06

Influence of phonon focusing effect on the diamond thermal conductivity

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The thermal conductivity of diamond samples at low temperatures is calculated taking into account the phonon focusing effect based on the McCurdy, Maris and Elbaum theory in the frame of purely diffuse boundary scattering of phonons. Data on the focusing effect for transverse and longitudinal phonon modes are obtained. The calculated values of thermal conductivity are compared with experimental data for diamond samples in the form of square plates with different axes along [100] and [110]. At low temperatures near 5 K, experiment and theory showed satisfactory agreement, but above 10 K, anisotropy is not observed experimentally. Possible causes of this discrepancy are discussed.

Keywords: anisotropy, solid state, phonons, wide-bandgap semiconductors.

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Introduction

Bulk diamond single crystals have the highest thermal conductivity — about 24 W/(cm·K) [1], — and therefore may be considered for a wide range of applications in modern electronics. One of them is the use of diamond in dark matter sensors where interaction between a particle and crystal lattice gives rise to transfer of a part of energy and, thus, to appearance of acoustic phonons subject to recording [2]. To ensure maximum efficiency of such detection, probability of scattering of the emerging phonons on lattice defects and detector boundaries must be minimized, which implies thorough selection of crystal parameters such as crystal sizes, crystal-lattice orientation and surface treatment quality. Moreover, phonon behavior shall be accurately simulated and calculated, including, in particular, the phonon focusing effect.

Cubic symmetry of the diamond crystal causes the equality of three components of crystal's thermal conductivity tensor. But at low temperatures or in case of small crystal sizes where the free path of thermal phonons becomes comparable with the sample sizes, thermal conductivity of even a cubic crystal depends on the sample geometry and orientation due to the phonon focusing effect [3]. This effect is defined as nonuniform distribution of group phonon velocities even with isotropic phase vectors, which causes distribution anisotropy of various phonon modes and, thus, to thermal conductivity anisotropy. In the low temperature region where phonon scattering occurs almost exclusively on the sample surface, it can be detected experimentally using the thermal pulse procedure [4]. It was first demonstrated for LiF and KCl crystals, for which it was found that phonons with longitudinal polarization prevailed in the temperature ranges of 2−3.6 K in the [100] direction for LiF, and phonons with transverse polarization prevailed for KCl [5].

Thermal conductivity theory that takes into account the phonon focusing effect was proposed by McCurdy, Maris and Elbaum [3]. This theory is the generalization of classical Carimir heat transfer theory where the sample boundaries are treated as an absolute black body (i.e. phonon scattering on boundaries is of diffuse type) and the phonon mode velocity is isotropic [6], for the case of anisotropy of the phase and group phonon mode velocities. It may be used to explain the existing experimental findings for various crystals at low temperatures, including cubic Si, CaF_2, GaN single crystals [3,7–9] and low-dimensional SiGe structures [10].

The experiment [9] has shown that in case of, for example, Si, thermal conductivity of samples in the form of parallelepipeds with a length of 40 mm and cross-section of 4×4 mm is 38% as high for orientation along the [100] direction as along [110] in the diffuse boundary scattering mode at low temperatures. For diamond, experimental data [11] agree only qualitatively with the theory, which requires additional study of the phonon focusing effect on the magnitude and anisotropy of diamond's thermal conductivity at low temperatures.

This work calculates the thermal conductivity of diamond samples taking into account the phonon focusing effect on the basis of McCurdy, Maris and Elbaum theory. Theoretical data was obtained for focusing of transverse and longitudinal phonon modes. Calculated thermal conductivity data is compared with the experimental data for diamond samples in the form of plates with the (100) and (110) orientations. Quantitative agreement was achieved between

the experiment and calculation in the very low temperature region. It was analyzed why the phonon focusing effect in diamond appears in the experiment only below 10 K and is almost not observed at higher temperatures.

1. Samples and methods

Two diamond plate samples were cut from a diamond single crystal grown using the HPHT technique with the (100) orientation of the largest facet. Samples D100 and D110 had a form of $0.54 \times 4.03 \times 4.03$ mm and $0.52 \times 4.03 \times 4.03$ mm parallelepipeds with the long facet oriented along [100] and [110], respectively. According to the scanning force microscopy data, surface roughness of polished samples was lower than 5 nm.

To measure thermal conductivity of diamond samples in the temperature range of 5–410 K, a longitudinal heat flux method was used. For measurements, heat flux was oriented along the largest facet in the [100] and [110] directions for samples D100 and D110, respectively. Thus, thermal conductivity along the [100] and [110] directions was measured. The experimental procedure is described in detail in [1,12]. The experimental measurement error does not exceed 3% in the main measurement range, but increases by several times at helium temperatures.

Thermal conductivity of samples was calculated using the McCurdy, Maris and Elbaum model [3]. Phase velocities s of elastic plane phonon modes in a crystal are determined from its elastic constants using the Christoffel equation $\Sigma_{ij}[M_{ij} - s^2\delta_{ij}]s_j = 0$, where M_{ij} are the Christoffel matrix elements related to the elastic crystal constants C as $M_{ij} = \Sigma_{nm}k_nC_{inmj}k_m$, where vector $\mathbf{k}$ is the wave vector, δ_{ij} is the delta function, s_{Pj} is the phonon mode polarization (index j equal to 0 corresponds to the quasi longitudinal mode L, 1 and 2 correspond to transverse modes $T1$ and $T2$).

The Christoffel equation for cubic lattice was solved using Christoffel software package [13]. The calculation was performed using the 720×2880 grid for the polar angle θ and azimuthal angle ρ , respectively. The calculation used the density of 3515 kg/m^3 and elastic constants of $c_{11} = 1079$ GPa, $c_{12} = 124$ GPa and $c_{44} = 578$ GPa.

Knowing the phase velocity distribution of phonon modes, the Casimir velocity v_C, Debye velocity v_D may be calculated by averaging over the full solid angle, and, moreover, the specific heat capacity of the crystal C_v and the Debye temperature T_D^{el} may be calculated in terms of the Debye model as [14]:

$$v_C = \frac{\langle s^{-2}\rangle}{\langle s^{-3}\rangle},$$

$$v_D = (\langle s^{-3}\rangle)^{-1/3},$$

$$C_v = k_B\,\frac{2\pi^2}{5}\Big(\frac{k_BT}{\hbar}\Big)^3 v_D^{-3},$$

$$T_D^{el} = v_D\Big(\frac{6\pi^2}{V_0}\Big)^{1/3}\frac{\hbar}{k_B},$$

where T is the temperature, V_0 is the atomic volume, and $\langle s^{-2}\rangle$ and $\langle s^{-3}\rangle$ are the mean inverse squares and inverse cubes of phase velocities of all phonon modes over the full solid angle ($d\Omega = \sin\theta d\theta d\varphi$, $0 < \theta < \pi$, $0 < \varphi < 2\pi$):

$$\langle s^{-n}\rangle = \frac{1}{3}\,\frac{1}{4\pi}\sum_j \int\limits_{\Omega}^{\square} \frac{d\Omega}{s^n(\mathbf{k}j)}.$$

The calculation provided the following values that corresponded to the experimental data: $v_C = 13.103 \cdot 10^5$ cm/s, $v_D = 13.443 \cdot 10^5$ cm/s, $C_v/T^3 = 0.503$ erg/(K^4·cm^3) and $T_D^{el} = 2244$ K.

Knowing the phase velocities of phonon modes, group velocities $v_g = \nabla s$ may be calculated [15]. The calculated group velocity surfaces are shown in Figure 1.

Thermal conductivity in the diffuse boundary scattering mode in terms of the McCurdy model is determined as [16]:

$$\kappa = \frac{C_v v_D^3}{24\pi A}\sum_j \int\limits_{\Omega}^{\square} \frac{I(\mathbf{k}j)}{s^3(\mathbf{k}j)}\,d\Omega,$$

where A is the sample cross section and I is the integral depending on the sample geometry, for example, for a sample with round cross section, it is equal to

$$I_o(\mathbf{k}j) = \frac{16R^3}{3}\,\frac{v_3^2(\mathbf{k}j)}{v_1(\mathbf{k}j)},$$

where R is the round sample radius, $v_3(\mathbf{k}j)$ is the group velocity component along the sample axis, $v_1(\mathbf{k}j)$ is the group velocity component in the sample cross section plane. For a rectangular cross-section sample, this integral is calculated as

$$I_{\blacksquare}(\mathbf{k}j) = \begin{cases} \frac{D^3}{3}\,\frac{v_3^2(\mathbf{k}j)}{v_1(\mathbf{k}j)}\,\frac{3n\sin\phi - \cos\phi}{\sin^2\phi}, & \text{if } \tan\phi > \frac{1}{n}, \\ \frac{D^3}{3}\,\frac{v_3^2(\mathbf{k}j)}{v_1(\mathbf{k}j)}\,\frac{3n^2\cos\phi - n^3\sin\phi}{\cos^2\phi}, & \text{if } \tan\phi < \frac{1}{n}, \end{cases}$$

where D and nD are the cross section side dimensions, and ϕ is the angle between $v_1(\mathbf{k}j)$and nD side.

To calculate thermal conductivity for a finite bar, it is also important to introduce a length correction. The same correction as in [16] was used. To determine the phonon focusing effect on the thermal conductivity magnitude, thermal conductivity was calculated in all sample axis orientations at 1° intervals over polar and azimuthal angles for a cylindrical sample with a length of 30 mm and diameter of 3 mm.

2. Findings and discussion

Figure 2 shows the calculated thermal conductivity in the cylindrical diamond sample in the ab plane taking into account the phonon focusing effect. The calculated values

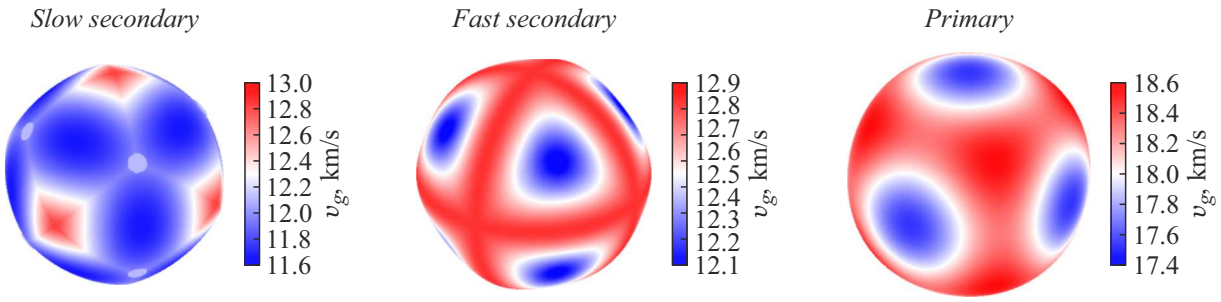

Figure 1. Group velocity surfaces of phonon modes in the diamond (left to right — $T1$, $T2$, L).

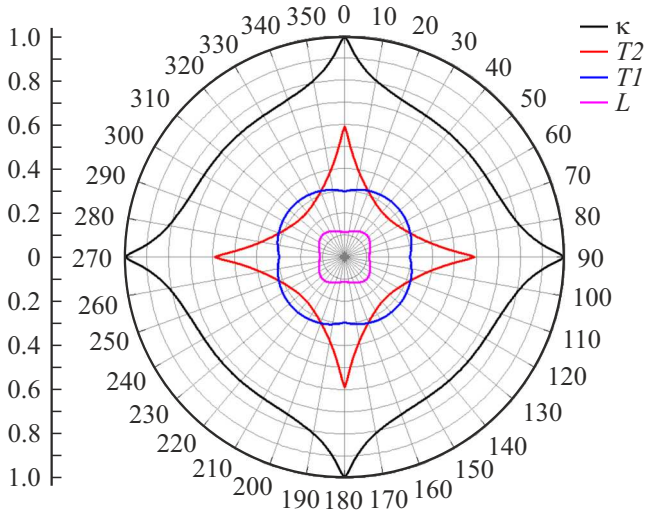

Figure 2. Thermal conductivity of the cylindrical diamond sample with a length of 30 mm and diameter of 3 mm at low temperatures taking into account phonon focusing depending on the sample orientation in the 100 plane.

are normalized to the thermal conductivity in the [100] direction. Due to the cubic crystal symmetry, the same dependence of thermal conductivity is observed in the bc and ac plane. The maximum focusing effect is observed in the major axes — a, b, c ([100], [010], [001]). The maximum thermal conductivity in the ab plane is observed for and in the vicinity of the [110] direction within 25° where the thermal conductivity appears to be more than 26% as low as that in the major axis directions. The main contribution to this dependence is made by the slow transverse mode $T2$ that appears to be focused in the major directions and defocused in the [110] direction. The behavior of other modes is opposite — their group velocity surfaces are focused in the [110] direction and defocused in the [100] and [010] major crystallographic axes, but due to a lower velocity, the mode $T2$ makes a higher contribution to the general thermal conductivity (the mean contribution of the longitudinal mode L in this plane is about 13%, of transverse modes $T1$ and $T2$ is 32% and 55%, respectively). Minimum thermal conductivity in the full solid angle is observed for the [111] direction — with such crystal orientation, the thermal conductivity decreases by 28% with respect to the [100] axis.

Calculation of the thermal conductivity for samples D100 and D110 taking into account the phonon focusing effect gives 0.1795 and 0.1336 W/(m·K^4), i.e. the phonon focusing effect would have caused a 1.34 times higher thermal conductivity in the sample oriented along the [100] axis compared with the sample oriented along the [110] axis. Experimental and calculated data for the boundary diffuse scattering mode, including the phonon focusing effect, is shown in Figure 3. Experimental thermal conductivity measurement gives a close relation at the lowest measurement temperatures (5 K), but starting rom 10 K and higher, measured thermal conductivities of these samples almost coincide. However, the free path lengths determined from the experimental data are 2.6 times as long as those for these samples. Moreover, even at low temperatures, the measured temperature dependence of thermal conductivity is not cubic. These experimental results indicate an important role of mirror-like scattering in heat transfer in the diamond at low temperatures. Mirror-like scattering presumably prevents the phonon focusing effect from appearing to the

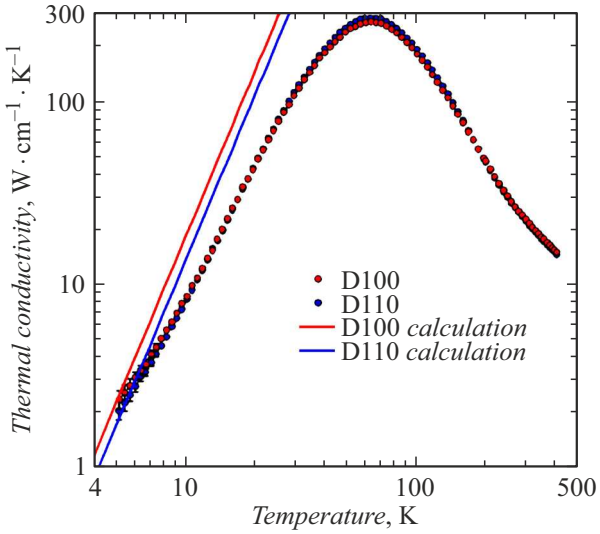

Figure 3. Dependence of thermal conductivity of the diamond samples on temperature (dots — experimental data, lines — calculated data in the diffuse scattering approximation).

full extent. To make the highest contribution, this effect requires the diffuse boundary phonon scattering mode.

Conclusion

Diamond's thermal conductivity was calculated in the diffuse boundary scattering mode taking into account phonon focusing. It is shown that defocusing in the [110] and [111] directions leads to a decrease in thermal conductivity by 26% and 28%, respectively, compared with the [100] direction, with the main contribution made by the slow quasi transverse mode $T2$.

At low temperatures, the phonon focusing effect is observed experimentally, the measured thermal conductivity anisotropy coincides with the calculated value taking into account the sample geometry. Thermal conductivity anisotropy isn't observed at higher (above 10 K) temperatures. Such behavior is presumably caused by the deviation from the diffuse boundary phonon scattering mode due to mirror-like phonon scattering at the boundary, which is confirmed by the deviation of the temperature dependence of thermal conductivity from the cubic one and by the free path length that is more than twice as high as the theoretical value.

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Conflict of interest

The authors declare no conflict of interest.

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