# Contributions of various phonon relaxation mechanisms to the thermal resistance of the crystal lattice of bismuth at temperatures below 2°K

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The contribution of various phonon relaxation mechanisms (scattering of phonons by phonons, by carriers, or by the sample surface) to the thermal resistance of the crystal lattice of massive perfect bismuth crystals at temperatures below the thermal conductivity maximum (0.1–2 °K) is discussed. The effective phonon mean free path $l_{\text{eff}}$ in the crystal lattice is calculated by the Monte Carlo method at various relations between the mean free path in normal ($l^N$) or resistive ($l^R$) scattering of phonons within the sample and the sample diameter $d$. Estimates are obtained of the magnitude and possibility of observing the Knudsen minimum in the heat conduction on going from Poiseuille to Knudsen phonon gas flow are estimated (the depth of the corresponding minimum on the $(l_{\text{eff}}(T)$ curve on decrease of temperature is about 20% of $d$). The magnitude and temperature dependence of the effective phonon-carrier scattering length $l_{pe}$ in bismuth are calculated in two limiting cases: $l^N \equiv 0$ and $l^N \to \infty$. To remove the divergences, diffuse scattering of phonons by the sample surface is introduced. In both cases the increase of the number of phonons interacting with the carriers with decreasing temperature should lead to an increase of the corresponding contribution to the thermal resistance of the lattice (decrease of $l_{pe}$) down to 0.5–0.2 °K. At temperatures below 0.1 °K, at which scattering by the carriers can be neglected, the principal role is again assumed by scattering of the phonons by the sample surface.

## 1. INTRODUCTION

This paper is devoted to a calculation of the contribution made by various phonon-relaxation mechanisms to the thermal resistance of the bismuth crystal lattice at temperatures below the maximum of the thermal conductivity, i.e., in the region where elastic[1)] phonon-phonon collisions and phonon scattering by carriers can play an important role in addition to phonon scattering by the surface of a bulky sample. This question was not considered theoretically before, since the analytic calculation is quite complicated, and the experimental results cited in the literature pertain to samples of approximately equal dimensions and quality (a detailed review of the experimental data accumulated by 1970 is given in the monograph of Mogilevskiĭ and Chudnovskiĭ [1]), and only recently, following the developments of methods for obtaining highly perfected large bismuth crystals [2], did it become possible to observe the change of the thermal conductivity with successively decreasing sample thickness [3]. It was shown experimentally [1] that the principal role in the heat-transport processes in bismuth at liquid-helium temperatures is played by phonons; the contribution of the carriers is small and amounts to $\leq 1\%$ of the total thermal conductivity at 3°K and $\leq 15\%$ at 1.3°K. No investigations were made at lower temperaperatures.

Just as in a typical dielectric, the thermal resistance in the crystal lattice of bismuth at temperatures above the maximum of the thermal conductivity ($T_{max}$) is due to inelastic scattering of the phonons by phonons (U processes), the probability of which decreases exponentially with decreasing temperature, i.e., the effective phonon mean free path calculated from the measured thermal conductivity $\kappa$,

$$l_{\text{eff}} = 3\kappa / C\bar{s} \qquad (1)$$

(where C is the specific heat and $\bar{s}$ is the average speed of sound) increases exponentially with decreasing temperature in the interval $T > T_{max}$.

At temperatures $T \lesssim T_{max}$, the behavior of $l_{\text{eff}}$ in a dielectric depends on the relation between the effective mean free path $l^N$ of the phonons at normal collisions in the volume (N processes), the mean free path $l^R$ corresponding to the phonon inelastic scattering in the volume (U processes, scattering by microscopic stacking faults of the crystal lattice, or scattering by carriers in bismuth), and the characteristic dimensions, for example the diameter d in the case of a cylindrical sample [4]. If

$$l^N \ll d \ll l^R \text{ and } d^2/l^N l^R \ll 1, \qquad (2)$$

the motion of the phonons under the influence of the applied temperature gradient similar to the flow of a viscous liquid or gas in a pipe under the influence of an external force (Poiseuille flow). The effective mean free path of the phonons is in this case $l_{\text{eff}} \sim d^2/l^N$ and can greatly exceed the characteristic dimensions of the sample. With decreasing temperature, $l_{\text{eff}}$ decreases in proportion to $1/l^N$, i.e., when condition (2) is satisfied the experimental data make it possible in principle to calculate $l^N$ directly.

With further decrease of temperature $T \ll T_{max}$ (and in most crystals obtained at the present time also at $T \lesssim T_{max}$), a different situation is observed, wherein

$$l^N,\ l^R \gg d, \qquad (3)$$

and the phonon motion is similar to the Knudsen flow of a real gas, i.e., $l_{\text{eff}}$ increases slightly with decreasing temperature and tends asymptotically to d.

As indicated in Ziman's book [5], the feasibility of Poiseuille flow in a phonon gas was predicted back in the 30's by Peierls, who also raised the question of whether the Knudsen minimum appears on going from the Poiseuille flow to the Knudsen flow with decreasing sam-

ple temperature. So far, the conditions (2) could be satisfied only in experiments with highly perfect solid-helium crystals [6,7], the temperature dependence of the thermal conductivity of which near $T_{max}$ can be described well within the framework of theoretical models [8-10]. As to bismuth [3], and apparently also most other substances, one should expect more readily a transition regime at the characteristic crystal dimensions $d \leq 1$ cm and at temperatures $T \leq T_{max}$, while in perfect samples at $T \ll T_{max}$ one should expect a Knudsen flow of the phonon gas.

However, an exact analytic description of the behavior of $l_{eff}(T)$ in the transition regime, when the Poiseuille flow gives way to Knudsen flow of the phonon gas, cannot be obtained by the previously employed methods [8,9] while the method proposed by Guer and Krumhansl [10] for numerically integrating the Callaway integrals for a smooth transition from one asymptotic form to another employs a switching function which, as noted by the authors themselves, is arbitrarily chosen.

We have undertaken a numerical calculation of $l_{eff}(T)$ in the general case. The Monte Carlo method was used to calculate the values of $l_{eff}/d$ as a function of $d/l^N$ at the different values of the ratio $l^R/l^N$, which was used as a parameter. The calculation program and plots of $l_{eff}/d$ as function of $d/l^N$ are given in Sec. 2. It is appropriate to note here that the values of $l_{eff}$ calculated by means of the formulas previously obtained [9] and [8,10] at specified values of $l^N(T)$ and d differ numerically in the region of Poiseuille flow by a factor of 5, apparently as a result of a difference in the definition of $l^N$. The $l_{eff}(T, d)$ curve obtained by computer calculation lies practically halfway between them. The calculation predicts the appearance of a Knudsen minimum on the $l_{eff}(T)$ curve, with a depth $\approx 20\%$ of d, in the temperature region where $d/l^N \approx 1$ (naturally, at lower temperatures we have $d/l^N \ll 1$ and $l_{eff}$ tends to d).

The experimentally observed oscillations of the phonon thermal conductivity of bismuth (at 1.5°K, the amplitudes of the oscillations in strong transverse magnetic fields amounted to several percent of the total thermal conductivity [1]) point to the need of taking the interaction of the phonons with the carriers into account. Inasmuch as this question was not considered theoretically before, we have attempted to calculate the behavior of the effective length $l_{pe}$ in the temperature interval 0.1—2°K in two limiting cases: 1) when the most frequent phonon-scattering processes are N processes, i.e., $l^N = 0$, and the only resistive process is the scattering of phonons by carriers; and 2) when the normal collisions can be neglected, $l^N \to \infty$, and the thermal resistance is the result of inelastic scattering of the phonons by the carriers and by the surface of a sample of specified diameter.

The results of the calculations are given in Sec. 3. In both cases it turned out that $l_{pe}(T, d)$ decreases substantially with decreasing temperature at $T < 1.5$°K, reaches a minimum at $T \approx 0.3$—0.4°K, and then again increases.

A comparison of the results with the experimental data [3] shows that in perfect crystals with characteristic dimensions $d \lesssim 1$ cm, the thermal resistance near the maximum of the thermal conductivity (i.e., in the interval 2—3°K) is due mainly to diffuse scattering of the phonons from the surface of the sample. The decrease of $l_{eff}$ with decreasing temperature in this region is due to the appearance of a transition regime of phonon-gas flow, which is caused by the frequent normal phonon-phonon collisions ($d/l^N \gg 1$ in the volume of the sample). At temperatures below 1.5°K we have $d/l^N \sim 1$, but at the same time the role of the volume resistance, which is connected with the scattering of the phonons by the carriers, increases. Calculation predicts the appearance of a deep minimum, several times deeper than the Knudsen minimum, on the $l_{eff}(T)$ curves at temperatures 0.3—0.5°K, when the characteristic momenta of the thermal phonons too become comparable with the transverse dimension $2p_F$ of the electron ellipsoid. At lower temperatures, $l_{pe}$ in bismuth, as in a normal metal, increases with decreasing temperature, so that at $T < 0.1$°K the principal role in the thermal resistance of the lattice is again played by the scattering of the phonons on the surface of the sample—Knudsen flow, $l_{eff} = d$. A similar minimum on the $l_{eff}(T)$ curve is predicted in Ziman's monograph [5] for pure semiconductors with low concentration of the free carriers.

## 2. CALCULATION OF THE EFFECTIVE PHONON MEAN FREE PATH AT DIFFERENT RELATIONS BETWEEN d, $l^N$, AND $l^R$

The numerical calculations of the ratio $l_{eff}/d$ as a function of $d/l^N$ for a specified parameter $l^R/l^N$ were performed with the BÉSM-6 computer by the Monte Carlo method. The idea of the calculations was as follows: In a cylinder of given diameter d, we chose an arbitrary point for the start of the motion of the quasiparticles, and specified the mean free path $l^R$ in the volume with loss of quasimomentum, and the average step, i.e., the mean free path for normal phonon-phonon collisions $l^N$. For convenience in the calculations it was assumed that the mean value is $l^N \equiv 1$, i.e., all the lengths were measured in relative units. From the specified mean values we generated the following random quantities: the mean free path $l^{R*}$ in the volume with loss of quasimomentum, and also the length of the step $l^{N*}$ of the particle prior to the next collision, as well as the azimuthal and polar angles $\varphi^*$ and $\vartheta^*$ which determine the direction of motion at the given instant. After each step, we calculated the coordinates of the particle and the length of the trajectory from the initial point. As soon as the trajectory length exceeded $l^{R*}$ or the particle crossed the surface of the cylinder, the calculation was stopped, the length of the trajectory of this particle was fixed, and the motion of the next particle was then simulated. The trajectories were averaged over all the initial particle-emission points uniformly distributed over the cross section of the cylinder, after which the phonon effective mean free path $l_{eff}$, which enters in Eq. (1), was calculated. The number of particles over which the averaging was carried out was chosen such that the average error in the calculation of $l_{eff}$ did not exceed 3%.

It is natural to assume, when specifying the random mean free path, that the probability of phonon scattering in the volume, in the time interval dt, does not depend on the distance traversed by the particle from the instant of the last collision. Therefore the probability that the particle will negotiate a path of length between $l$ and $l + dl$ from the instant of the last collision is equal to $(1/\lambda)\exp(-l/\lambda)dl$ at a mean free path $\lambda$. Accordingly, it can be assumed that the random value $l^{R*} = -l^R \ln x$, where x is a random quantity, is uniformly distributed in the interval $\{0, 1\}$. Analogously, assuming isotropic

scattering in normal collisions of the phonons, the differential distribution with respect to the mean free path in the direction of motion is described by the expression

$$dP(\lambda, \vartheta, \varphi) = (1/4\pi\lambda)\, e^{-l/\lambda} \sin\vartheta\, dl\, d\vartheta\, d\varphi,$$

where $\varphi$ and $\vartheta$ are the azimuthal and polar angles, and $\lambda \equiv l^N = 1$. Hence $l^{N*} = -\ln x_1$, $\cos\vartheta^* = 2x_2 - 1$, and $\varphi^* = 2\pi x_3$, where $x_1$, $x_2$, and $x_3$ are random numbers uniformly distributed in the interval $\{0, 1\}$. (Similar problems are described in greater detail in [11,12].)

The Monte Carlo method is equivalent to calculating multiple integrals, the multiplicity of which is comparable with the number of steps made by the particle before it leaves the cylinder, amounting to $10^4$ if $d/l^N \sim 100$. The fact that the calculations are all of the same type, and that no large-capacity memory is required, make this method exceedingly convenient for programming, and for the given calculations it is perhaps the only one possible.

The results of the calculations are shown in Fig. 1. As expected, at $d \ll l^N, l^R$, i.e., in the Knudsen limit, $l_{eff}/d$ tends to unity. With increasing ratio $d/l^N$, the value of $l_{eff}/d$ decreases, reaches a minimum at $d/l^N \approx 1$—the Knudsen minimum (the minimum value is $l_{eff}/d \approx 0.75$—$0.80$), and then begins to increase. The behavior of $l_{eff}/d$ in the region $d/l^N \gg 1$ depends essentially on the value of the parameter $l^R/l^N$. Thus, at $l^R/l^N \gtrsim 300$ and $d/l^N \gg 10$ the value of $l_{eff}/d$ increases in proportion to the increase of $d/l^N$—the Poiseuille flow of the phonon gas. It follows from the diagrams that in this region $l_{eff} \approx 0.1 d^2/l^N$. The coefficient 0.1 lies between the values 5/32 and 1/32 obtained in [8,10] and [4,9], respectively; the probable reason is the difference in the definition of the mean free path $l^N$. In any case, owing to the presence of the small coefficient, the developed Poiseuille flow ($l_{eff} \gg d$ and is proportional to $d^2/l^N$) can be observed only if the following condition, which is more rigorous than (2), is satisfied:

$$l^R/d \gg d/l^N \gg 10. \qquad (4)$$

If the requirements (4) are violated, then $l_{eff}$ does not increase as steeply with increasing $d/l^N$, one should speak more readily of the appearance of the transition flow regime (this can be easily traced in Fig. 1), and to calculate $l^N$ from the experimental data it is necessary to use the presented plots, since the analytic methods used in the theories of [8,9] are not suitable for the description of the transition from the Poiseuille flow to the Knudsen flow, while in the method proposed in [10] for numerically integrating the Callaway integrals corresponding separately to the Knudsen and Poiseuille limits this transition is described by an arbitrarily chosen switching function, which is equivalent to drawing an arbitrary smooth curve between the two asymptotic curves (naturally, the question of the existence of the Knudsen minimum does not even arise in this approximation).

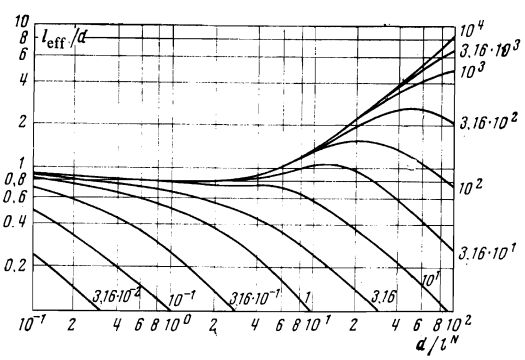


FIG. 1. Plots of $l_{eff}/d$ against $d/l^N$ for the different $l^R/l^N$ values marked on the curves.

By using the approximate estimates of the corresponding volume free paths of the phonons (for example, those given in the book [5]), it can be estimated that in order to satisfy the requirements (4), i.e., to observe a developed Poiseuille flow in a dielectric with characteristic dimensions on the order of 1 cm, the concentration of the point stacking faults of the crystal lattice (impurity atoms, vacancies) must be $\lesssim 10^{-5}\%$. It is not surprising that Poiseuille flow could be observed heretofore only in helium crystals [6,7] grown from the chemically purest material available at present, and the slopes of the $l_{eff}(T)$ curves in the region of the Poiseuille flow (and the maximum values of the thermal conductivity), as shown by comparison of the results [6] and [7], are much higher in the case when the crystals were grown from the isotopically purified material [6] (the concentration of the $He^3$ isotope in the $He^4$ in natural gas is $\sim 10^{-4}$—$10^{-5}\%$ and can be easily lowered by more than one order of magnitude).

Bismuth has a single isotope, and the certified purity of the metal is at present $\sim 10^{-4}\%$ (Bi-0000), while zone melting in deep vacuum [2] can greatly decrease the content of the dissolved gases, which usually are not taken into account in the chemical analysis. Although the exact values of the length $l^N$ in bismuth at liquid-helium temperatures are not known, and the estimates given by various authors [13,14] differ by a factor of 7, namely $l^N \approx (3$—$0.4)T^{-4}$ cm, it can be estimated that at $T \approx 2.7°K$, which corresponds to the maximum $l_{eff}$ in [3], we have a ratio $d/l^N \approx 10$—$60$ for a sample of 0.5 cm diameter, and this ratio is decreased by a factor 16 when the temperature is lowered to 1.3°K, that is to say, if one neglects the possible scattering by impurities, structure defects, and carriers, then a transition phonon-gas flow should appear in samples of diameter $d \leq 0.5$ cm, and one should observe the Knudsen minimum in $l_{eff}$ at temperatures $\sim 1°K$.

The experimental investigations were carried out at $T \geq 1.3°K$, and the accuracy of the calculation of $l_{eff}$ is low, inasmuch as the qualitative estimates of [3] took no account of the difference between the phonon and total thermal conductivity (the values of $l_{eff}$ at 1.3°K should be decreased by 10—15%, i.e., the slopes of the $l_{eff}(T)$ curves are somewhat steeper than those given in Fig. 2 of [3]). Therefore the experimental data alone do not make it possible to identify the mechanisms (scattering by carriers or by structure defects [15] and impurities) that limit the growth of $l_{eff}$ near the maximum. A comparison of the results of the calculations and experiments and the subsequent discussion will be continued in Sec. 4.

## 3. CALCULATION OF THE INFLUENCE OF PHONON-CARRIER INTERACTION ON HEAT TRANSPORT BY THE PHONON SYSTEM

The need for taking into account the interaction of the phonons with the carriers is evidenced by the observations of oscillations of the phonon thermal conductivity of bismuth in strong transverse magnetic fields [1]; the amplitude of the oscillations in fields $\lesssim 10$ kOe amounts to several percent of the total thermal conductivity at

1.5–2°K. So far, however, this question has never been investigated.

## 1. Thermal-conductivity Tensor

The thermal-conductivity tensor $\kappa_{ik}$ can be calculated in only two cases: a) in the Zeeman limit $l^N = 0$, and b) at $l^N = \infty$. To eliminate the divergences in the thermal conductivity it is necessary to take into account the diffuse scattering of the phonons from the surface of a sample of given diameter d. In the intermediate case, an important role is played by the particular form of the phonon-phonon collision integral.

We derive the corresponding formulas with allowance for the anisotropy of the crystal structure of the bismuth [16]. The kinetic equation for the distribution function

$$\tilde{N}_q = N_q - \frac{\partial N_q}{\partial \hbar\omega_q}\psi_q$$

($N_q$ is the equilibrium distribution) takes the form

$$\left(-\frac{\partial N_q}{\partial \hbar\omega_q}\right)\mathbf{v}\left(\frac{\hbar\omega_q}{T}\nabla T + \nabla\psi_q\right) = I_q + \nu(\mathbf{q})\frac{\partial N_q}{\partial \hbar\omega_q}\psi_q, \qquad (5)$$

where $I_q$ is the normal-collision integral, $\nu(\mathbf{q})$ is the frequency of the collisions of a phonon with momentum $\mathbf{q}$ with the carriers, and $\mathbf{v} = \partial\hbar\omega_q/\partial\mathbf{q}$.

a) $l^N = 0$. It is possible to omit the term with $\nabla\psi_q$ from Eq. (5). To solve this equation we use a method of successive approximations [4]. In the zeroth approximation we have

$$\psi_q = \mathbf{q}\mathbf{u},$$

where the drift velocity $\mathbf{u}$ does not depend on $\mathbf{q}$ and on the polarization, and is determined from the momentum conservation law

$$\sum\int \mathbf{q} I_q d^3q = 0$$

(the summation is over the phonon polarizations). For the components of the vector $\mathbf{u}$ we obtain

$$u_i = -S_{ph}(\nabla T)_i / \langle q_i^2 \nu(\mathbf{q})\rangle, \qquad (6)$$

where $S_{ph}$ is the specific entropy of the phonon gas,

$$\langle F(\mathbf{q})\rangle \equiv \sum\int \frac{d^3q}{(2\pi\hbar)^3}\left(-\frac{\partial N_q}{\partial \hbar\omega_q}\right)F(\mathbf{q}).$$

We choose a coordinate system consisting of the binary (X), bisector (Y), and trigonal (Z) axis of the crystal. Calculating the heat flux

$$\mathbf{Q} \equiv \left\langle \hbar\omega_q \frac{\partial \hbar\omega_q}{\partial \mathbf{q}}\psi_q \right\rangle = S_{ph} T \mathbf{u}, \qquad (7)$$

we obtain the components of the thermal-conductivity tensor:

$$\varkappa_{ik} = T S_{ph}^2 / \langle q_i^2 \nu(\mathbf{q})\rangle. \qquad (8)$$

b) $l^N = \infty$. The solution of Eq. (5) without $I_q$ for pure diffuse reflection from the boundaries takes the form [5]

$$\psi_q = -\frac{\hbar\omega_q}{T\nu(\mathbf{q})}\mathbf{v}\nabla T[1-\exp(-\nu(\mathbf{q})t)], \qquad (9)$$

where t is the time elapsed since the last collision of the phonon with the wall. If we denote by $\mathbf{v}_s$ the projection of $\mathbf{v}$ on the cross section plane and chose the axes $\xi \parallel \mathbf{v}_s$ and $\eta \perp \mathbf{v}_s$ in this plane, then we obtain for a cylindrical sample of radius R

$$t = [\xi + (R^2-\eta^2)^{1/2}]/|\mathbf{v}_s|. \qquad (10)$$

Calculating the heat flux and averaging it over the cross section, we obtain

$$\varkappa_{ik} = \frac{1}{T}\left\langle \frac{(\hbar\omega_q)^2}{\nu(\mathbf{q})} v_i v_k [1-\beta(z)] \right\rangle, \qquad (11)$$

$$\beta(z) = \frac{4}{\pi}\int_0^1 (1-x^2)^{1/2} e^{-zx}\,dx, \quad z = \frac{2R\nu(\mathbf{q})}{|\mathbf{v}_s|}. \qquad (12)$$

We note that, owing to the presence of the boundaries, the quantity $\kappa_{ik}$ in (11) is not a tensor, for physical properties of the sample are altered when the crystal axes are rotated relative to the boundaries. Consequently, the components $\kappa_{xx}$ and $\kappa_{yy}$ are independent (in a bulky sample we have $\kappa_{xx} = \kappa_{yy}$, inasmuch as z is a threefold axis.

## 2. Phonon-electron Collision Frequency

Bismuth has a strongly anisotropic Fermi surface, the dimensions of which are of the order of the momentum of the thermal phonon at helium temperature. In addition, the carrier dispersion law is not quadratic. These factors greatly influence the character and intensity of the phonon-electron scattering, as will be seen from the formula derived below for the collision frequency.

The frequency of the collisions between a phonon of given polarization and carriers belonging to one valley is conveniently expressed in the form

$$\nu(\mathbf{q}) = \frac{\pi(\mathbf{e}\hat{C}\mathbf{q})^2}{\hbar^2 D\omega_q(N_q+1)}\int_0^\infty f(\varepsilon)[1-f(\varepsilon+\hbar\omega_q)]\chi_q(\varepsilon)\,d\varepsilon, \qquad (13)$$

where $\omega_q$ and $\mathbf{e}$ are the frequency and polarization vector of the phonon with momentum $\mathbf{q}$, $\hat{C}$ is the deformation-potential tensor, D is the density of the crystal, $f(\epsilon)$ is the Fermi distribution, and

$$\chi_q(\varepsilon) = \int \delta(\varepsilon-\varepsilon_p)\delta(\varepsilon_{p+q}-\varepsilon_p-\hbar\omega_q)\frac{2d^3p}{(2\pi\hbar)^3}. \qquad (14)$$

The carrier dispersion $\epsilon_p$ is determined from the equation

$$E(\varepsilon_p) \equiv \varepsilon_p\left(1+\frac{\varepsilon_p}{\varepsilon_g}\right) = \frac{1}{2m_0}\mathbf{p}\hat{\alpha}\mathbf{p}, \qquad (15)$$

where $m_0$ is the mass of the free electron, $\epsilon_g$ is the magnitude of the gap, and $\hat{\alpha}/m_0$ is the reciprocal-mass tensor.

The integration in (14) can be easily carried out after changing over to the proper axes of the tensor $\hat{\alpha}$:

$$\chi_q(\varepsilon) = \frac{3n|E'(\varepsilon)|^2}{8(E^3(\varepsilon_F)E(\varepsilon_q))^{1/2}}\theta[E(\varepsilon)-E(\varepsilon_0)], \qquad (16)$$

where n is the carrier density in the valley, $\epsilon_F$ is the Fermi energy,

$$E(\varepsilon_0) = \frac{1}{4E(\varepsilon_q)}[E(\varepsilon_q)-E'(\varepsilon_0)\hbar\omega_q]^2, \qquad (17)$$

$$\theta(x) = \begin{cases} 1 & (x>0) \\ 0 & (x<0) \end{cases}.$$

Substituting (16) in (13) and taking the slowly varying factor $|E'(\epsilon)|^2$ outside the integral sign at $\epsilon = \epsilon_F$, we obtain after integration

$$\nu(\mathbf{q}) = \frac{3\pi n|E'(\varepsilon_F)|^2(\mathbf{e}\hat{C}\mathbf{q})^2}{8\hbar D(E^3(\varepsilon_F)E(\varepsilon_q))^{1/2}}\left[1-\frac{kT}{\hbar\omega_q}\ln\frac{\exp[(\varepsilon_0-\varepsilon_F+\hbar\omega_q)/kT]+1}{\exp[(\varepsilon_0-\varepsilon_F)/kT]+1}\right] \qquad (18)$$

In the case of a quadratic isotropic dispersion, this formula agrees with the Zeeman formula [17].

Under conditions of Fermi degeneracy, the expression

Fermi-surface parameters and deformation potential of bismuth

| | $n$, $10^{17}$ cm$^{-3}$ | $\epsilon_F$, MeV | $\epsilon_g$, MeV | $\alpha_{xx}$ | $\alpha_{yy}$ | $\alpha_{zz}$ | $\alpha_{yz}$ | $\hat{C}_{xx}$, eV | $\hat{C}_{yy}$, eV | $\hat{C}_{zz}$, eV | $\hat{C}_{yz}$, eV |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Electrons | 0.92 | 27.6 | 15.3 | 924 | 9.75 | 397 | −49.2 | 2.24 | −5.6 | 1.68 | −1.4 |
| Holes | 2.75 | 10.9 | ∞ | 15.62 | 15.62 | 1.45 | 0 | 1.16 | 1.16 | −1.2 | 0 |
| References | [20] | | [21] | [22] | | | | [23, 24] | | | |

Notation: n—carrier density per valley, $\epsilon_F$—Fermi energy, $\epsilon_g$—energy gap, $\alpha_{ik}/m_0$—reciprocal-mass tensor, $m_0$—free-electron mass, $\hat{C}_{ik}$—deformation-potential tensor.

in the square brackets in (18) can be replaced by the step function

$$\theta(\varepsilon_F-\varepsilon_0)\equiv\theta[E(\varepsilon_F)-E(\varepsilon_0)]\approx\theta[E(\varepsilon_F)-{}^1/_4E(\varepsilon_q)].$$

We introduce the notation

$$B=\frac{3\pi n}{8\hbar D}\left[\frac{E'(\varepsilon_F)}{E(\varepsilon_F)}\right]^2,\quad v_\omega(\mathbf{n})=\left(\frac{2m_0E(\varepsilon_F)}{\mathbf{n}\hat{\alpha}\mathbf{n}}\right)^{1/2},\quad \mathbf{n}=\frac{\mathbf{q}}{q}. \tag{19}$$

As a result, (18) takes the form

$$\nu(\mathbf{q})=Bqp_F(\mathbf{n})\,(e\hat{C}\mathbf{n})^2\theta[2p_F(\mathbf{n})-q]. \tag{20}$$

It is seen from (20) that the only phonons that are scattered are those whose momenta do not exceed in absolute magnitude the diameter of the Fermi surface in the **n** direction.

## 3. Numerical Calculations

The phonon spectrum of bismuth can be described, with accuracy 15%, by the formula [18,19]

$$\hbar\omega_{\mathbf{q}}=s(q_x^2+q_y^2+rq_z^2)^{1/2}. \tag{21}$$

The parameters s and r and the polarization vectors take the following form, in the transverse mode $t_1$, $s = 1.5\times10^5$ cm/sec, r = 0.58,

$$e_x=-n_y/n_\perp,\quad e_y=n_x/n_\perp,\quad e_z=0;$$

in the quasitransverse mode $t_2$, $s = 1.1\times10^5$ cm/sec, r = 1

$$e_x=-n_xn_z/n_\perp k,\quad e_y=-n_yn_z/n_\perp k,\quad e_z=(1+f)^{1/2}n_\perp/k;$$

in the quasilongitudinal mode $l$, $s = 2.6\times10^5$ cm/sec, r = 0.59,

$$e_x=(1+f)^{1/2}n_x/k,\quad e_y=(1+f)^{1/2}n_y/k,\quad e_z=n_z/k,$$

where

$$n_\perp=(n_x^2+n_y^2)^{1/2},\quad k=(1+fn_\perp^2)^{1/2},$$
$$f=(c_{11}-c_{33})/(c_{33}-c_{44})=1.03,$$

$c_{ik}$ are the elastic constants, and s and r are the parameters of the phonon spectrum (see (21)).

The table lists the values of the Fermi-surface parameters and the components of the deformation-potential tensor. The electron Fermi surface consists of three equivalent valleys, therefore the table lists the values of the components of $\hat{\alpha}$ and $\hat{C}$ for one valley, for which one of the principal axes coincides with the X axis.

We define the phonon effective mean free path by the relation

$$l_{ii}=\varkappa_{ii}/S_{ph}\bar{s},$$

where $\bar{s} = 1.1\times10^5$ cm/sec. Numerical calculations of $\kappa_{ii}$ were carried out with the BÉSM-6 computer in accordance with formula (8) for the case $l^N = 0$, and in accordance with formulas (11) and (12) for the case $l^N = \infty$. The function $\beta(z)$ (see (12)) was approximated by the expression

$$\beta(z)=\frac{az+b}{z^2+cz+b}, \tag{12'}$$

where $a = 4/\pi$, $b = 5$, and $c = 8(1 + b/3)$. This approximation introduces an error less than 5%. The integration with respect to **q** was carried out by the Gauss method. The results of the calculations are given in Fig. 2.

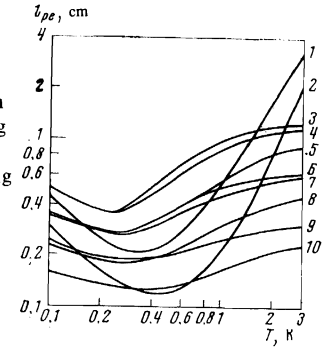


FIG. 2. Dependence of the effective length $l_{pe}$ on the temperature with account taken of the phonon scattering by the carriers in two limiting cases: a) $l^N \equiv 0$, $d\to\infty$: 1—sample oriented along X axis, 2—along Z axis; b) $l^N\to\infty$: 3, 4, 5—d = 1.0 cm (sample oriented along X, Y, and Z, respectively); 6, 7, 8—the same for d = 0.9 cm; 9, 10—d = 0.26 cm (X and Z axes).

If the normal phonon-phonon collisions were to be neglected, allowance for phonon scattering by the carriers only would lead to an infinite thermal conductivity at $T > 0.5$°K, since the characteristic momenta of the thermal phonons $q_T$ in bismuth at helium temperatures can exceed the characteristic dimensions of the electron and hole Fermi surfaces $2p_F$ (thus, at 1°K we have $q_T \approx 10\times10^{-22}$ g-cm/sec, and $p_F = 5\times10^{-22}$ and $15\times10^{-22}$ g-cm/sec for the electrons and holes, respectively). Therefore, by virtue of the conservation laws, only long-wave phonons corresponding to temperatures $\lesssim 1$°K can interact with the carriers. Allowance for diffuse scattering of the phonons from the surface of a sample with finite dimensions leads, naturally, to a finite thermal conductivity, the value of which depends on the dimensions of the sample and on the conditions of scattering from the surface. These circumstances must be taken into account also when calculating, for example, the phonon-drag thermoelectric power in bismuth at low temperatures.

In the opposite case, at $l^N = 0$, the finite thermal resistance in an infinite sample is due to the scattering of the phonons by the carriers (the mutual-dragging effects call for a special investigation and are not considered here), since frequent normal collisions between the phonons make it possible to transfer the total momentum from the phonon system to the carrier system, even though only the long-wave phonons interact with the latter. (A similar situation arises also in the solution of the problem of the behavior of the phonon-drag thermoelectric power in semiconductors with a small number of carriers [25].)

On all curves, a minimum is observed at $T \approx 0.2$–$0.5$°K and corresponds to a transition from $q_T < 2p_F$ to $q_T > 2p_F$. The possible existence of such a minimum in the thermal conductivity of semiconductors was first pointed out by Zeeman [5]. At temperatures below the minimum, phonon scattering by carriers in bismuth is analogous to scattering in a typical metal.

## 4. COMPARISON WITH EXPERIMENT; TEMPERATURE DEPENDENCE OF $l_{eff}$ AT TEMPERATURES BELOW 1.5° K

For convenience in comparison, Fig. 3 shows the experimental curves describing a plot of $l_{eff}(T)$ for one of

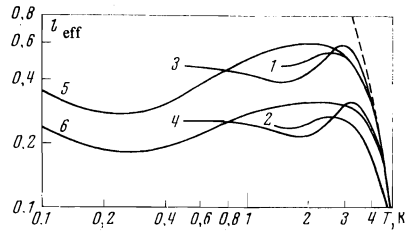


FIG. 3. Comparison of the experimental data with the calculated ones. Curves 1, 2—experimentally measured plots of $l_{eff}$ for sample Bi-4 of diameter d = 0.48 and d = 0.26 cm from [3]; curves 3, 4—plots of $l_{eff}$ calculated from the plots of Fig. 1 for the same diameters; $l^N = 3T^{-4}$, and $l^R$ is determined from the continuation of the high-temperature branch of the experimental $l_{eff}$ curve (the interaction with the carriers is disregarded); curves 5, 6—plots of $l_{eff} = l_{pe}$ neglecting the normal collisions between the phonons (correspond to curves 6 and 9 in Fig. 2; it is natural to expect $l_{eff} \approx l_{pe}$ at $T < 1°K$) (the calculation was carried out for the case when $\nabla T$ is parallel to the X axis).

the samples [3] at d = 0.48 cm (curve 1) and d = 0.26 cm (curve 2), and also the calculated plots for the same diameters without allowance for the inelastic scattering of the phonons by the defects or by the carriers (curves 3 and 4) and with allowance for scattering only by carriers and by the surface of the sample (curves 5 and 6). When plotting curves 3 and 4 it was assumed that the only inelastic-scattering mechanism in the volume is that of inelastic phonon-phonon collisions (U-processes), the effective mean free path $l^U$ of which can be easily calculated from the exponential branch of the experimental $l_{eff}(T)$ curve, and that $l^N = 3T^{-4}$ cm. [13] The value of $l_{eff}$ was determined from the plots of Fig. 1 using the calculated values of $d/l^N$ and $l^U/l^N$ at the given temperature. Curves 5 and 6 are the results of the calculation of $l_{pe}$ for the given dimensions under the condition $l^N \to \infty$ (Fig. 2), since we are interested mainly in the prediction of the behavior of $l_{eff}$ at temperatures below 1.5°K, where $d/l^N < 1$.

It is seen from a comparison of curves 1, 2 with 3, 4 that the values and temperature dependences of the experimentally obtained lengths $l_{eff}(T)$ are smaller than those calculated neglecting scattering by carriers and structure defects. Unfortunately, the accuracy of the experimental measurements is insufficient to be able to determine, from the experimental curves and from the plots of Fig. 1, the temperature dependence of the length $l^R$ due to the additional scattering of the phonons in the volume. The value of $l^R$ is several times larger than the maximum diameter, namely, $l^R \approx 2$ cm at 2°K. This resistance is attributed in [3] to the appearance of the interaction of phonons with carriers under conditions of hydrodynamic flow of the phonon gas. A numerical calculation of $l_{pe}$ with allowance for the real ratio $d/l^N \approx 10$ would require excessively long computer time, but a comparison of this estimate with the results given in Sec. 3 (in the limit $l^N = 0$ and $d \to \infty$ we have $l_{pe} \approx 1$ cm at 2°K), and also with the experimental data (oscillations of the thermal conductivity in strong transverse magnetic fields [1], damping of the thermal momenta at 1.5°K [13], the behavior of the phonon-drag thermoelectric power [3]) confirms the validity of this assumption. Thus, in perfect bismuth samples with diameter $\lesssim 1$ cm, in the interval 2—2.7°K, the thermal resistance is due mainly to phonon scattering by the surface; the relatively weaker scattering of the phonons by the carriers prevents a considerable increase of $l_{eff}$ from being produced by the frequent normal collisions of the phonons in the volume.

In the phonon system, the N processes play here a twofold role: on the one hand they lead to a redistribution of the momenta in the phonon system and by the same token increase the probability of phonon scattering by the carriers (this is clearly seen from Fig. 2, which shows the calculations of $l_{pe}$ in the limiting cases $l^N \to 0$ and $l^N \to \infty$); on the other hand, they increase the effective phonon mean free path as a result of the appearance of hydrodynamic flow of the phonon gas. At lower temperatures we have $d/l^N \sim 1$, and in the absence of carriers one should expect the appearance of the Knudsen minimum on the $l_{eff}(T)$ curve at the temperature $\sim 1.5°K$ (curves 3 and 4), followed by an increase to $l_{eff} = d$. If account is taken of the phonon-carrier scattering, the role of which greatly increases with decreasing temperature, especially at temperatures $\leq 1°K$, then $l_{eff}$ should practically coincide with $l_{pe}$ (curves 5, 6) when the temperature decreases to $T < 1°K$, where the contributions of the phonon scattering by the sample surface and by the carriers are close in magnitude. As a result, when the temperature drops below 1°K one should expect the phonon effective mean free path, which determines the magnitude and character of the temperature dependence of the lattice thermal conductivity, to decrease, to reach a minimum at $T \lesssim 0.5°K$, and then again to increase to $l_{eff} \approx d$ (the Knudsen limit).

## 5. CONCLUSION

As seen from a comparison of the results of the calculations with the experimental data, the existing information on the properties of the phonon and electron systems in bismuth is perfectly sufficient to be able to obtain, without any fit parameters, results that agree closely with the experimental observations, and to estimate the role of the different mechanisms of the phonon relaxation at lower temperatures. Computer simulation of the heat transport processes in a dielectric crystal has made it possible not only to refine the conditions under which the hydrodynamic transport mechanism manifests itself, but also to calculate the behavior of the system in the transition regime, to predict the existence of a Knudsen minimum on going from the Poiseuille flow to the Knudsen flow of the phonon gas, and the depth of the minimum.[2)] With increasing chemical purity and perfection of the crystal structure, in samples with $\sim 1$ cm diameter, at a point-defect concentration $\leq 10^{-5}\%$, the hydrodynamic situation can arise in most dielectrics (at least those with a Debye temperature $\lesssim 100°K$), so that this calculation is also of independent significance.

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[1)] By elastic (or inelastic) scattering we mean here and throughout processes in which the total quasimomentum of the phonon system is conserved (or is not conserved).

[2)] The possibility of the appearance of a Knudsen minimum on the $l_{eff}(T)$ curves in crystals of $He^4$ was pointed out to one of us by Yu. M. Kagan in a discussion of the experiments of [6].

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