PHONON THERMAL CONDUCTIVITY

THESIS

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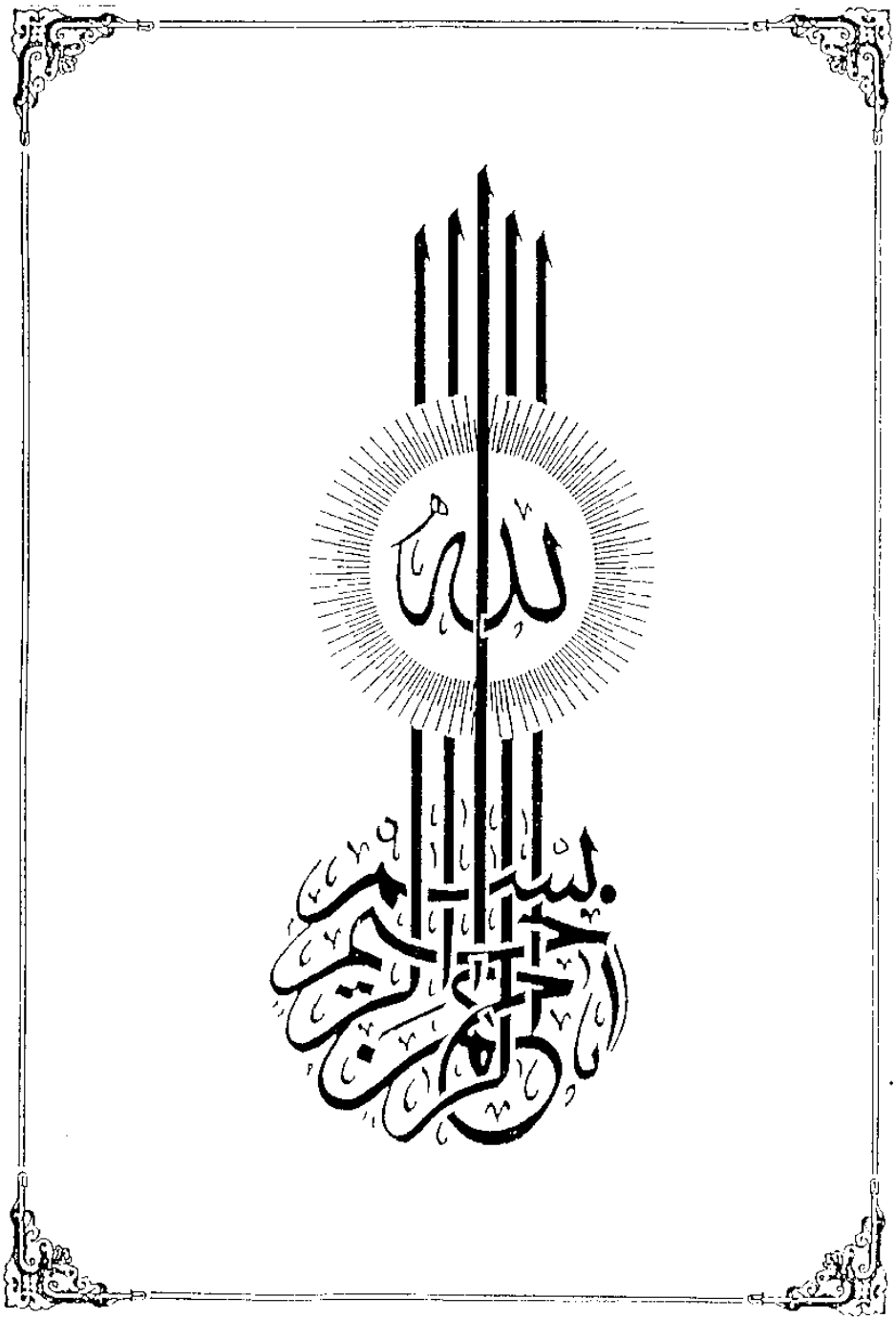

ABSTRACT

A theoretical study is given of the phonon heat conduction in nonmetallic materials. The complementary variational principle is used to obtain sequences of lower and upper bounds for the phonon thermal conductivity. In this technique the phonon collision operator should be decomposed into two parts, each of which should satisfy certain properties. The necessary conditions for the convergence of the sequences of lower and upper bounds as well as the best way of decomposing the phonon collision operator are explored in a more rigorous manner than was done hitherto. The study has been performed in quite a general way so that the results obtained can also be used for the calculation of other transport coefficients.

Further, a new model operator for umklapp processes is formulated in such a way that the quasi-conservation of wavenumber is taken into account. In comparison with the models used in earlier work the present model has the advantage that the reciprocal lattice vectors need not be grouped in a certain manner. It also yielded a new expression for thermal conductivity which, in turn, gave a reasonable quantitative agreement with the experimental data for Ge and LiF, without using any fitting

parameters. The analysis shows, further, that the quasi-conservation of wavenumber in the umklapp process gives a negative contribution to the thermal conductivity of the same order of magnitude as that found in previous work.

Also it seems to us that in some previous treatments the reciprocal lattice vectors involved in certain types of umklapp interactions as well as the areas and limits of some of the integrals needed in the calculations were incorrectly determined. In the present work these points have been amended and more accurately considered. Moreover, we have derived and used general expressions for the strengths of all types of three-phonon interactions, rather than using the approximate special forms reported in earlier work.

CONTENTS

CHAPTER ONE

" INTRODUCTION"

The thermal conductivity is the coefficient which measures the thermal transport properties of solids. In general both phonons (lattice vibrations) and charge carriers (electrons and holes) contribute to the heat current and consequently to the thermal conductivity coefficient. In pure metals the electronic contribution is dominant at all temperatures and therefore the thermal conductivity satisfies the Wiedemann-Franz law. For dielectric and most of intrinsic semiconductor materials phonons play the essential role in heat conduction and the thermal conductivity is almost entirely due to the phonon contribution. In semimetals, extrinsic semiconductors and metals containing large amounts of impurities both the contributions from charge carriers and phonons are of importance. Korenblit et al [1] and Uher and Goldsmid [2], however, introduced a method which could be used to separate the electronic and phonon parts of thermal conductivity in semimetals. Similar analysis was also recently used for the case of metals by Amundsen et al [3] and Tausch et al [4].

In the present work we confine ourselves to the thermal conductivity of phonons and thus consider the calculation of this coefficient in dielectries and intrinsic semiconductors where the effect of charge

carriers on thermal conduction can be entirely neglected. However, the results obtained can be applied to the phonon part of thermal conductivity for other materials, if the effect of the electron phonon interaction is taken into account (see for example Borchi et al [5]). For the calculation of the phonon thermal conductivity two main approaches are usually adopted. The first is based on the Kubo formula for the energy current (Kubo et al [6]) and on Van Hove's theory of the time evolution of dissipative systems (Van Hove [7] , [8]). This approach was used in the work of Mori [9] , Luttinger [10] , Martin [11] and Kirczenow [12] . The second approach is established on the Boltzmann equation which describes the flow of phonons in the presence of a temperature gradient. The main results of this approach are reviewed in Klemens [13] , [14] , Ziman [15] , Carruthers [16], Parrott and Stuckes [17] , Berman [18] and Callaway [19] . The first approach is outside the intended scope of the present work. We thus restrict our attention to the second approach which in fact is more applicable and much simpler.

The phonon Boltzmann equation consists of two terms. The first depends on the temperature gradient (the driving force) and the phonon distribution while the second represents the phonon collision operator. The

different types of interactions which phonons can undergo in nonmetallic materials are boundary scattering, dislocation scattering, interactions with mass defects and three-phonon interactions both normal and umklapp. All of these types of interactions are supposed to conserve the energy of phonons within the limits of the uncertainty principle. However, the only type of these interactions which conserves wavenumber (wave vector) is the three-phonon normal process. The other types of interactions are, therefore, termed resistive processes. Umklapp processes are also distinguishable from other resistive interactions by the fact that they quasi-conserve wavenumber (the wavenumber is allowed to vary with a reciprocal lattice vector in each interaction).

In view of what has been mentioned above it is clear that the difficulty in solving the phonon Boltzmann equation arises from the complexity of the collision operator which represents the phonon scattering mechanism. The form of this operator, however, can be substantially simplified by considering only the first order deviations from the phonon equilibrium distribution. This approximation linearises both the phonon collision operator and the Boltzmann equation. In spite of the considerable simplifications which result from such approximation no exact solution exists for the resulting linear Boltzmann

equation. Approximate methods and techniques must therefore be utilized to obtain the solution. The most important techniques used for such purpose are i) the relaxation time approximation, ii) the replacement of the exact collision operator by a model operator which possesses the same important properties , iii) the variational principle.

In the ordinary relaxation time approximation the diagonal part of the collision operator is only retained while the other off-diagonal terms are completely neglected This approximation can be justified mathematically in very few cases. It, however, has a good interpretation from the physical point of view since the diagonal part of the collision operator can be related to the relaxation time needed to retain the phonon equilibrium distribution. The main objection to the relaxation time approximation is that it does not preserve the important features of the exact collision operator. In this respect it is clear that in this approximation neither the energy nor the wavenumber are conserved and consequently no distinction is made between normal and resistive processes. The role of normal processes, however, has been studied more carefully by using a modified relaxation time technique (Callaway [20]). In this technique Callaway used two

different relaxation times to represent normal and resistive processes. He, further, assumed that these two kinds of processes relax phonons to different equilibrium distributions. The equilibrium distribution for each kind has been chosen so that the required conservation conditions are satisfied. The equilibrium distribution of resistive processes was thus taken to be the ordinary Bose Einstein (Planck's) distribution. For normal processes, however, Callaway used a modified form for the Bose Einstein equilibrium distribution which depended on a new parameter (drift velocity) whose value was inferred from the wavenumber consevation condition. The expression for thermal conductivity obtained by Callaway [20] consists of two terms. The first is identical with the result found in earlier work by using the ordinary relaxation time approximation (Klemens [21]). The second term represents the effect of the normal process conservation of wavenumber. Also, it reflects, in a sense, the effect of the off-diagonal part of the normal process collision operator which was neglected in the ordinary relaxation time technique.

A more adequate derivation for the Callaway expression for thermal conductivity was given later by Krumhansl [22] and Guyer and Krumhansl [23] . Also in the

original analysis of Callaway [20] the longitudinal and transverse branches of the dispersion relation were replaced by one average branch. Parrott [24] and Simons [25] generalized independently the Callaway expression to take into consideration the different contributions from longitudinal and transverse phonons, after an incorrect attempt by Kosarev et al [26] .

For the calculation of thermal conductivity from the Callaway result one needs suitable expressions for the relaxation times representing the different phonon scattering mechanisms. The relaxation times of boundary, dislocation and mass defects scattering were respectively obtained by Casimir [27] ; Klemens [21] and [28] . As regards normal and umklapp processes, the problem of calculating the relaxation times is quite complicated. Only approximate formulae which hold for phonons of low frequencies were derived for the normal process relaxation time by Herring [29] and for the umklapp process relaxation time by Klemens [21] , [13] and by Mikhail and Simons [30] . The Callaway expression for thermal conductivity was used successfully to fit the experimental data of several dielectric and semiconductor materials over wide temperature ranges. In this connection we refer

to the work of Callaway [20] on germanium, the work of Berman and Brock [31] on lithium fluoride, the work of Jackson and Walker [32] on sodium fluoride, the work of Kimber and Rogers [33] on solid , neon and the work of Parrott [34], [35] on germanium-silicon alloys. It is, however, a general characteristic of all of these analyses that the approximate forms of the normal and umklapp relaxation times which are only valid for phonons of low frequencies were used throughout. Also, the parameters specifying these relaxation times were treated as adjustable parameters whose values were obtained from the best fit to the experimental results.

A more rigorous technique which has been more recently utilised to solve the linearised phonon Boltzmann equation is to replace the exact collision operator by a model operator which possesses the same important properties. The model operator would of course has a simple structure than the exact operator so that the solution of the Boltzmann equation can be easily obtained. The important properties which should be satisfied by the model operator are stated clearly in § 2.1 and § 4.1 in the present work. However, we emphasize here

that the model operator representing resistive processes should conserve energy while the model operator representing normal processes should conserve both energy and wavenumber. The first attempt along this direction was due to Simons [36]. In this attempt Simons [36] formulated the model operator in such a way which is almost equivalent to the approaches of Callaway [20] and Krumhansl [22]. However in a more recent article Simons [37] presented a new method for formulating model operators. This new formulation has enabled him to derive a model operator for umklapp processes in which the quasi-conservation of wavenumber is preserved. This important property of umklapp processes has not been taken into account in all the earlier treatments, reviewed above, since in these treatments umklapp processes have been treated as a part of the whole resistive scattering mechanism. The Simons model [37] was then used by Mikhail [38] to represent the umklapp part of the phonon collision operator. A new expression for thermal conductivity has accordingly been obtained. This new expression involve the two ordinary terms of the Callaway expression in addition to a new term which arises naturally because of the more accurate treatment of umklapp processes. The correction term, therefore, represents the effect of the quasi conservation of wavenumber in the umklapp