Investigation of the kinetic coefficients of bismuth at helium temperatures

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The thermal conductivity κ, electric conductivity σ, and thermo-emf α of perfect $[\rho(300°K)/\rho(4.2°K) \approx 650–680]$ massive bismuth crystals with characteristic dimensions $d \lesssim 0.6$ cm and length $l \approx 6$ cm are investigated between 1.3 and 7°K. It is shown that the magnitude and temperature dependences of the kinetic coefficients depend essentially on the characteristic dimensions of the sample and on the quality of its surface. A $\kappa(T)$ dependence stronger than cubic and observed at temperatures below the thermal conductivity maximum can be attributed to the appearance of a hydrodynamic situation in the phonon system evoked by frequent normal collisions between phonons. Thermo-emf measurements in massive and sufficiently perfect crystals show that $\alpha(T)$ grows exponentially with diminishing temperature, in analogy with $\kappa(T)$. This indicates the appearance of a new drag mechanism, viz., phonon-phonon carrier drag produced as a result of frequent normal collisions between phonons at temperatures for which the exponentially increasing thermal phonon drift velocity becomes comparable to the drift velocity of long-wave phonons interacting with the carriers. The dependence of the electric resistance of bismuth on temperature and sample size may be expressed by the formula $\rho = \rho_0(d) + \rho(T)$; the first term rapidly increases with decrease of d and then levels out; the second term weakly depends on the size. A discussion of the dependence $\rho(d)$ observed is carried out within the framework of the diffusion size-effect theory.

1. INTRODUCTION

Transport processes in bismuth are being extensively investigated in various laboratories. The great interest in its properties is quite understandable. Bismuth is a semimetal with small free-carrier density ($\sim 10^{-5}$ per atom) and has a low Debye temperature ($\sim 120°$ K); there is no isotopic scattering in it, and the chemical purity of the experimental batches is quite high ($\sim 10^{-4}$% of impurities in accordance with the official specifications). All this makes it possible to investigate the excitation relaxation processes in the phonon and electron systems and to study thoroughly the character of the interaction between them.

The electronic properties of bismuth at low temperatures have been investigated in sufficient detail[1]. At the same time, characteristics of practical importance such as the thermal conductivity, the electric conductivity, and the thermoelectric power of bismuth crystals at temperatures below 4.2° K have been less investigated both experimentally and theoretically.

Thus, the thermal conductivity κ was investigated at helium temperatures in samples of approximately equal dimensions (cross section area $S \lesssim 0.1$ cm^2) and approximately equal quality[2-5] (a detailed review of the results of these investigations is given in[6]); it was shown that at $T < 20°$K the principal role in the thermal conductivity of bismuth is played by phonons. The contribution of the electronic component, down to 1.3° K, does not exceed several percent, and the temperature dependence of $\kappa(T)$ is close to that observed in typical dielectrics.

However, the study of the thermal conductivity of bismuth at helium temperatures cannot be regarded as complete. In fact, the following problems are encountered:

1) The effective phonon mean free path l^{eff} at the lowest temperatures, calculated from the measured thermal conductivity of the better samples, turned out to be several times smaller than the characteristic dimensions of the samples, and no direct data have been obtained on the effect of the dimensions on the sample thermal conductivity.

2) The oscillations of $\kappa(H)$ in strong transverse magnetic fields indicate that phonon-electron scattering affects the thermal conductivity of bismuth at temperatures below $T_{\kappa\,\text{max}}$.

3) The mean free path in normal phonon-phonon collisions is $l^{\text{n}} \ll d$ at $T \approx T_{\kappa\text{max}}$, as follows from the estimates given in[3]. In such a situation, Poiseuil flow of the phonon gas can occur in a sufficiently pure and bulky dielectric sample, and can lead to an appreciable increase of the thermal conductivity and to a change of its temperature dependence at temperatures below the maximum of the thermal conductivity[7-10]; that is to say, if the phonon-electron interaction is small, one should expect the appearance of a hydrodynamic mechanism in the thermal conductivity of perfect bismuth samples with characteristic dimensions of the order of 1 cm.

A number of questions arise also in the study of the thermoelectric power α due to phonon dragging and of the electric conductivity κ of bismuth at helium temperatures. For example, in[11], in an estimate of the maximum of α, it was assumed that the phonon mean free path is limited by phonon scattering from carriers and not from the sample boundaries. Although for some orientations the obtained values of α_{max} were close to the experimentally observed ones, for other orientations they differed even in sign[12].

The nature of the size effect in the electric conductivity of bismuth, which is observed in high-grade samples as well as in samples with defects, remains unclear.

To solve these problems it is necessary to investigate experimentally the influence of the dimensions, of the quality of the crystal structure, and of the surface properties on the kinetic coefficients of sufficiently perfect bulky bismuth samples. Preliminary measurements performed by us on different samples with characteristic dimensions 0.25 and 0.6 cm in the temperature interval

1.3–7° K have shown that the dimensions of the samples and the quality of the crystal structure have a significant effect on the values and temperature dependences of κ, α, and σ[13,14]. As a result of the strong anisotropy of the bismuth properties, however, it is difficult to obtain quantitative estimates from measurements performed on different samples; it was therefore necessary to develop a procedure for obtaining perfect samples and for measuring the influence of the dimensions and the surface quality on the properties of one and the same sample.

The results reported here were obtained with samples grown by zone melting of free standing cylindrical blanks in deep vacuum (~ 10^{-6} Torr). (The sample preparation procedure will be described in detail separately.) The sample dimensions were decreased during the course of the investigations by etching in concentrated nitric acid. The initial sample was oval in cross section with characteristic dimensions 0.4 × 0.6 cm and length $l \approx 6$ cm, and had a mirror-smooth surface. The first etching removed a thin surface layer (the cross-section area changed by less than 5%). The surface then became dull in appearance and revealed readily crystal facets that made it possible to assess the single-crystal character of the sample.

That the initial samples were of high grade is evidenced by the ratio of the resistances measured at room and helium temperatures: $\gamma = \rho(300°\,\mathrm{K})/(4.2°\,\mathrm{K}) \approx 650$–$680$ (correspondingly $\rho(300°\,\mathrm{K})/\rho(T \to 0) \gtrsim 2000$).

The sample was placed on an insulating substrate inside a vacuum chamber in a cryostat. The carbon thermometers, the current and potential leads, the heaters, and the copper cold finger were soldered to the sample with easy-melting solder. The thermometers and the potential contacts were placed in the central part, at distances ~2 cm from the ends of the sample. When the heaters and thermometers were mounted, the sample was placed horizontally on an insulating substrate made of a segment of thin-wall stainless tube and covered with a thin layer of epoxy resin. To prevent thermal shock due to soldering, the sample, and the substrate were smoothly heated to a temperature close to the melting point of Wood's alloy. As shown by control measurements, the results obtained by repeated soldering were reproducible, i.e., accurate soldering did not affect the sample quality significantly.

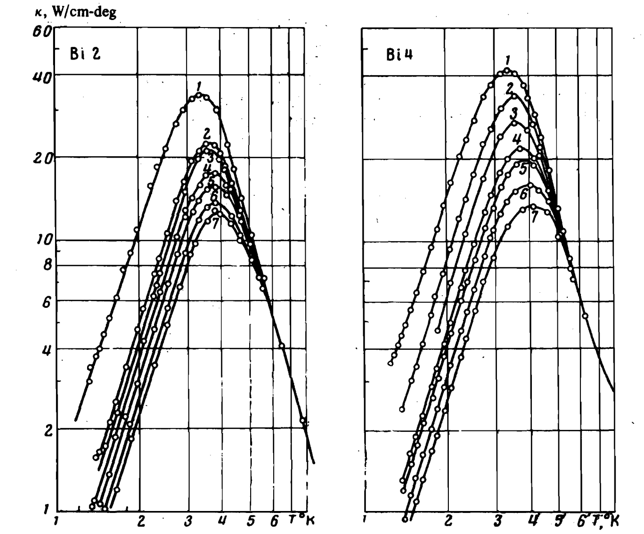

FIG. 1. Dependence of the thermal conductivity of perfect samples on the temperature and on the characteristic dimensions. Sample Bi2: C_3 axis inclined ~45° to the sample axis, Curve 1–initial sample, d = 0.51 cm; 2–after light etching of the surface, same dimensions; 3–d = 0.45 cm; 4–d = 0.39 cm; 5–d = 0.33 cm; 6–d = 0.30 cm; 7–d = 0.26 cm. Sample Bi4: the orientation differs somewhat from the orientation of Bi2; curve 1–initial sample; d = 0.48 cm; 2–after light etching of the surface; 3–d = 0.37 cm; 4–d = 0.34 cm; 5–d = 0.27 cm; 6–d = 0.19 cm; 7–d = 0.15 cm.

The measurements were performed by a standard method using an R-308 potentiometer. The thermometer calibration curves were calculated by least squares with a computer[15]. Below 4.2° K, the thermometers were calibrated against He^4 vapor pressure. To establish the temperature scale above 4.2° K, we used the superconducting transition point of pure lead. The temperature drop along the sample usually amounted to ~0.01° K, so that the error in the measurement of ΔT did not exceed 2%. The current flowing through the sample during the resistance measurement was 100–300 mA, and the accuracy with which ρ was measured at the lowest temperature was ~ 4% and increased with increasing temperature and with decreasing sample cross section. The external magnetic field did not exceed $\lesssim 0.3$ Oe and its influence on the properties of the samples was neglected in this study.

2. THERMAL CONDUCTIVITY

As indicated in the review[6], the thermal conductivity of the better of the previously investigated samples reached a maximum with decreasing temperature at $T \approx 3.6$–$4.2°$ K ($\kappa_{\max} \approx 15$–20 W/cm-deg), and then decreased in nearly cubic fashion, like $T^{2.7 \pm 0.2}$. The results of the measurements of the thermal conductivity of the two best samples investigated by us, with different orientations, are shown in Fig. 1.

The upper curves correspond to a sample with mirror finish while the curves that follow illustrate the change in the thermal conductivity following removal of a thin surface layer by etching (dull surface). This is followed in turn by the change of the temperature variation of the thermal conductivity of the same sample following a decrease in its characteristic dimensions (the surfaces of all the etched samples were similar in appearance). The thermal conductivity of a perfect bulky sample increases exponentially with decreasing temperature, reaching a maximum at $T \approx 3.4°$ K, beyond which it decreases again. The maximum thermal conductivity ($\kappa_{\max} \approx 40$ W/cm-deg) is double the thermal conductivity of the better of the samples described in the literature[6], and the position of the maximum is shifted towards lower temperatures. Etching of the surface layer leads to a decrease of κ and increases somewhat the slope of the low-temperature branch of the $\kappa(T)$ curve. In the interval 1.5–2.4° K, the $\kappa(T)$ dependence is stronger than cubic and is close to $\kappa \propto T^{3.5 \pm 0.1}$, which agrees qualitatively with the results of[5] and our preliminary observations[7]. After subsequent etching, the value of κ at $T = 1.4°$ K decreases in approximate proportion to the mean diameter d of the sample (defined as $\sqrt{d_1 d_2}$, where d_1 and d_2 are the largest and smallest cross-section diameters), and the position of the maximum shifts towards higher temperatures. (A decrease of d from ~0.5 to 0.1 cm changes the position of the maximum by 0.6° K.)

We have indicated above that in the working interval the thermal conductivity of bismuth is determined mainly by the lattice component. According to our measurements and the data of[5], the contribution of the carriers to the heat transfer is less than 1% at $T \gtrsim 2^\circ$ K and less than 10% at $T \approx 1.3^\circ$ K. Thus, the phonon conductivity at $T \gtrsim 2^\circ$ K practically coincides with the total measured conductivity, and below 2° K, after subtracting the electronic thermal conductivity, the low-temperature branch of the phonon conductivity is steeper than that shown in Fig. 1.

Neglecting in the qualitative treatment the difference between the phonon and total thermal conductivity, it is convenient to examine the behavior of the effective phonon mean free path l^{eff}, determined from the kinetic relation $\kappa = (1/3)\mathrm{C}s\, l^{\mathrm{eff}}$, whence

$$l^{\mathrm{eff}} = 3\kappa / Cs, \tag{1}$$

where $C \approx 5.5 \times 10^{-5}\, T^3 [\mathrm{J/cm^3 deg^4}]$ is the phonon specific heat in the Debye approximation and $s \approx 1.1 \times 10^5$ cm/sec is the average speed of sound in bismuth. The plots of l^{eff} for the same samples as before as shown in Fig. 2.

Above 4.5° K, the value of l^{eff} decreases exponentially with increasing temperatures, i.e., the principal role in the thermal conductivity of perfect samples is played by phonon-phonon processes with Umklapp (U-processes), $l^{\mathrm{U}} \approx 6.3 \times 10^{-5} \mathrm{E}^{33/T}$ [cm] for sample Bi^2 and $l^{\mathrm{U}} \approx 5 \times 10^{-5} \mathrm{E}^{40/T}$ [cm] for Bi4, and is practically independent of the sample dimensions. Below 4° K, the magnitude and temperature dependence of l^{eff} is noticeably influenced by the change of the sample dimensions and of its surface quality (Fig. 3). For example, at the lowest temperatures we have $l^{\mathrm{eff}} \approx 0.7$ and 0.9 cm for the initial samples with characteristic dimensions $d \approx 0.51$ and 0.48 cm, respectively, and decreases to 0.3 and 0.45 cm after light etching of the surface layer.

The decrease of l^{eff} to less than one-half following light etching of the mirror surface can be naturally attributed to the decrease of the degree of specular scattering of the phonons by the boundary. The coefficient p of specular scattering of the phonons by the boundary can be estimated from the simple relation[16]

$$l^{\mathrm{eff}}_{\mathrm{spec}} = l^{\mathrm{eff}}_{\mathrm{diff}} \frac{1+p}{1-p}. \tag{2}$$

From this we have for the surface of a bismuth sample grown in vacuum $p \approx 0.3-0.4$ at $T \approx 1.4^\circ$ K. It was assumed in the estimate that the thermal resistance is due to scattering of the phonons by the sample boundary (as is evidenced by the practically linear $l^{\mathrm{eff}}(d)$ dependence for the etched samples), and that etching makes the surface completely diffusing.

As shown by the preliminary investigations[14], in less perfect bismuth crystals phonon scattering by crystal-structure defects can become significant. Thus, introduction of $\sim 10^7\ \mathrm{cm}^{-2}$ dislocations into a sample with the same dimensions would reduce l^{eff} to half its value at the same temperature, and would lead to a weaker dependence of l^{eff} on the characteristic dimensions and on the temperature.

From the plots shown in Fig. 2 it is evident that as the temperature drops l^{eff} reaches a maximum at $T \approx 2.5^\circ$ K, after which it decreases smoothly (in etched samples we have $l^{\mathrm{eff}} \propto T^{0.5 \pm 0.1}$), flattening out at $T \lesssim 1.5^\circ$ K. The presence of a maximum on the $l^{\mathrm{eff}}(T)$ curve distinguishes significantly the behavior of this curve from that observed in less perfect samples[3,4]. To explain this phenomenon, it is useful to determine the relation between different phonon mean free paths and the sample dimensions. The mean free path l^{U}, which is determined by Umklapp processes and governs the behavior of the high temperature branch of the $\kappa(T)$ curve, increases exponentially with decreasing temperature, so that below $T_{\kappa\max}$ we have $l^{\mathrm{U}} \gtrsim d$. The phonon mean free path in normal collisions, l^{N}, can be estimated from the published data at $l^{\mathrm{N}} \approx 0.4T^{-4}$ [cm][3] or $l^{\mathrm{N}} \approx 3T^{-4}$ [cm][17]. In either variant, at $T \gtrsim 2.5^\circ$ K the mean free path l^{N} is much smaller than d and becomes comparable with the characteristic dimensions of the sample at $T \approx 1-1.5^\circ$ K. This means that at $T \sim T_{\kappa\max}$ the hydrodynamic situation is in the phonon system[8] is described by

$$l^{N} \ll d < l^{U} \tag{3}$$

and frequent normal phonon-phonon collisions can greatly influence the magnitude and temperature dependence of sufficiently perfect and bulky samples in a temperature interval near $T_{\kappa\max}$.

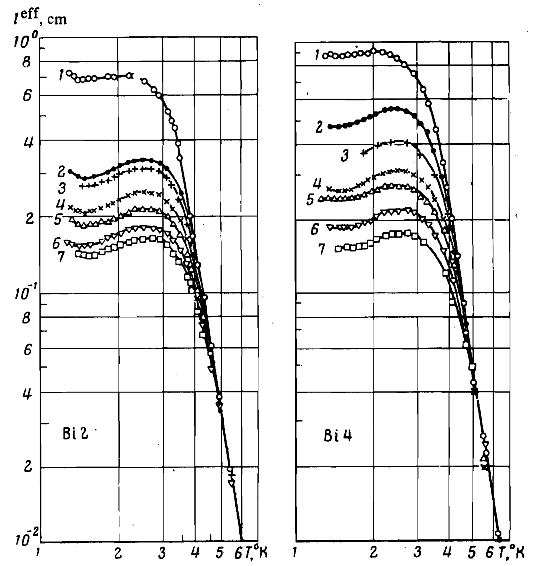

FIG. 2. Influence of dimensions on the effective phonon mean free path; the curve labels are the same as in Fig. 1.

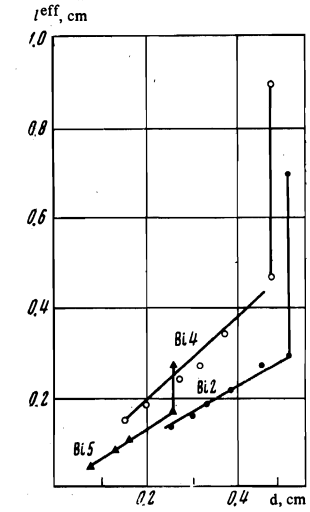

FIG. 3. Dependence of $l^{\mathrm{eff}}(d)$ at T = 1.4°K on the characteristic dimensions for samples Bi2 and Bi4. The plot of $l^{\mathrm{eff}}(d)$ for sample Bi5 with initial d = 0.26 cm is shown for comparison.

In order for Poiseuil flow of the phonon gas to set in, it is necessary and sufficient to satisfy the condition[8]

$$l^{N} \ll d, \quad d^2 / l^{N} \ll l^{R}, \tag{4}$$

where l^{R} is the effective mean free path of the phonons in the volume of the sample without allowance for the N-collisions. If additional volume scattering (l_{pi}) is present besides the phonon-phonon scattering, say by the structure defects, then $(l^R)^{-1} = (l^U)^{-1} + l_{pi}^{-1}$, in accordance with the Mathiessen rule.

When conditions (4) are satisfied we have $l^{eff} = 5d^2/32l^N$, i.e., the effective phonon mean free path can greatly exceed the characteristic dimension of the sample, and its dependence on the dimensions and on the temperature, which is expected for conditions of developed hydrodynamic flow of the phonon gas, takes the form $l^{eff} \propto d^2T^4$[8,9]. When the temperature or the characteristic dimension is appreciably decreased, the first condition of (4) can be violated, and the Poiseuil flow of the phonon gas gives way to a Knudsen flow (at $l^N \gg d$ we get correspondingly $l^{eff} \to d$), which is indeed usually observed in the thermal conductivity of perfect dielectric crystals with characteristic dimensions on the order of several millimeters (so far, the conditions (4) could be satisfied and Poiseuil flow observed in pure form only in perfect solid-helium crystals of diameter $d \approx 0.25$ cm[10]). Unfortunately, the problem of the behavior of $l^{eff}(T)$ in gradual transition from Poiseuil flow to Knudsen flow cannot be solved in general form by the methods used in[8,9], and the method proposed in[9] for numerically integrating the Callaway integrals is based on an arbitrarily chosen switching function describing the decrease of the contribution of the hydrodynamic term to the thermal conductivity with decreasing ratio d/l^N. We hope to calculate numerically the behavior of the thermal conductivity in the transition regime in the general case, but in the present paper, for a qualitative description of the phenomenon, it is convenient to use the modified Mathiessen rule:

$$(l^{eff})^{-1} \approx \left(d + \frac{5}{32}\frac{d^2}{l^N}\right)^{-1} + [(l^U)^{-1} + l_{pi}^{-1}], \tag{5}$$

where the first term describe the contribution of phonon scattering by the sample boundaries and the second describes exchange scattering with loss of quasimomentum.

In the limiting cases $l^N \ll d$ and $l^N \gg d$, expression (5) coincides with the generally accepted formulas.

It is seen from (5) that when the hydrodynamic situation (3) sets in, even volume scattering of the phonons by the crystal-lattice structure or by the carriers, which may be negligible in the Knudsen limit, is capable of greatly altering l^{eff}, i.e., of decreasing noticeably the velocity of the hydrodynamic flow of the phonon gas, owing to viscous losses in the phonon system.

To explain the role of different mechanisms in the thermal conductivity of perfect bismuth crystals at temperatures close to the maximum of thermal conductivity, let us list briefly the presently available experimental facts:

1) The $l^{eff}(T)$ curve has a maximum, thus distinguishing it from the l^{eff} plots of typical perfect dielectrics, in which the free path increases weakly with decreasing temperature at $T < T_{\kappa max}$, and approaches d asymptotically.

2) At $T \approx 2.5°$ K, the conditions (3) are satisfied, with $l^N \propto 1/T^4$ and the free path l^N becoming comparable with d at $T \approx 1-1.5°$ K.

3) The dependence of l^{eff} on the characteristic dimensions of the sample is close to linear at $T = 1.4°$ K, i.e., the principal role in the development of the thermal resistance is played by phonon scattering from the sample boundaries, but the observed oscillations of the lattice thermal conductivity in strong transverse magnetic fields (the oscillation amplitude is of the order of several percent at H = 5 kOe and $T \leq 2°$ K) indicate that it is necessary to take phonon scattering by carriers into account.

The foregoing facts offer evidence that a hydrodynamic situation is produced in perfect bismuth samples at temperatures near the maximum thermal conductivity, but an appreciable increase in the phonon drift by heat flow through the sample is prevented by the additional scattering of the phonons by the carriers.

Using (5), we were able to estimate the effective phonon mean free path l_{pe} for phonon-carrier scattering from the results of the thermal-conductivity measurements, and obtained $l_{pe} \approx 2$ cm at $T = 2°$ K (if we assume in accordance with[17] that $l^N \approx 3T^{-4}$ cm). This estimate will be useful to us later in the discussion of the results of measurements of the thermoelectric power.

The conclusion that a hydrodynamic situation is produced in bulky perfect bismuth crystals, which we have drawn on the basis of the results of the preliminary investigations[7], is confirmed also by recent observations of second sound, i.e., of weakly damped high-frequency temperature waves in perfect crystals[17], for the existence of which it suffices to satisfy the conditions (3).

3. THERMOELECTRIC POWER

The dependence of the thermoelectric power α of samples Bi2 and Bi4 on the temperature, dimensions, and surface quality is illustrated in Figs. 4 and 5.

We see that the thermoelectric power has a maximum at $T \approx 2.2-2.8°$ K. The maximum value of α, the position of the maximum, and the slope of the high-temperature branch of $\alpha(T)$ vary greatly from sample to sample; with decreasing characteristic dimensions and degree of specularity of the surface, the maximum drops (from ~70 μV/deg for large (d = 0.5 cm) perfect samples with partially specular surface to ~20 μV/deg for etched samples with characteristic dimension $d \approx 0.2$ cm), the position of the maximum shifts towards higher temperatures, and the exponential growth of the thermoelectric power gives way to a weaker power-law growth. In the low-temperature region (at $T < T_{\alpha max}$), the temperature dependence of $\alpha(T)$ remains practically unchanged with changing sample dimensions, and stays close to $\alpha \propto T^{1-1.5}$.

After the first etching, α_{max} decreases by almost one-half (Fig. 5). With subsequent etching thermoelectric power first decreases and then increases slightly (at d = 0.32 and 0.28 cm for samples Bi2 and Bi4), and then starts to decrease again.

Let us discuss the temperature dependence of α, as observed in our experiments. The expression for the thermoelectric power due to phonon dragging of carriers of one sign is[18]

$$\alpha = \frac{k}{e}\frac{m^*s^2}{kT}\frac{\tau_p{}^\alpha}{\tau_e{}^p}, \tag{6}$$

where k is Boltzmann's constant, e and m* are the charge and effective mass of the carriers, s is the speed of sound, τ_p^α is the effective relaxation time of the

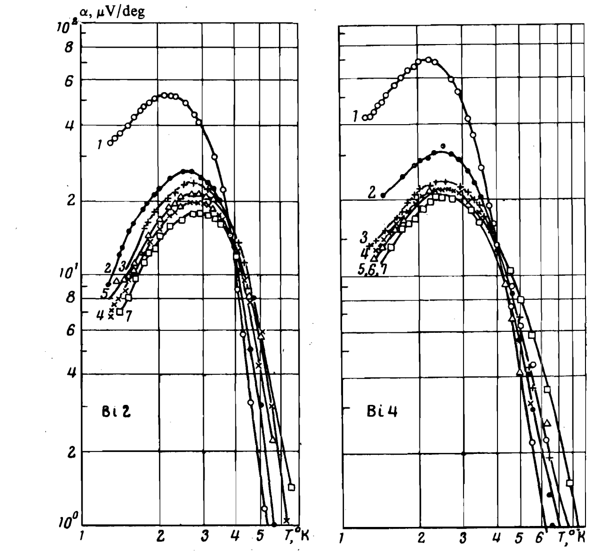

FIG. 4. Effect of the dimensions and of the conditions at the boundary the thermoelectric power of perfect bismuth samples. The curves are labeled as in Fig. 1.

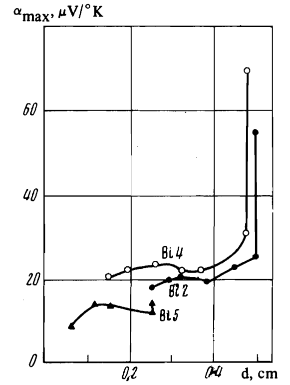

FIG. 5. Dependence of the maximum thermoelectric power on the characteristic dimensions for three bismuth samples.

phonons that determine the dragging, and τ_e^p is the relaxation time for carrier scattering by phonons. In the presence of several groups of carriers, the expression for the total thermoelectric power is

$$\alpha_{\text{tot}}=\sum\alpha_i\sigma_i\Big/\sum\sigma_i, \tag{7}$$

where α_i and σ_i are the partial thermoelectric powers and the conductivities of the individual groups. It is shown in[19] that τ_p^α in (6) should be taken to be the effective relaxation time of the phonons interacting with the carriers. If the characteristic momenta of the thermal phonons q_T greatly exceed the characteristic dimensions $2p_F$ of the Fermi surface, then by virtue of the conservation laws the carriers can interact only with phonons of less-than-thermal velocity (i.e., with longer wavelengths), and τ_p^α can differ noticeably from the thermal-phonon relaxation time that determines the thermal conductivity.

In bismuth, the smallest dimensions of the electron and hole Fermi surfaces are 5×10^{-22} and 15×10^{-22} g-cm/sec, and the characteristic momentum of the thermal phonon is $q_T = 10\times10^{-22}$ g/cm/sec at 1° K. Thus, at $T \gtrsim 1°$ K the phonons in bismuth (just as in semiconductors for which formula (6) is valid) can be conveniently divided into two groups: long-wave (interacting with the carriers) and thermal. The interaction between the groups is effected by the normal collisions. Allowance for his interaction can lead, as will be shown below, to a considerable change of the temperature dependence of α (to the onset of phonon-phonon dragging of the carriers[20]) in comparison with that predicted by the simple model[18] in perfect and sufficiently bulky samples.

A temperature gradient along the sample produces a constant heat flux proportional to the drift velocity v_T of the thermal phonons ($v_T \propto \tau^R$, where τ^R is the thermal-phonon relaxation time), and $\kappa \propto \tau^R$. The thermoelectric power is determined by the drift velocity of the long-wave phonons, which is conveniently represented in the form of the velocity of the group of long-wave phonons relative to the thermal phonons, $v_e \propto \tau_e^{NT}$, and the thermal-phonon velocity v_T. At high temperatures the phonons are scattered in the main by one another; if the relaxation time τ^R is small (low thermal conductivity), the normal collisions between the groups of phonons lead to a loss of the summary quasimomentum of the system of long-wave phonons, i.e., to a decrease of their drift velocity (the drift velocity of the thermal phonons can be neglected), and thermoelectric power is determined by the effective relaxation time τ_e^{NT} in the scattering of long-wave phonons by the thermal phonons in accordance with[19].

In sufficiently perfect and bulky samples, where τ^R increases exponentially with increasing temperature, the drift velocity of the thermal phonons can become comparable with or even exceed the drift velocity of the long-wave phonons (owing to the deceleration of the latter by the carriers). In this case, if the N-collisions between phonons belonging to different groups are frequent, $\tau_p^\alpha = \tau_e^{NT} + \tau^R$, and if the second term is predominant, the customarily observed power-law dependence gives way to an exponential dependence: from (6) it follows that

$$\alpha=\frac{k}{e}\frac{m^*s^2}{kT}\frac{\tau_e^{NT}+\tau^R}{\tau_e^p}. \tag{8}$$

Judging from the thermal conductivity of our samples, the mean free path of the phonons scattered by carriers at 2° K is $l_{pe} \approx 2$ cm. Since only long-wave phonons interact with the carriers, their path length for scattering by carriers is several times smaller than the mean free path, i.e., the long-wave phonons are slowed down appreciably by the carriers.

Thus, the considerable increase of $\alpha_{\max}$ of the samples investigated by us, in comparison with the better of the previously reported ones[12], and the observed change of the temperature dependence of the high-temperature branch of the $\alpha(T)$ curve with decreasing dimensions can be attributed to the appearance of a new mechanism, namely phonon-phonon dragging of the carriers.

The maximum attainable thermoelectric power $\alpha_{\max}$ for samples of given dimensions, and the behavior of $\alpha(T)$ at temperatures below the maximum, are determined by the relation between $\tau_d = d/s$ and the scattering time τ_{pe}^e of the long-wave phonons by the carriers, on the one hand, and the relative contribution of the phonon-phonon mechanism, on the other. If at low temperatures under phonon-phonon dragging conditions the thermal phonons are scattered mainly by the boundaries and the relaxation times of the electrons and holes on the phonons are nearly equal, i.e., $\tau_{ep} \sim \tau_{hp}$ (and in accordance with the data given in the next section we have $\tau_{ep} \propto T^{1.6}$), we have in accordance with (8) $\alpha \propto \tau_p^\alpha / T\tau_{ep} \propto T^{0.6}\tau_p^\alpha$ coincides with the relaxation time that determines the thermal conductivity. Under conditions of developed hydrodynamic phonon-gas flow, this would lead to a strong ($\propto T^{4.6}$) $\alpha(T)$ dependence at temperatures below the maximum of the thermoelectric power, but in our samples, as indicated earlier, $\tau_p \propto T^{0.5}$, i.e., the expected dependence should be somewhat stronger than linear, in qualitative agreement with the results of our experiments.

4. ELECTRIC CONDUCTIVITY

We did not compensate for the earth's magnetic field during the measurements of the electric conductivity, but estimates performed with the aid of Kohler's rule and the experimental data of[5], obtained with samples of nearly equal quality, a field of intensity 0.3 Oe increases the resistance of samples having a resistivity $\gtrsim 0.1$ μΩ-cm by not more than 3–4%, so that the influence of the field can be neglected in a qualitative analysis.

The dependence of the electric resistivity on the temperature and on the characteristic dimensions of the investigated samples is shown in Fig. 6 and 7. We see that when the surface quality changes, and when dimensions are subsequently changed, the resistivity of the samples increases in the entire investigated temperature interval, but the slope of the curves changes little, i.e., the dependence of the resistance on the temperature and on the characteristic dimensions can be represented in the form

$$\rho(d, T) = \rho_0(d) + \rho(T). \tag{9}$$

The temperature dependence of $\rho(T)$ is usually represented analytically in the form $\rho(T) = bT^n$, and the coefficients ρ_0 and b are determined assuming a fixed exponent n. Thus, n = 2 was assumed in[21] and in our paper[14]. In the present paper we determined ρ_0, b, and n from the experimental values of $\rho(d, T)$ by least squares with a computer. For the investigated samples, the minimum rms deviation (~0.5–1%) is obtained at $n = 1.6 \pm 0.1$. Substitution of n = 2 nearly doubles this deviation, i.e., the temperature dependence of the resistivity in the investigated temperature interval is close to

$$\rho = \rho_0 + bT^{1.6\pm0.1}; \tag{10}$$

the mean values of b for samples Bi2, Bi4, and Bi5 are respectively 0.012, 0.013, and 0.015 if ρ is expressed in μΩ-cm. When the characteristic dimensions of samples Bi2 and Bi4 is decreased, the coefficient b increases approximately 10%.

Figure 7 shows the dependence of the conductivity of the characteristics dimensions of the investigated samples at two fixed temperatures. We see that the initial rapid decrease of σ with decreasing dimensions gives way to a slower decrease.

A similar behavior of σ(d) in bismuth was observed in a number of investigations[22–25] of samples that differed from one another both in quality and in orientation. Various mechanisms were proposed to explain the observed dependence[23–25], but the authors themselves admitted that the explanations could not be reconciled with the experimental results even qualitatively.

The most satisfactory description of the observed dependence of the electric conductivity on the dimensions can be obtained, in our opinion, within the framework of the model of the diffusion size effect[26], the gist of which consists in the following.

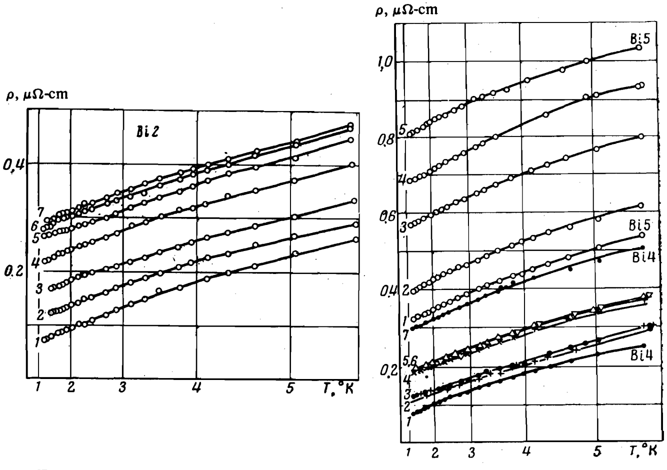

FIG. 6. Effect of sample dimensions on the electric conductivity; the curves are labled as in Fig. 1; curve 1 for Bi5 corresponds to a partially specular surface; the remaining results were obtained with etched samples having average dimensions 0.26 (1), 0.26 (2), 0.16 (3), 0.13 (4), and 0.07 cm (5).

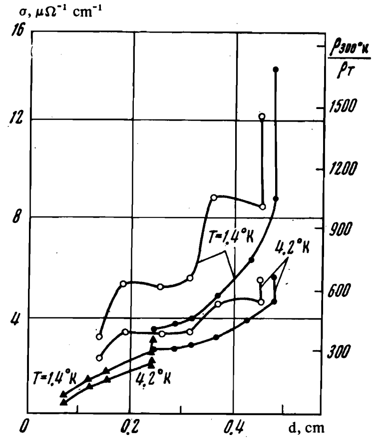

FIG. 7. Dependence of the electric conductivity on the sample dimensions at two temperatures: ●—sample Bi2, ○—Bi4, ▲—Bi5.

In very thin samples, the electric resistance is due mainly to carrier scattering by the crystal surface, i.e., σ ~ d. With increasing characteristic dimensions d, the intervalley collisions of the carriers in the volume of a perfect crystal, with characteristic relaxation time T, may become infrequent ($d \ll v_F T$) while the intravaelley collisions are quite frequent ($l \ll d$). If the probability of the intervalley collisions on the surface is small, then transverse gradients are produced in the concentrations of carriers belonging to different valleys, and as a result the effective conductivity at $l \ll d \ll v_F T$ turns out to be independent of the sample dimensions. With further increase of d, when the carrier trajectory in the sample ($\sim d^2/l$) becomes comparable in length with $v_F T$, the intervalley collisions in the surface lead to a vanishing of the transverse gradients. At $d \gg \sqrt{l v_F T} = L$ the conductivity is obviously independent of the sample dimensions.

Thus, under conditions when the diffusion size effect appears, the dependence of the electric conductivity on the sample dimensions can have two plateaus (at $d \gg L$ and $l \ll d \ll L$). If the conductivities on these plateaus differ strongly, then the σ(d) dependence in the transition region $d \approx L$ may turn out to be quite strong. (In bismuth the ratio of the conductivities on the plateau, according to estimates[28], can reach 25 for certain orientations.)

Allowance for the contribution of the intervalley scattering of the carriers on the surface does not change the value of the conductivity of a sample with large dimensions, but can come strongly into play in the intermediate region $l < d < L$, but the qualitative picture of the behavior of $\sigma(d)$ remains unchanged.

Calculation of the diffusion size effect in bismuth on the basis of the equations obtained in[27] was carried out in[28]. The results obtained in our experiments on the $\sigma(d)$, and also experiments by others, do not permit a detailed quantitative comparison with the calculation of[28], but the observed experimental $\sigma(d)$ agrees qualitatively with the theoretical one.

As seen from the plot (Figs. 6 and 7), the conductivity of the investigated samples decreases strongly after etching a thin surface layer. Within the framework of the diffusion size effect this fact can be attributed either to a decrease of the probability of the intervalley scattering by the surface, or an increase in the diffuseness of the surface relative to the intravalley scattering of the carriers, in the case when the sample dimension d does not greatly exceed l.

5. CONCLUSION

The main results of our investigations are as follows:

1. The thermal conductivity of perfect bismuth samples at temperatures below the maximum is determined mainly by the scattering of phonons by the sample boundaries. An influence of the surface quality on the thermal conductivity of the samples has been observed. The coefficient of specular scattering of phonons by the surface of molten samples is $p \geq 0.3$.

2. The stronger than cubic temperature dependence of the thermal conductivity in this temperature interval is due to the influence of frequent normal collisions between the phonons, which lead to the occurrence of the hydrodynamic situation in the thermal conductivity[8]. The velocity of the hydrodynamic viscous flow of the phonons in bismuth is small in comparison with the velocity observed by us earlier in crystals of solid helium[10], owing to the additional scattering of the phonons by the carriers in the volume of the sample, which increases the viscous loss in the phonon system.

3. The exponential growth of the thermoelectric power due to phonon dragging of the carriers in perfect and sufficiently bulky initial samples, when the temperature is decreased in the interval 7–3° K, is due to the appearance of a new quantum effect, namely phonon-phonon dragging of the carriers[20]. With decreasing characteristic dimensions of the sample, the exponential slope of the $\alpha(T)$ curve gives way to a weaker power-law slope, which can be attributed to a decrease in the contribution of the phonon-phonon dragging.

4. A size effect in the thermoelectric power was observed, namely, $\alpha_{\max}$ decreases slightly with decreasing characteristic dimensions, after which it practically flattens out. A detailed explanation of this effect calls for a quantitative analysis of the relations between the roles of the different phonon scattering mechanisms, but it is qualitatively clear that the weak dependence of the thermoelectric power of bismuth at $T \leq 2.5^\circ K$ on the dimensions of samples with characteristic dimensions 2–3 mm can be attributed to the influence of a stronger scattering of the long-wave phonons by the carriers than in the case of the thermal conductivity (the expression for the thermal conductivity contains the time of scattering by the carriers, averaged over all the phonons) and to the transition from the phonon-phonon mechanism of carrier dragging to the ordinary phonon mechanism.

As seen from the results and their discussion, the study of the question of the behavior of the thermoelectric power of perfect single crystals of bismuth at helium temperatures is of interest from the point of view of constructing a theory of the processes of mutual dragging of quasiparticles in perfect bulky crystals at low temperatures.

5. We have shown that the electric conductivity of bismuth at helium temperatures depends essentially not only on the chemical purity but also on the dimensions of the samples, the quality of the surface, and the perfection of the crystal structure of the samples. Unlike usual metals, the quality of the structure can greatly influence the electric conductivity of bismuth samples at low temperatures (the cross section for the scattering of electrons by defects in bismuth is approximately 10^4 times larger than in normal metals[14]), so that the chemical purity of the material cannot be assessed uniquely from the ratio $\rho(300^\circ K)/\rho(4.2^\circ K)$ of the resistances at room and helium temperatures.

6. The observed dependence of the electric conductivity on the dimensions of perfect samples with characteristic dimensions of several millimeters can be explained most fully within the framework of the theory of the diffusion size effect[26,27]. The conditions for the scattering of the electrons by the boundary have been seen to influence the electric conductivity of samples in the region of the diffusion size effect.

The size-effect phenomena described above, with the exception of the dependence of the electric conductivity on the dimensions, were observed by us in bismuth for the first time.

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76