurements of the materials are usually performed on specimens of thickness an order of magnitude larger than the actual coatings. In these measurements the radiative component forms a significant part of the conductivity at high temperatures. This is probably responsible for the observations that the thermal conductivity does not decrease with increasing temperature as rapidly as predicted for the lattice conductivity, and sometimes not at all [6]. For example, in recent measurements [1] of yttria-stabilized zirconia (dense specimens of 3 and 8 mol%), the radiative component is probably around $1 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at 1300 K of a total of 2.4 and $2.0 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, respectively. The specimens were 1.3 mm thick. Equation (14) with $n = 2.7$ yields a maximum value of $4 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$. The radiative component is thus substantially reduced by the decreased emissivity into the specimen of the front layer, which absorbs the laser flash. In actual thermal barrier coatings D is substantially less, and the radiative component should be even smaller.

The defect structure of thin films depends on the method of deposition. In plasma sprayed films, splat boundaries are produced, which are of

irregular shape but lie mainly in the plane of the film. These boundaries between deformed particles contain small voids and may be regarded as thin sheets of decreased density, with decreased elastic moduli and a decreased index of refraction. They scatter photons and reduce the effective attenuation length for heat transfer across the film. The reflection coefficient of a thin layer having a thickness t and refractive index n_2 embedded in a medium of refractive index n_1 is, for perpendicular incidence, given by [8]

$$R = \frac{2(n_1 - n_2)^2 \, (n_1 + n_2)^2 \, (1 - \cos 2\beta)}{(n_1 + n_2)^4 + (n_1 - n_2)^4 + (n_1 + n_2)^2 \, (n_1 - n_2)^2 \cos 2\beta} \tag{15}$$

where $\beta = 2\pi n_2 t f / c$ and f is the frequency. For splat boundaries thin compared to the wavelength in the boundary, i.e., for small β,

$$R = 4\beta^2 \frac{(n_1 - n_2)^2}{(n_1 + n_2)^2} \tag{16}$$

Thick splat boundaries are not of uniform thickness; therefore, the oscillatory terms in Eq. (15) can be disregarded, and independently of t

$$R \approx \frac{2(n_1 - n_2)^2 \, (n_1 + n_2)^2}{(n_1 + n_2)^4 + (n_1 - n_2)^4} \tag{17}$$

For cracks $n_1 = 1$, and if the cracks are thick, Eq. (17) applies, so that the cracks scatter as two independent interfaces. For zirconia, $n_2 = 2.7$, and the reflectivity of each interface is about 0.4. In the same material, if a thin splat boundary is about 1.5 μm thick and has a density about half of the surrounding material, so that $n_2 - n_1 = 0.9$, the maximum reflectivity occurs when $\beta = \pi/2$, i.e., when $f = c/(4n_2 t)$ or 2×10^{13} Hz. At that frequency $R \approx 0.2$ and averages about 0.1 over a wide frequency range. Cracks scatter more strongly than splat boundaries. However, splat boundaries are more numerous than cracks in plasma sprayed films.

In films grown by chemical vapor deposition, growth is in columns perpendicular to the film plane, and there may be empty spaces or cracks between these columns. Cracks of this orientation have only a small scattering effect for heat flow across the film, but when at a high concentration, they will reduce the average dielectric constant n^2 and thus reduce the radiative heat flow by the same factor as their fractional volume density. Radiative heat flow in the plane of the film will also be reduced due to scattering by these cracks in addition to the reduction of the dielectric constant.

4. LATTICE COMPONENT OF THIN FILMS

4.1. External Boundaries

In addition to all the factors which control the lattice conductivity in bulk samples, there are additional scattering processes. Obviously there may be more imperfections which scatter phonons, and there will be reductions in the phonon mean free path due to the external boundaries of the film. Again, one must distinguish between heat flow across the film and heat flow in the plane of the film. In heat flow normal to the film plane, the phonon mean free path is terminated at the external boundaries, so that L in Eq. (10) should be identified with the film thickness. In heat flow parallel to the film, the appropriate mean free path L_{ex} is increased, since only diffuse reflection processes limit the phonon mean free path. Thus,

$$\frac{1}{L_{ex}} \approx (1-s)\frac{1}{D} \tag{18}$$

where D is the film thickness, and s is the fraction of phonons reflected specularly. The diffuse fraction $(1-s)$ generally decreases with decreasing frequency and depends on the roughness of the boundary. If there are also internal defects, $1/L_{ex}$ is one of the terms which contribute to Eq. (6). External boundary scattering is important at low temperatures. At high temperatures, it is usually significant only for very thin (submicron) films.

4.2. Oxide Stoichiometry

Although there is a lack of observed data on the thermal conductivity of oxide films, one can draw on studies of the effect of oxygen stoichiometry in bulk samples to predict its effect in thin films. Only the lattice component is discussed, since the radiative component will be relatively small. The three systems discussed, uranium oxide, titanium oxide, and cubic zirconia, are each representative of different behavior.

In uranium oxide, and presumably in other actinide oxides, the oxygen ions are larger than the cations, and the oxygen sublattice is very stable. Changes in oxygen concentration, achieved by decreasing the oxygen chemical potential, do not produce oxygen vacancies; on the contrary, the thermal conductivity actually increases. However, an increase in oxygen content produces point defects, and the thermal conductivity is reduced [9]. The increase in thermal conductivity in substoichiometric UO_2 is attributed to the formation of metal colloids, large enough to enhance conduction. A similar effect has been seen in Simfuel, a mixture of oxides

which simulates the "burn-up" of UO_2. Some of these oxides have only limited solid solubility, and the excess solute cations also form colloids that increase the conductivity [10]. In the case of hyperstoichiometric UO_2, where the thermal conductivity is reduced, it is not clear whether the responsible point defects are interstitial oxygen [3] or cation vacancies. Further work in this area is needed.

The situation seems clearer in the case of oxygen-deficient TiO_2, where thermal conductivity data exist [11] and can be compared with the theory of Ratsifaritana and Klemens [12]. A vacancy scatters owing to the missing linkages, which belong to two atom sites at the missing atom, and also the missing kinetic energy of the missing atom. Thus, in Eqs. (7) and (8), $\Delta M/M$ becomes

$$\left(\frac{\Delta M}{M}\right)_{vac} = -2 - \frac{M_{vac}}{M_a} \tag{19}$$

where M_{vac} is the missing mass and M_a is the average atomic mass. For an oxygen vacancy in TiO_2, $(\Delta M/M)_{vac} = -2.60$. Substituting this into Eq. (8), one can calculate (ω_0/ω_m) and λ/λ_i from Eq. (9). For oxygen vacancy concentrations from 0.005 to 0.037 per molecule, the theoretical reductions [13] agree well with the observations of Siebeneck et al. [11].

Cubic zirconia, which can be stabilized by the addition of divalent or trivalent solutes, is used for fuel cells and oxygen sensors as well as for thermal barrier coatings, preferably in thin layers. It seems that the formation energy of oxygen vacancies is low, so that these solutes are accompanied by these vacancies. This is responsible for high values of oxygen diffusivity, and at the same time for the low thermal conductivity [6]. The stability of the cubic phase is presumably due to the entropy of solution of solutes and vacancies. Thermal conductivity measurements have been performed mostly on thick samples, and this enhances the radiative component. The conductivity is found to be sensitive to cracks [14]; both radiation and lattice conduction are presumably affected.

5. THE TWO-DIMENSIONAL PHONON GAS

The ultimate thin film is a monatomic layer; its vibrations form a two-dimensional phonon gas. In two dimensions the low frequencies play a larger role in heat transport than in three dimensions. Phonons in graphite behave like a two-dimensional gas over most of the frequency range of the acoustic modes, except below 4 THz, where there is propagation in the c-axis with very low velocities, since coupling between hexagonal planes is

very weak. In two dimensions the spectral specific heat has the form $C(\omega) \propto \omega$, but the intrinsic mean free path $l_i(\omega, T)$ has the same frequency dependence as in three dimensions, for it is governed by the anharmonic transition probabilities, and not by the locus of permitted three-phonon interactions in momentum space [15]. Thus, $l_i(\omega, T) \propto \omega^{-2}T^1$, $C(\omega) \, l_i(\omega) \propto \omega^{-1}$, and the intrinsic thermal conductivity integral has a logarithmic divergence at low frequencies. In graphite this divergence is removed at the angular frequency ω_c, where the phonon spectrum changes from two-dimensional to three-dimensional behavior, that is, at $\omega_c = 2.51 \times 10^{13}\ \text{s}^{-1}$. Therefore, the intrinsic thermal conductivity is [15]

$$\lambda_i = \frac{\rho v^4}{\gamma^2 \omega_m T} \ln \left(\frac{\omega_m}{\omega_c} \right) \tag{20}$$

Here v is the wave velocity in the basal or hexagonal plane, ρ is the density, γ is the Grüneisen anharmonicity parameter, and ω_m is the maximum frequency of the acoustic branch in a Debye approximation. With $\gamma = 2$, $\omega_m = 2.88 \times 10^{14}\ \text{s}^{-1}$, $\rho = 2.26 \times 10^3\ \text{kg} \cdot \text{m}^3$, since $\ln(\omega_m/\omega_c) = 2.44$, $\lambda_i = 5.73 \times 10^5/T\ \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, in agreement with measurements.

The single graphene sheet is two-dimensional down to zero frequency, since there are no waves propagating outside the basal plane. The logarithmic divergence is thus removed by a limitation on the mean free path. In an unsupported sheet, the mean free path cannot exceed the smallest linear dimension L of the sheet. Since

$$l_i = \frac{1}{2\gamma^2} \frac{Mv^2}{kT} \frac{\omega_m v}{\omega^2} \tag{21}$$

where M is the atomic mass, the condition $l_i(\omega_B, T) = L$ yields a cutoff for the divergence at a frequency ω_B given by

$$\omega_B^2 = \frac{1}{2\gamma^2} \frac{Mv^2}{kT} \frac{\omega_m v}{L} \tag{22}$$

or $\omega_B = 5.8 \times 10^{11}L^{-1/2}T^{1/2}$, where L and T are in meters and K, respectively. For $L = 1\ \text{mm}$ and $T = 300\ \text{K}$, $\omega_B = 1.06 \times 10^{12}\ \text{s}^{-1}$. The thermal conductivity of a free-standing sheet with 1 mm smallest dimension is then $\lambda = 4.4 \times 10^4\ \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$. Since the thickness of this single layer is $3.3 \times 10^{-10}\ \text{m}$, the conductance of such a sheet is about $1.5 \times 10^{-5}\ \text{W} \cdot \text{K}^{-1}$. If the graphene sheet lies on a substrate which has a lower phonon velocity than that of graphene ($v = 1.86 \times 10^4\ \text{m} \cdot \text{s}^{-1}$), its conductivity is reduced, because wave energy leaks into the substrate. This increases ω_B by an

amount which depends on the velocity difference and reduces the conductivity by 20 to 50%. If the substrate is itself a thin film of low thermal conductivity, the additional conductance of the graphene sheet may be just observable.

ACKNOWLEDGMENTS

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