Influence of isotope scattering on the thermal conductivity of diamond

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The thermal conductivity of diamond crystals with different isotope contents is evaluated in the framework of a microscopic model that considers acoustic- and optical-phonon branches. The phonon Boltzmann equation is solved iteratively, with the phonon wave vectors taken in the real Brillouin zone and the three-phonon normal and umklapp collisions, with the isotope scattering, rigorously treated. As a consequence, the evaluation of the thermal conductivity is done avoiding the relaxation-time approximation for the scattering mechanisms. Good agreement with the experimental data is obtained. The calculation reveals a fundamental role of the optical phonons in determining the thermal resistivity of diamond. Comparison of the theoretical results with the recent experimental data for germanium and silicon is also proposed.

I. INTRODUCTION

Besides its very efficient thermal transport at room temperatures, an important feature of diamond thermal conductivity has to be emphasized: the large enhancement of the conductivity obtained when the isotopic purity is increased.[1] It was observed that it amounts to 50% at room temperature when the ^{12}C concentration goes from 98.9 to 99.9%.

The present paper discusses the thermal conductivity and the role of the isotope scattering in diamond with the framework of a recently introduced approach to the solution of the phonon transport equation.[2] In Ref. 2, the thermal conductivity of crystals with diamond structure, germanium and silicon, was approached with a numerical iterative procedure to solve the phonon transport equation, and reference was made to the real Brillouin zone of the crystal. Such a theory avoids the approximations usually introduced in the literature to solve the Boltzmann equation (relaxation time, trial functions in variational methods, etc.) and to describe the structure of the solid (continuum model, with all the difficulties deriving from its use in the treatment of the umklapp processes and optical phonons). The only approximation introduced in Ref. 2 was connected with a central pair potential responsible for the interaction between atoms. In spite of its simplicity, such a potential was shown to provide good dispersion curves for phonon frequencies in germanium and silicon.

It is then very interesting to study the diamond thermal conductivity, and the isotope role too. The discovery of this great isotope effect[1] was followed by many experimental investigations in diamond[3-5] and in materials with diamond structure, particularly germanium and silicon.[6,7] The possibility to reach a high thermal transport at room temperature is very stimulating in the case of silicon,[8-10] since it could be exploited in the technology of chemical vapor deposition (CVD) films, actually proposed for diamond.[11-13]

Many attempts have been made in the literature to explain the role of isotopic effect in diamond. All these attempts were weakened by the approximations used in the calculations (relaxation-time approximations, Debye-like spectrum, and so on).

To explain the variation of the diamond thermal conductivity related to the isotope content, an approach of the Klemens-Callaway type[14,15] was tried by Onn *et al.*[4] This theoretical approach was suggested by the failure of the classical Ziman calculation.[16] However, in Ref. 4, in order to obtain a good agreement with the experimental data, a further source of phonon scattering was introduced by assuming an increase of the number of vacancies in natural diamond. Against this interpretation, it was argued that large isotope effects are not inconsistent with the existing theories.[17]

In the frame of a Callaway approach, based on the relaxation-time approximation, the effect of isotopes was afterwards discussed by Olson *et al.*,[5] Lanhua Wei *et al.*,[3] and by Novikov *et al.*[18] It was pointed out in Ref. 3, that the scattering mechanisms relevant to enhance the isotopic effect are the normal rather than the umklapp processes.

A two-step model for the normal processes was also proposed for diamond:[19] in the first step, the normal processes transfer low-frequency phonons into the high-frequency region, in the second step, phonons undergo the resistive processes.

It is then interesting to inquire if the observed isotopic effect can be explained by a model where the approach to the solution of the transport equation is avoiding relaxation-time approximations and the real crystal structure is taken into account: in other words, a model where umklapp processes and optical phonons are rigorously introduced as a consequence of the lattice dynamics. Although in the case of diamond the use of a pair potential leads to some discrepancies between experimental and theoretical phonon-dispersion curves, the theory developed in Ref. 2 seems at present to provide the simplest and, at the same time, most reliable model to discuss the thermal conductivity of such a material.

The Boltzmann transport equation is solved through an iterative procedure.[20] The iterative solution allows the simultaneous treatment of all the scattering phonon processes (normal, umklapp, and isotope scattering processes) due to account being taken of the interference among different scattering mechanisms. Actually, the effect of isotopes in germanium and silicon was already discussed in Ref. 21, but in the framework of an isotropic lattice model, where optical
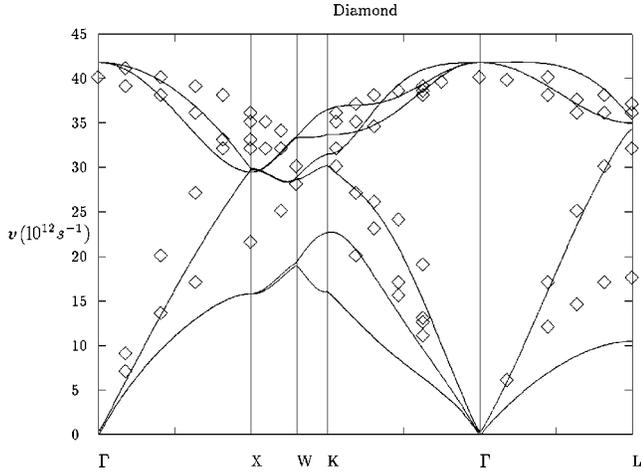
FIG. 1. Theoretical phonon dispersion curves (continuous lines) for diamond, in comparison with experimental data.[23]

phonons were not treated in a rigorous way.

In the present paper, a discussion of the thermal conductivity of diamond and the role of the isotopic defects is presented. Calculations for germanium and silicon are reproposed in comparison with interesting experimental data.[6,7] The model does not consider the presence of other lattice defects, such as vacancies, dislocations, and grain boundaries, that further reduce thermal conductivity.

II. RESULTS FOR DIAMOND AND COMPARISON WITH EXPERIMENTAL DATA

The central potential is described in terms of six parameters denoted by $\rho, \rho', \beta, \beta', \epsilon, \epsilon'$ whose definition was given in Ref. 2. The parameters $\rho, \rho', \beta, \beta'$ appear in the equation of the atomic motion[22] and can be derived by imposing the best fit of the theoretical phonon-dispersion curves to the experimental points as given in Ref. 23.

In Fig. 1 the result of the calculation of phonon dispersions for diamond is shown: the parameters turn out to be $\rho = 0.15$ and $\beta = 4.2, \beta' = 0.17$ (β, β' are in units of 10^{20} g cm^{-2} s^{-2}). The value of ρ' is assumed to be $\rho' = -\rho/8$, as obtained in Ref. 2. ρ, ρ' are dimensionless parameters.

The anharmonic parameters $\varepsilon, \varepsilon'$, involved in the phonon-phonon interaction, require the knowledge of the Grüneisen high-temperature parameter (in the case of diamond $\gamma_G = 0.57$, Ref. 19): the values of ε and ε' turn out to be 35 and 0.4, respectively. Such a set of parameters $\rho, \rho', \beta, \beta', \epsilon, \epsilon'$ fits the experimental value of the thermal conductivity at 300 K for natural diamond. For the calculation the cell spacing parameter was taken as $a = 0.356$ nm.

The isotope scattering is characterized by a mass difference ΔM which is assumed to be present in a fraction f_i of the atoms belonging to the crystal. The probability rate for the scattering due to a single center used for the calculation is the same as proposed by Srivastava (see Ref. 22, p. 179). The scattering centers are assumed randomly distributed and f_i is assumed to be so small that any interference effect between any two centers is excluded.
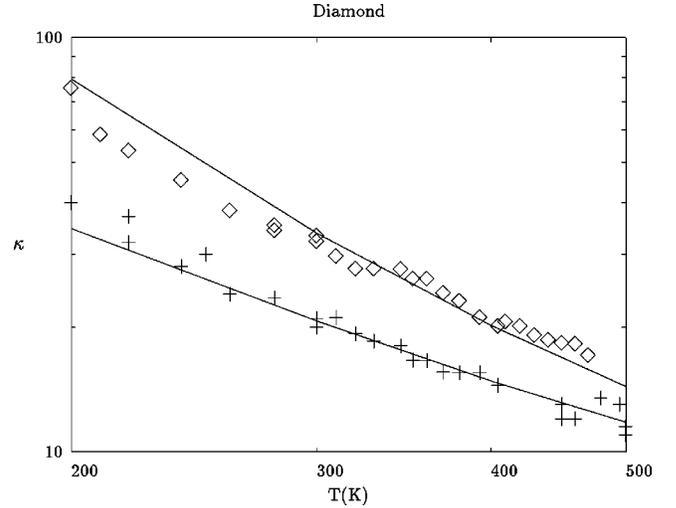

FIG. 2. Temperature dependence of thermal conductivity (in W cm^{-1} K^{-1}) for natural diamond (1.1% of ^{13}C, lower curve) and for isotopically enriched diamond (0.1% of ^{13}C, upper curve). The experimental data points of the natural and enriched samples are indicated by (+) and ($\diamond$), respectively (Refs. 3 and 4).

Through the iterative procedure described in Ref. 20 one obtains the thermal conductivity of natural diamond and of isotopically enriched diamond, using for $f_i(\Delta M/M)^2$ the values of 6.9×10^{-5} and 7×10^{-6} respectively. The corresponding concentrations of ^{13}C are 1.1% and 0.1%.

At 400 K, one obtains $\kappa = 14.8$ W cm^{-1} K^{-1} for natural diamond and $\kappa = 20.2$ W cm^{-1} K^{-1} for the enriched material, in full agreement with the experimental conductivities (14 and 20 W cm^{-1} K^{-1}, respectively[4]). The result is satisfactory because it follows from a microscopic calculation, the parameters employed in the theory having been justified through the harmonic and anharmonic vibrational properties of the crystal.

The relaxation-time approximation is completely avoided, since boundary scattering (the only scattering mechanism treated with this approach) is not relevant at high temperatures.

Figure 2 shows the theoretical behavior of thermal conductivity for natural and isotopically enriched diamond as a function of temperature in the range between 200 and 500 K. The experimental data are those reported by Onn *et al.* and by Lanhua *et al.*[3,4]

For the low-temperature region, the thermal conductivity was determined by treating the boundary scattering through a relaxation time, that is

$$\tau_p = LF/s_p, \qquad (1)$$

where L is the Casimir length, F a correction factor depending on the width to length ratio of the sample,[24,25] and s_p the velocity of sound for a phonon with polarization index p. s_p is taken as the value referring to an isotropic model,[21] in which the two transverse acoustic branches have a common value, s_T, to be distinguished from the value s_L of the longitudinal acoustic phonons: s_T and s_L are considered independent of the wave vector. Boundary scattering of optical
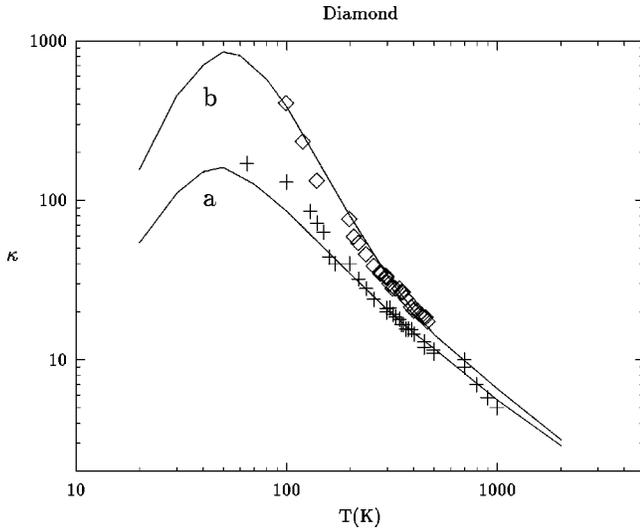
FIG. 3. Thermal conductivity (in $W\,cm^{-1}\,K^{-1}$) for natural (curve a) and isotopically enriched (curve b) diamond, in the entire temperature range. The experimental data of the natural and enriched samples are indicated by (+) and ($\diamond$), respectively (Refs. 3 and 4).

modes is neglected. For L and F we use the Casimir length $L=0.3$ cm and the correction factor $F=0.5$.

Figure 3 shows the behavior of the thermal conductivity in the whole temperature range. Below 200 K, the behaviors of the theoretical and experimental curves for the natural sample are slightly different. The discrepancy is probably due to the inadequacy of the theoretical dispersion curve for the lower acoustic branch. In fact, below 200 K acoustic phonons are expected to play a dominant role in determining the transport properties.

The microscopic model allows the evaluation of the role of optical phonons both in the three-phonon processes and in isotope scattering mechanisms. Table I lists the values of κ, referring to calculations for natural diamond (1.1% of ^{13}C) in the first two columns, and isotopically enriched diamond (0.1% of ^{13}C) in columns 3 and 4. Columns 1 and 3 show the result of the calculation in which both acoustic and optical phonons are taken into account; columns 2 and 4 are obtained by considering only acoustic phonons.

At high temperatures the value of the thermal conductivity, when only acoustic phonons are considered, is remarkably higher than the value obtained when all phonons are included. Thus optical phonons provide the main source of the thermal resistance in the range above 200 K.

Because of their small group velocity, they carry a negligible amount of heat but scatter the acoustic phonons, to which heat transport is committed. This role of optical phonons in the three-phonon processes for crystals with diamond structure was previously discussed by Srivastava,[26,27] using relaxation times for phonon scatterings and Debye and Einstein phonon dispersion laws, approximations avoided in this paper.

The isotopic effect in diamond is clearly dominant at 200 K. At this temperature, the enhancement of the conductivity in the isotopically enriched sample is slightly different (of 10%) when only acoustic phonons are considered. At higher temperatures the difference is $\sim 20\%$: this is in agreement with the fact that isotope scattering is enhanced by the high-frequency phonons.

At lower temperatures, boundary and isotope scattering are the only active processes: due to the time-relaxation approximation used for the boundary scattering, the theoretical results must be considered only qualitatively. Since, to the author's knowledge, low temperature data for single crystals are not available, any further discussion is avoided.

Comparison between the experimental data of germanium and silicon and the microscopic calculations is presented in Figs. 4 and 5. Figure 4 shows the result of calculations for germanium with different percentages of isotope contents.

The microscopic potential parameters for germanium are the ones introduced in Ref. 2 and, for the isotope factor $f_i(\Delta M/M)^2$, use was made of the parameter g of the mass variance defined by Eq. (1) of Ref. 6 and given in Table I of the same reference. From the same table, the value L_E is taken as the value of FL in boundary scattering. The experimental data shown in the figure are those corresponding to ^{70}Ge (99.99%), ^{70}Ge (96.3%), ^{nat}Ge, $^{70/76}Ge$. The agreement of the present calculation is good for ^{70}Ge (96.3%) and for ^{nat}Ge.

Figure 5 shows results of the calculations on silicon with the microscopic potential parameters as in Ref. 2 in the case of natural (isotope factor 2.7×10^{-4}) and isotopically enriched (99.7% of ^{28}Si) samples.[28] Comparison with the experimental data[29,30] of natural silicon gives a good agreement, that is also found for the high-temperature values of the thermal conductivity of the enriched sample.[7] For the data at 100 K, the discrepancy is high: a better agreement can be obtained if the value of the anharmonic parameters ε,ε' is changed with temperature.

TABLE I. Thermal conductivity (in $W\,cm^{-1}\,K^{-1}$) of natural diamond (columns 1 and 2) and isotopically enriched diamond (columns 3 and 4) at selected temperatures. Columns 1 and 3 show the result of the calculation with both acoustic and optical phonons taken into account; columns 2 and 4 are obtained by considering only acoustic phonons.

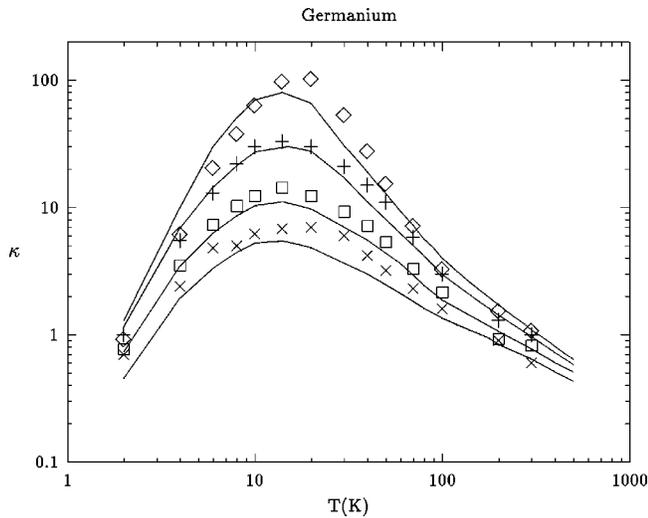| T (K)	Natural ($A+O$)	Natural (A)	Enriched ($A+O$)	Enriched (A)
100	85.4	85.4	383	389
200	34.6	37.6	79.3	95
500	11.8	20.0	14.4	29.5
1000	5.6	11.1	6.6	15.6

FIG. 4. Thermal conductivities (in $W\,cm^{-1}\,K^{-1}$) for germanium as a function of temperature. The experimental data points correspond to ^{70}Ge (99.99%) ($\diamond$), ^{70}Ge (96.3%) ($+$), ^{nat}Ge (squares), $^{70/76}Ge$ ($\times$) (Ref. 6).

III. CONCLUSIONS

In the calculations of thermal conductivity performed in this paper no continuum approximation is done, since the lattice is described according to its real structure, both in the direct and in the reciprocal space. The matrix elements for phonon-phonon interaction are also given in terms of the geometrical parameters of the Brillouin zone, allowing a rigorous treatment of umklapp processes.

Moreover, the calculation of thermal conductivity automatically includes both acoustic and optical modes with dispersion. Let us stress that the calculation rigorously considers normal and unklapp scatterings.

The paper is mainly devoted to the discussion of the isotope effect in the diamond thermal conductivity. The thermal
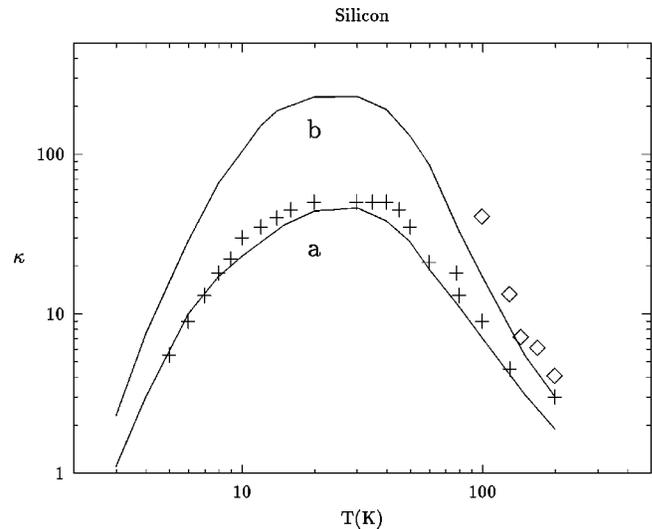

FIG. 5. Thermal conductivities (in $W\,cm^{-1}\,K^{-1}$) for natural (curve a) and isotopically enriched (curve b) silicon as a function of temperature. The experimental data points for natural silicon are indicated by ($+$) (Refs. 29 and 30). and for the enriched silicon by ($\diamond$) (Ref. 8).

conductivity of diamond crystals with different isotope contents is evaluated with a theoretical framework that completely avoids the relaxation-time approximations for the scattering mechanisms. The discussion of the thermal conductivity and of the isotope effect with such a kind of theory and the good agreement obtained with the experimental data turns out to be relevant for the present renewed interest in the thermal transport phenomena.

Moreover, comparison with very recent experimental data on germanium and silicon, previously not available, are also included. The mass difference of isotopes completely explains the variation of the thermal conductivity in diamond and germanium.

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