THERMAL EMF AND THERMOMAGNETIC PROPERTIES OF BISMUTH AT LOW TEMPERATURES

I. Ya. KORENBLIT, M. E. KUSNETSOV, and S. S. SHALYT

A. F. Ioffe Physico-technical Institute, USSR Academy of Sciences; Leningrad Pedagogical Institute; Semiconductor Institute, USSR Academy of Science

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The thermal emf and thermomagnetic phenomena of pure bismuth and of bismuth doped with tin or tellurium are studied. In the latter case the ratio of the number of electrons and holes can be changed. The measurements were performed with single crystals of various crystallographic orientations, at temperatures between 3 and 80°K and magnetic field strengths between 0 and 25 kOe. A strong phonon dragging of the carriers is observed at $T < 20°K$; at $T \approx 4°K$ the Nernst coefficient in pure Bi is very large, of the order of 10^{-5} V/deg-Oe. In those cases when the electron and hole contributions do not cancel each other, the thermal emf is of the order of 100–300 μV/deg, which is larger by two orders of magnitude than the values of these coefficients in the diffusion transport mechanism. A turning (Umkehr) effect is observed for fields parallel to the binary axis in electron Bi at low temperatures, when the drag effect is operative. The electron and hole thermal emf's exhibit a pronounced anisotropy. The experimental results can be satisfactorily explained by the previously developed detailed theory[7].

EXPERIMENTAL data are presently available on the thermal emf and on the thermomagnetic properties of bismuth at $T > 80°K$ and $T < 5°K$. In the latter case, principal attention has been paid to oscillations of various kinetic coefficients of this semimetal in quantizing magnetic fields[1,2]. The thermal emf and the thermomagnetic effect in bismuth in the intermediate region of low temperatures 5–80°K, when the magnetic field H does not exceed the classical limits, have not been investigated until recently either experimentally or theoretically.

It is shown in recent theoretical papers[3-7] that at low temperatures, dragging of the carriers by phonons can appear in semimetals of the bismuth type; this dragging changes radically the temperature variation and the magnitude of the thermal emf and of the Nernst[1)] effect in the hitherto uninvestigated temperature region.

Unlike metals, in semimetals at low temperatures, when intervalley transfers are insignificant, only long-wave phonons, with momenta lying in the range $q < 2p_F \ll q_m$ in the case of an isotropic spectrum, interact with the carriers (p_F is the electron formula momentum and q_m is the maximum phonon momentum). Therefore the characteristic temperature for electronic kinetic coefficients of a semimetal is not the Debye temperature Θ, but the temperature $T_0 = 2p_F S/k \ll \Theta$ (S—speed of sound, k—Boltzmann's constant). In the interval $T_0 \ll T \ll \Theta$ there are many phonons interacting with the carriers ($N_q \approx kT/qS \gg 1$). In this case the dragging effect can appear in full measure if the temperature T_0 is small enough to make the role of phonon scattering insignificant. The partial thermal emf of each species of carriers of the semimetal can grow in this case to values on the order of k/e, which greatly exceeds the diffusion thermal emf of a degenerate electron gas $\alpha_d \approx k^2T/e\zeta$ (e—electron charge, ζ—Fermi energy). When $T < T_0$, thermal phonons ($\hbar\omega_q \approx kT$) interact with the carriers; the number of these phonons decreases in proportion to T^3, and therefore the thermal emf should vary under these conditions like $\alpha \approx (k/e)(T/T_0)^3$ (if the phonon-phonon scattering is negligible). The dragging greatly influences the Nernst coefficient Q if there are several groups of carriers. In this case Q can reach values ku/ec (u is the mobility), which are characteristic of nondegenerate semiconductors[4,6,7] (as against the values $uk^2T/ec\zeta$ characteristic of a degenerate electron gas in the absence of dragging). If mutual dragging takes place, Q may increase even more[6].

The foregoing general considerations pertain qualitatively also to bismuth, whose carrier energy spectrum has a complicated structure. A complete theoretical analysis of this question is given in[7].

In this paper we report experimental results of an investigation of the thermal emf and thermal magnetic effects in the temperature interval 3–80°K and in the range of magnetic fields 0–25 kOe. We investigated both pure bismuth single crystals, and those doped with tellurium or tin. The doping made it possible to change the ratio of the concentrations of the electrons and the holes in the investigated samples. The experimental results are analyzed on the basis of the theory of[7 2)]. It is shown that this theory describes correctly the main dependences of α and Q on T and H, and that in many cases perfectly satisfactory quantitative agreement is obtained for the absolute values of α and Q.

[1)] The Nernst effect is the appearance of an electric field perpendicular to the temperature gradient and to the magnetic field.

[2)] References to formulas and sections of this paper will henceforth be accompanied by the letter K.

The experimental fact that the phonon dragging influences α and Q in bismuth was demonstrated in a brief communication[8].

EXPERIMENTAL RESULTS

The thermal emf α_0 in the absence of a magnetic field, the thermomagnetic effects Q(H, T), and the change of the thermal emf $\Delta\alpha(H)$ in a magnetic field were measured in Bi single crystals with different orientations of the crystallographic axes, which are designated as follows: C_3(Oz)—principal threefold axis of the crystal, C_2(Ox)—the binary axis perpendicular to it, and C_1(Oy)—bisector axis perpendicular to the other two. The investigated sample was soldered to the bottom of a vacuum chamber (diameter ≈20 mm) immersed in the thermostatic liquid (nitrogen, hydrogen, helium). The temperature was measured at two points of the sample (diameter ≈2–3 mm, length ≈50–60 mm) at a constant heat flux by means of copper-constantan thermocouples in the T = 30–80°K region and by carbon resistors in the T = 3–40°K region. The thermal emf of the investigated samples was measured relative to copper, from which it was found that its absolute thermal emf does not exceed 1 μV/deg in the entire investigated temperature range. All the experimental data are presented below without this circumstance taken into account. The available data[9] allow us to assume that addition of one tellurium atom introduces 0.7 electrons, while one tin atom introduces 0.27 holes. The impurity concentration is indicated in atomic percent. Since in pure bismuth the electron and hole concentrations are equal and they compete in the formation of the thermal emf, to reveal more clearly the effect of dragging on the thermal emf we investigated, besides pure bismuth single crystals, also single crystals doped with Te or Sn. The main characteristics of the investigated samples are listed in the table, which indicates the contents of the Te and Sn impurities (in at.%) and the orientations of the current j or of the gradient temperature ∇T relative to the crystallographic axes.

Figure 1 shows the temperature dependences of the electric conductivities of the investigated pure and doped Bi single crystals. Figures 2–4 show the results of the measurements of the thermal emf α_0 in the absence of a magnetic field. The numbers of the curves in all the figures correspond to the numbers of the samples in the table. We see that the dragging causes the thermal emf α_0 in n-type and p-type Bi to reach the theoretically predicted values on the order

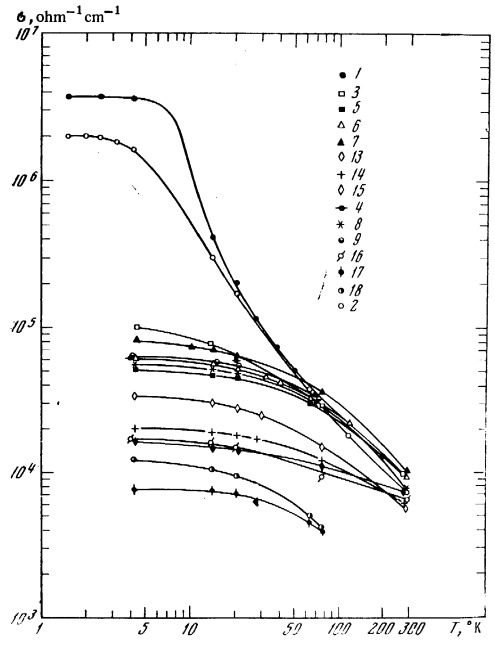

FIG. 1. Temperature dependence of the electric conductivity σ of the investigated Bi single crystals. The numbers of the curves correspond to the numbers of the samples in the table.

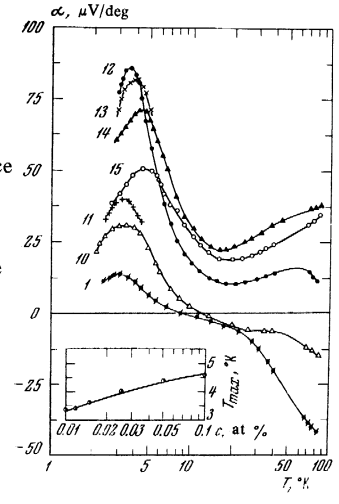

FIG. 2. Temperature dependence of the thermal emf α_0 of the investigated Bi single crystals (pure and doped with tin), $\nabla T \perp C_3$. The numbers of the curves correspond to the number of the samples in the table. The insert, in the lower part of the figure, shows the dependence of T_{max} on the tin concentration c.

of k/e = 86 μV/deg., instead of values of α_0 on the order of 1 μV/deg, which would be produced in this case by the diffusion mechanism. The same figures

Sample number	Impurity content at. %	Orientation	Sample number	Impurity content at. %	Orientation
1	Pure Bi, B=390*	$j \parallel \nabla T \perp C_3$	10	Sn 0.01	
			11	Sn 0.012	
2	Pure Bi, B=280*	$j \parallel \nabla T \parallel C_3$	12	Sn 0.015	
			13	Sn 0.025	$j \parallel \nabla T \perp C_3$
			14	Sn 0.05	
3	Te 0.001		15	Sn 0.1	
4	Te 0.0025		16	Sn 0.015	
5	Te 0.005	$j \parallel \nabla T \perp C_3$	17	Sn 0.025	$j \parallel \nabla T \parallel C_3$
6	Te 0.01		18	Sn 0.05	
7	Te 0.05		19	Sn 0.01	
8	Te 0.025	$j \parallel \nabla T \parallel C_3$			
9	Te 0.01				

*B = R(290°)/R(4.2°): R – electric resistance.

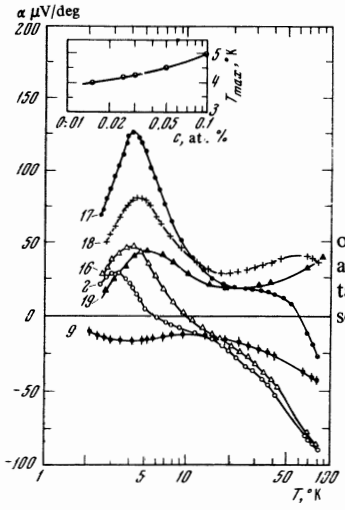

FIG. 3. Temperature dependence of the thermal emf of the investigated Bi single crystals at an orientation $\nabla T \parallel C_3$. The curve in the insert is the same as in Fig. 2.

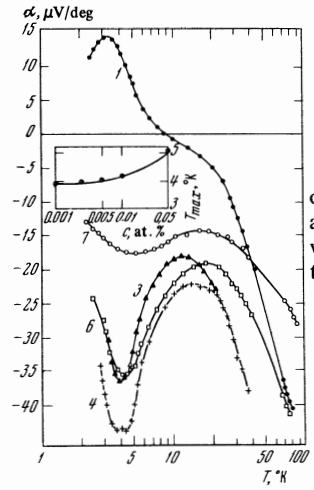

FIG. 4. Temperature dependence of the thermal emf of the investigated Bi single crystals (pure and doped with tellurium), $\nabla T \perp C_3$. The curve in the insert is the same as in Fig. 2.

show how the temperature at which α_0 reaches a maximum (T_{max}) shifts as a function of the impurity concentration (i.e., essentially as a function of the carrier density, which determines the aforementioned characteristic temperature T_0). For α_0 at the maximum, the dependence on the density of the Te or Sn impurity is not monotonic as for T_{max}. The optimal values of these concentrations are obtained from the experimental data of Figs. 2–4. The decrease of α_0 at $T < T_{max}$ is due mainly to the "freezing out" of the phonons that interact with the carriers. This feature distinguishes the effect of dragging in semimetals from the dragging in weakly doped semiconductors, where the decrease of α_0 at $T < T_{max}$ is due mainly not to the "freezing out" of the phonons but to their scattering by the boundaries of the sample.

Figure 5 shows the influence of the dragging effect on the anisotropy of the thermal emf of pure, n-type, and p-type bismuth. We see that in the region $T > 50°K$, where the dragging effect does not appear noticeably, the thermal emf of the n-type and p-type Bi isotropic. A strong anisotropy appears in the dragging region.

Figure 6 shows the action of the turning (Umkehr) effect due to the turning of the electronic ellipsoids relative to the basal plane of the crystal, and manifest in a change of the value of α when $H \parallel C_2$ is rotated

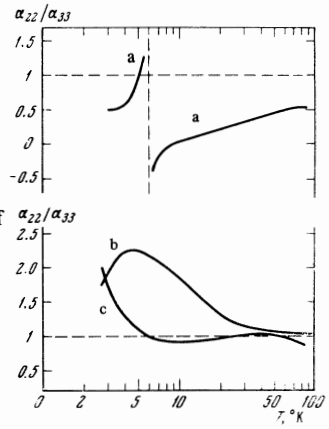

FIG. 5. Temperature dependence of the anisotropy of the thermal emf of pure (a), n-type (0.01% Te) (b), and p-type (0.0% Sn) (c) Bi.

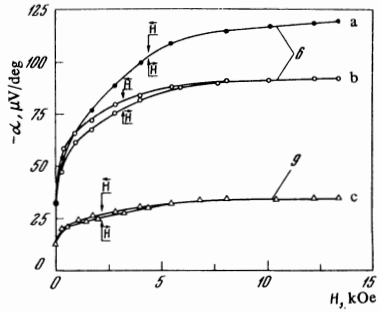

FIG. 6. Dependence of the thermal emf on the intensity of the transverse magnetic field for samples No. 6 and No. 9 at $T \approx 4°K$, which reveals a turning (Umkehr) effect in the region where the dragging effect takes place: a – $H \parallel C_3$, b and c – $H \parallel C_2$.

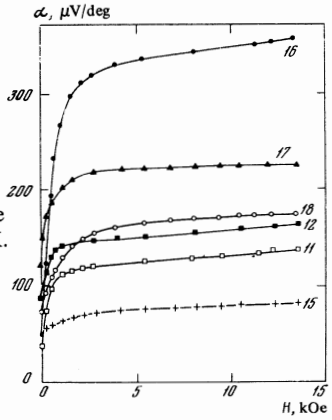

FIG. 7. Dependence of the thermal emf of several tin-doped Bi single crystals on the intensity of the transverse magnetic field at $T \approx 4°K$. $H \parallel C_2$ for curves 16, 17, and 18 and $H \parallel C_3$ for curves 11, 12, and 15.

through 180°. As expected, such a rotation does not influence α when $H \parallel C_3$.

It is seen from Fig. 7 that at the optimal tin-impurity concentration (0.015%) the thermal-emf of p-Bi almost reaches the value predicted by the theory: $\alpha \approx 5\ k/e$. The curve of Fig. 8 at $T = 4.1°K$ in a strong longitudinal field exhibits quantum oscillations, which we have not investigated in this work.

Figure 9 shows the dependence of the Nernst coefficient on the field for pure, n-type, and p-type Bi. All the curves of this figure have the theoretically expected

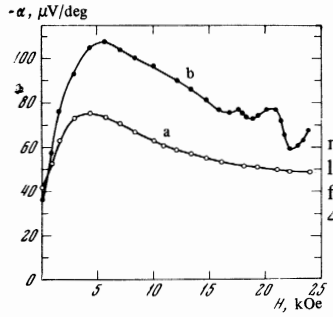

FIG. 8. Dependence of the thermal emf on the intensity of the longitudinal magnetic field ($\mathbf{H} \parallel C_1$) for sample No. 6 at 81°K (a) and 4.1°K (b).

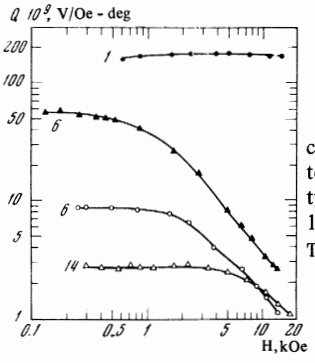

FIG. 9. Dependence of the Nernst coefficient on the magnetic field intensity for single crystals of pure, n-type, and p-type Bi: 1 – T = 20°K, 14 – T = 4°K; 6 – T = 4°K (▲) and T = 20°K (○).

form, namely, if the carriers are all of the same sign Q decreases with increasing H (in the strong-field region), and in the presence of electrons and holes (pure Bi) Q retains a large value also in strong fields.

Whereas for a stronger manifestation of the dragging effect in the thermal emf of Bi it is necessary to shift the electron/hole concentration ratio by doping, the most favorable conditions for the manifestation of the phonon dragging in the Nernst effect are produced when these concentrations are equal, in pure Bi. This is evidenced by the curves of Fig. 10. We see that at $T \approx 4°K$ the quantity Q reaches the value ku/ec predicted by the theory. The large value $Q \approx 10^{-5}$ V/Oe-deg is due in this case to both the dragging effect, which increases Q by a factor ζ/kT compared with the diffusion Nernst coefficient, and to the large carrier mobility in the pure Bi. This value of the Nernst coefficient is very large in absolute magnitude (even if one bears in mind nondegenerate semiconductors), thus ensuring for bismuth a relatively large (but still very small in practice) efficiency z of thermomagnetic cooling at helium temperatures ($z = 1.1 \times 10^{-3}$ deg^{-1} at 4°K, for a comparison see[10]). A special experiment aimed at clarifying the comparative influence of the transverse dimensions of the sample on the thermal conductivity and on the Nernst coefficient has shown that when $T \approx T_{max}$ the size effect has a much smaller influence on the Nernst coefficient than on the thermal conductivity. The subsequent decrease of Q (and α) when $T < T_{max}$ is mainly the consequence of the "freezing out" of the phonons.

The small values of Q for n- and p-type Bi on Fig. 10 are due mainly to the sharp decrease of the mobility when the Bi is doped. Thus, in the n-type sample (0.01% Te) the mobility is decreased by a factor of 450, and in the p-type sample (0.05% Sn) by a factor of 3000.

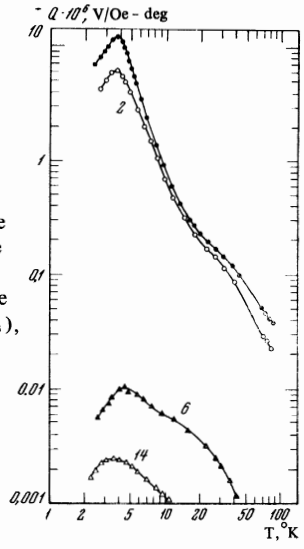

FIG. 10. Temperature dependence of the Nernst coefficient for two pure Bi single crystals – curve 1 ($\mathbf{H} \parallel C_3$) and 2 ($\mathbf{H} \parallel C_2$), and also n - Bi – curve 6 ($\mathbf{H} \parallel C_3$) and p - Bi curve 14 ($\mathbf{H} \parallel C_3$), H = 5 Koe.

ANALYSIS OF EXPERIMENTAL RESULTS

A. Thermal Emf in the Absence of a Magnetic Field

As is well known, the energy spectrum of bismuth consists of one hole ellipsoid and three electron ellipsoids[11]. The following expression was derived earlier[7] for the tensor of the partial dragging thermal emf due to carriers of group s:[3)]

$$\alpha_{kl}^{(s)} = \frac{1}{n^{(s)}e^{(s)}(kT)^2}\sum_{\mu=1}^{3}\int_{\Omega_s}\frac{d^3q}{(2\pi\hbar)^3}\frac{\exp(\hbar\omega_q^{(\mu)}/kT)\hbar\omega_q^{(\mu)}}{[\exp(\hbar\omega_q^{(\mu)}/kT)-1]^2}\frac{\nu^{(\mu,s)}(\mathbf{q})}{\nu^{(\mu)}(\mathbf{q})}S_l^{(\mu)}q_k. \quad (1)$$

Here $n^{(s)}$ and $e^{(s)}$ are the concentration and charge of the carrier group s, μ is the number of the polarization of the acoustic branch of the phonons, $S_l^{(\mu)}$ is the l-th component of the group velocity of the phonons with polarization μ, $\nu^{(\mu,s)}$ is the relaxation frequency of the phonons with polarization μ on the carriers of group s, $\nu^{(\mu)}$ is the total relaxation frequency, including the frequency ν_f of the phonon-phonon relaxation, the frequency ν_d of relaxation of phonons by the defects and boundaries of the sample, and the relaxation frequency of the phonons on carriers of all groups:

$$\nu^{(\mu)}(\mathbf{q}) = \nu_f(\mathbf{q}) + \nu_d(\mathbf{q}) + \sum_{s'}\nu^{(\mu,s')}(\mathbf{q}). \quad (2)$$

The integration in (1) is carried out over the region Ω_s filled by the phonons interacting with the carriers of group s. It constitutes an ellipsoid whose semiaxes are twice as large as the semiaxes of the constant-energy surface $\epsilon_s(\mathbf{p}) = \zeta_s$. The frequency $\nu^{(\mu,s)}(\mathbf{q})$ obviously differs from zero only when $\mathbf{q}$ is inside Ω_s, and for all $\mathbf{q}$ outside Ω_s we have $\nu^{(\mu,s)}(\mathbf{q}) = 0$.

We have already noted that in an isotropic semimetal the characteristic temperature in the kinetic coefficients is $T_0 = 2p_F S/k$, above which only sub-

[3)] We shall henceforth replace the two tensor indices of the partial thermal emf of one ellipsoid by a single index in accordance with the rule 11→1, 22→2, 33→3, 32→4, and 23→5. We retain two indices for the total thermal emf of n - Bi and pure Bi.

thermal phonons ($\hbar\omega < kT$) interact with the electrons, and below which only thermal phonons interact. In the anisotropic case, a similar rule is played by the temperatures $T_0^{(\mu+)}$ and $T_0^{(\mu-)}$, above which the exponentials in the corresponding terms of the sum (1) can be expanded in powers of $\hbar\omega_q^{(\mu)}/kT$. For bismuth, the temperatures $T_0^{(\mu,s)}$ lie in the interval 3–12°K[7]. When $T > T_0$, the temperature dependence of $\alpha_i(s)$ is determined completely by the temperature dependence of the frequency $\nu^{(\mu)}$. It can be shown that under these conditions the frequency $\nu^{(\mu,s)}(q)$ does not depend on the temperature in the anisotropic case, just as in the isotropic case. Since ν_d is likewise independent of T, the entire temperature dependence of $\nu^{(\mu)}$ is due to the phonon-phonon relaxation frequency ν_f, so that $\nu^{(\mu)}$ decreases with decreasing T until it reaches the minimum value equal to $\nu_d + \sum_{s'} \nu^{(\mu,s')}$. At $T \leq T^{(\mu,s)}$ the interaction between the thermal phonons and the carriers becomes appreciable, and the decrease of the number of thermal phonons with T contributes to a decrease of the thermal emf. Thus, the following two variants of temperature dependence of the partial thermal emf are possible: 1) if the temperature T_1, at which the contribution of ν_f to the total frequency is small compared with the contribution of ν_d and $\nu^{(\mu,s)}$, exceeds the temperature T_0, then $\alpha_i^{(s)}$ increases with decreasing T when $T > T_1$, is independent of T in the interval $T_0 < T < T_1$, and decreases with T at $T < T_0$; 2) if $T_1 < T_0$, then there is no plateau, and $\alpha_i^{(s)}$ reaches a maximum at a certain temperature smaller than T_0; this maximum is smaller than in the preceding case.

The partial emf's $\alpha_i^{(s)}$ for $T > T_0$ were calculated in[7] under the assumption that a) the phonon-phonon scattering is negligible, i.e., $T_0 < T < T_1$, and b) the contribution to the dragging of the phonons interacting with the carriers of all groups is negligibly small compared with the contribution of the phonons interacting with the carriers of one group only.

The second of the indicated assumptions means that in the calculation of $\alpha_i^{(s)}$ it is possible to discard in (2) all the $\nu^{(\mu,s')}$ with $s' \neq s$. The values of $\alpha_i^{(s)}$ obtained in this manner depend only on the anisotropy of the spectra of the carriers and phonons. At the same time, when $T \leq T^{(\mu,s)}$, the thermal emf depends on $T^{(\mu,s)}$, and consequently on the carrier concentration in the sample.

We shall see subsequently that the maximum thermal emf is reached in bismuth at $T \leq T_0^{(\mu)}$, and that the second assumption is likewise not always satisfied. Consequently the calculated values of the partial thermal emf are overestimated.

It is seen from the presented calculated data that the partial thermal emf is strongly anisotropic when $T > T_0$. This is connected with the anisotropy of the region Ω_s over which the integration is carried out in (1). When $T < T_0$, the anisotropy should decrease, since phonons with large q are frozen out earlier than phonons with small q. In the limit of very low temperatures, $T \ll T_0$, the integration in (1) is actually limited to the surface $\hbar\omega = kT$, which lies entirely inside the ellipsoid Ω_s, so that the anisotropy of the thermal emf is small and is due only to the anisotropy of the phonon spectrum. In the case of p-Bi, we confirmed these considerations by direct calculation of the thermal emf at $T \ll T_0$.

Let us proceed to analyze the experimental data. The temperature region in which the dragging is significant can be established from the temperature dependence of the thermal emf in samples with unequal electron and hole concentrations (Fig. 2–4). We see that below 10–20°K, the region in which the principal role is played by the diffusion thermal emf and α_0 decreases with temperature is followed by a temperature region in which α_0 increases with decreasing T.

In the region 3–5°K, the value of α_0 reaches a maximum. In none of the diagrams (Figs. 2–4) do we see a horizontal section, and consequently, in all cases T_1 is smaller than at least one of the temperatures $T_0^{(\mu,s)}$. The fact that α_0 increases down to 3–5°K indicates that, at least down to these temperatures, the frequency of the phonon-phonon scattering is comparable with $\nu^{(\mu,s)} + \nu_d$. From the fact that in the investigated temperature region α_0 is practically independent of the dimensions of the sample it follows that $\nu_d \ll \nu^{(\mu,s)}$.

In pure bismuth at high temperatures, the thermal emf is negative, since the electron mobility exceeds the hole mobility, and the partial thermal emf is practically independent of the number of the group s. With decreasing temperature α_0 reverses sign and only then does it reach a small maximum. Thus, the contribution of the holes to the dragging thermal emf exceeds in this case the contribution of the electrons. The partial thermal emf of the electron and hole ellipsoids in the axes of the crystal have been calculated (K, Sec. 3). They can be used to determine the total thermal emf with the aid of formulas (K.27) and (K.28), if the mobility ratios are known. We shall use the values of the mobilities measured in[12]. Although in the region of the impurity conductivity the mobilities vary from sample to sample, their ratios can be assumed to be insensitive to the impurity concentration.

For pure bismuth we obtain

$$\alpha_{22}^{\text{theor}}(0) = \mu\text{V/deg}\ , \quad \alpha_{33}^{\text{theor}}(0) = -45\ \mu\text{V/deg}.$$

The exceedingly small value of $\alpha_{22}(0)$ is connected with the fact that the contributions to the thermal emf of the electrons and the holes practically cancel each other. The experimental value of the thermal emf at the maximum, $\alpha_{22}(0) = 15\ \mu$V/deg (Fig. 4), agrees sufficiently well with the theoretical one, if it is recognized that the calculated value of $\alpha_{22}(0)$ is obtained in the form of a small difference of large numbers. For $\alpha_{33}^{\text{exp}}(0)$ at the maximum we have the value + 30 μV/deg (Fig. 3). Here, too, we have an appreciable cancellation of the contributions of the electrons and holes. However, $\alpha_{33}^{\text{theor}}(0) < 0$, but $\alpha_{33}^{\text{exp}}(0) > 0$, i.e., the contribution of the electrons to the total dragging thermal emf was strongly overestimated in the calculation. It seems to us that the main source of the error in this case is the second of the indicated as-

sumptions. This assumption is based on the fact that the number of phonons common to all the ellipsoids Ω_s (s = 1–4) is much smaller than the number of phonons belonging to each of them. In the case of the electron ellipsoids, the common phonons include also the phonons whose momenta are almost parallel to Oz. Their number is actually small, but their contribution to $\alpha_{33}(0)$ can be comparable or even greater than the contribution of the remaining phonons. In this case we have in (2) $\sum_{s'=1}^{3} \nu^{(\mu,s)} \approx 3\nu^{(\mu,1)}$, so that the calculated value of α_3^- is overestimated by a factor of approximately 3. Phonons with wave vectors almost parallel to Oz also make a contribution to α_3^+, but these vectors are much larger in absolute magnitude than those that make a contribution to α_3^-, to that the second assumption holds true for α_3^+. (The indices +(−) correspond to holes (electrons)).

We note that the source of the appreciable error may also be the fact that in (K.28) the large thermal emf α_3^+ is multiplied by u_3^+, and this mobility component was determined by Zitter[12] with accuracy ±100%. From Figs. 2–4 we see that at a given temperature α_0 is a nonmonotonic function of the density of the carriers of either sign. Such a behavior is explained as follows: on the one hand, when the concentration of carriers of one sign increases, the mutual cancellation of the contributions of the electrons and holes decreases, and this contributes to an increase of the total thermal emf. On the other hand, an increase of the concentration of the holes (or electrons) leads to an increase of their Fermi energy ζ, and consequently also of the temperature $T^{(\mu)} \sim \sqrt{\zeta}$. The wave vectors of the phonons interacting with the carriers increase simultaneously, and this leads to a more rapid increase of ν_f compared with $\nu^{(\mu)}$. As a net result, the partial thermal emf of the holes (electrodes) decreases, and the total thermal emf as a maximum at a certain optimal concentration of the holes and electrons. With increasing concentration, the maximum of α_0 as a function of the temperature shifts monotonically towards high temperatures (Figs. 2–4). This is also connected with the increase of $T_0^{(\mu)}$.

The maximal thermal emf $\alpha_{22}(0)$ of n-Bi is $\alpha_{22}^-(0)$ = 44 − μV/deg and is reached at T = 4° in the sample Bi(0.0025% Te), while in the sample Bi(0.01% Te) we have $\alpha_{33}^-(0) = -17$ μV/deg.

According to Zitter[12], we have for the mobilities $u_3^- u_1^- \gg u_2^- u_4^-$. This relation between the mobilities is due to the mass anisotropy and is presumably retained also in n-Bi doped with tellurium. We shall show later that in the discussed samples α_2^- is smaller by several times than in pure bismuth. In view of this, it follows from (K.12) and (K.13) that $\alpha_{11}^-(0) = \alpha_{22}^-(0) \approx \alpha_1^-$ and $\alpha_{33}^-(0) \approx \alpha_3^-$, so that in the sample Bi(0.0025% Te) at T = 4°K we have $\alpha_1^- = -44$ μV/deg, while in the sample Bi(0.01% Te) we have $\alpha_3^- = -17$ μV/deg.

At $T_0 < T < T_1$ we would have according to the theory $\alpha_1^- = -58$ μV/deg and $\alpha_3^- = -67$ μV/deg. The difference for α_1^- is small, although $T_0^{(\mu)}$ in n-Bi is much higher than in pure bismuth, for which, as already noted, the largest $T_0^{(\mu)}$ equals 12° K. This offers evidence that α_1^- decreases slowly with T when $T < T_0$. In addition, it can be concluded that at T ≈ 4°K, ν_f is already smaller than the phonon-electron relaxation frequency.

As regards α_3^-, the large difference between the experimental value and the calculated one is connected, as already noted, with the fact that in this case the assumption II [sic!] is not satisfied. α_2^- makes practically no contribution to $\alpha_{22}^-(0)$ and $\alpha_{33}^-(0)$. This component of the partial thermal emf can be determined from measurements of α in a strong field. In samples in which holes predominate, the thermal emf reaches relatively large values: 130 and 86 μV/deg respectively along and cross the trigonal axis. Inasmuch as the mobility of the electron is larger than that of the holes, even the small admixture of electrons contained in our samples can make an appreciable contribution to the thermal emf. It is easy to show that when $n^+ \neq n^-$ and H = 0 we have

$$\alpha_{22}(0) = \frac{2n^+\alpha_1^+u_1^+ + n^-(\alpha_1^-u_1^- + \alpha_2^-u_2^- + \alpha_4^-u_4^-)}{2n^+u_1^+ + n^-(u_1^- + u_2^-)}, \quad (3)$$

$$\alpha_{33}(0) = \frac{n^+\alpha_3^+u_3^+ + n^-(\alpha_3^-u_3^- + \alpha_5^-u_4^-)}{n^+u_3^+ + n^-u_3^-}. \quad (4)$$

Here $u_i^{\pm}$ are the components of the hole and electron mobility tensors. Bearing in mind that, according to[12], $2u_1^+$ differs from $u_1^- + u_2^-$ by only a factor of 2, and u_3^+ is 30 times smaller than u_3^-, we conclude that a small admixture of electrons have little influence on the component $\alpha_{22}(0)$, which in this case coincides with α_1^+ and greatly decreases $\alpha_{33}(0)$ compared with α_3^+. We shall show below that α_3^+ can be determined knowing α_{33}^+ in a strong magnetic field. The strong influence of the small admixture of electrons on α_{33} is apparently the reason why the anisotropy of the thermal emf in p-Bi, unlike n-Bi, does not go through a maximum (see Fig. 5).

B. Dependence of Thermal Emf on Magnetic Field

The dependence of the thermal emf on the field in bismuth with an excess of electrons or holes is shown in Figs. 7–9. A turning effect is observed for α_{22}^- and α_{33}^- when H ∥ C_2; this effect reaches a maximum, in accordance with the theory[7], in intermediate fields. In accord with[7], it is larger for α_{22}^- than for α_{33}^-. The turning effect is due to the anisotropy of the partial dragging thermal emf of the electron ellipsoid (see (K.17) and (K.19)). At high values of T, when the partial thermal emf is isotropic, no turning effect is observed in n-Bi with H ∥ C_2[13].

If we take into account the fact that, according to[12], $w_-^2 \equiv u_2^-u_3^- - (u_4^-)^2 \ll u_1^-u_3^-$, then the expression (K.23) for $\alpha_{22}^-(\infty)$ at H ∥ C_2 can be rewritten in the form

$$\alpha_{22}^-(\infty) \approx {}^1/_3(2\alpha_1^- + \alpha_2^-). \quad (5)$$

Using now the experimental value $\alpha_{22}^-(\infty) = -92$ μV/deg for the sample Bi(0.01% Te) at H ∥ C_2, and the value $\alpha_1^- = -36$ μV/deg, obtained at T = 4°K for this sample from the condition $\alpha_{22}^-(0) = \alpha_1^-$, we get $\alpha_2^- = -204$ μV/deg. From a comparison with the theoretical value $\alpha_2^- = -1000$ μV/deg, obtained at $T > T_0$, it follows that α_2^-, unlike α_1^-, decreases rapidly with T when $T < T_0$. This means that when $T < T_0^{(\mu)}$, the anisotropy of the thermal emf is smaller than when $T > T_0^{(\mu)}$, in qualitative agreement with the considerations advanced

above.

When $H \parallel C_3$, we have from (K.14)

$$\alpha_{22}^-(\infty) = {}^1/_2(\alpha_1^- + \alpha_2^- + \alpha_4^- u_4^- / u_2^-). \quad (6)$$

It is shown in[7] that, along the principal axes of the ellipsoid

$$\alpha_4^- \approx \frac{m_3^-}{m_2^-}\eta\frac{k}{e} \ll \frac{k}{e},$$

where η is the angle of rotation of the mass ellipsoid around the crystallographic axis Ox. Bearing in mind that $\eta \approx 0.1$, we get along the axes of the crystal

$$\alpha_4^- \approx (\alpha_3^- - \alpha_2^-)\eta = 19\ \mu V/deg.$$

To calculate $\alpha_{22}^-(\infty)$ it is also necessary to know u_4^-/u_2^-. We assume for this ratio the value obtained by Zitter[12] for pure bismuth. Then $\alpha_{22}^-(\infty) = -67$ $\mu V/deg$, whereas the experimental value is $\alpha_{22}^-(\infty) = -120$ mV/deg. The reason for this discrepancy is unclear. We note that it is apparently impossible to obtain agreement between the theoretical and experimental values of $\alpha_{22}^-(\infty)$ by varying u_4^-/u_2^- in reasonable limits. The component α_{33}^- increases in the field slightly compared with α_{22}^-, in qualitative agreement with the theory (see (K.24), (K.13)).

We now proceed to samples in which holes predominate. When $n^+ \neq n^-$, we can obtain for the thermal emf in a strong magnetic field the following expressions:

$H \parallel C_3$,

$$\alpha_{22}(\infty) = \frac{1}{n^+ - n^-}\left[n^+\alpha_1^+ - \frac{n^-}{2}\left(\alpha_1^- + \alpha_2^- + \alpha_4^-\frac{u_4^-}{u_2^-}\right)\right]; \quad (7)$$

$H \parallel C_2$,

$$\alpha_{33}(\infty) = \frac{1}{n^+ - n^-}\left[n^+\alpha_3^+ - n^-\left(\alpha_3^- + 2\alpha_5^-\frac{u_1^- u_4^-}{3u_1^- u_3^- + w^2}\right)\right]. \quad (8)$$

When $n^- \to 0$, the values of α_{ii} do not depend on H[7]. Therefore α_{22} hardly changes with the field in the sample Bi(0.1% Sn) (Fig. 8). From a comparison of (7) and (8) with (3) and (4) it follows that the addition of electrons to a p-type sample causes the thermal emf to increase in the magnetic field. This is precisely the dependence observed in the experiment.

Since $\alpha_3^+ > \alpha_3^-$, it follows from (8) that $\alpha_{33}(\infty) \approx \alpha_3^+$ when $n^- \ll n^+$: Under the same condition, we get from (3) $\alpha_{22}(0) \approx \alpha_1^+$. The inequality $n^- \ll n^+$ is sufficiently well satisfied in the sample Bi(0.015% Sn). Consequently, experiment yields for this sample

$$\alpha_{22}(0) = \alpha_1^+ = 86\ \mu V/deg,\quad \alpha_{33}(\infty) = \alpha_3^+ = 360\ \mu V/deg$$

The theoretical values calculated for $T > T_0$, namely $\alpha_1^+ = 120$ $\mu V/deg$ and $\alpha_1^+ = 430$ $\mu V/deg$, do not differ very strongly from the experimental ones obtained at $T < T_0^{(\mu)}$. The anisotropy of the hole thermal emf, as well as the electronic one, is smaller at $T < T_0^{(\mu)}$ than at $T > T_0^{(\mu)}$, as it should be.

C. The Nernst Coefficient

The contribution of the electrons and holes to the Nernst coefficient Q are additive. Therefore Q reaches its maximum values in pure bismuth. At $T < 70°$ K, the coefficient Q increases with decreasing T and, like the thermal emf, reaches a maximum at $T \approx 3$–$4°$K (Fig. 10). In the interval 70–3°K, the value of Q increases by almost 300 times. We note that the diffusion contribution to Q, which is proportional to uT, increases in this interval by approximately only three times.

The maximum values of Q at $H \parallel C_3$, $\nabla T \parallel C_1$, and $H \parallel C_2$, $\nabla T \parallel C_3$ in strong magnetic fields (H = 5 kOe) are respectively 1.2×10^{-5} and 6×10^{-6} V/Oe-deg (Fig. 10).

The theoretical values calculated from formulas (K.32) and (K.39) with the aid of the numerical values given in (K, Sec. 3) for α_i (in the notation of[7], we are dealing here with the components α_{12}/H and α_{23}/H), are equal to 4.7×10^{-6} and 4.8×10^{-6} V/Oe-deg, respectively. If we take into account the fact that the average carrier mobility in the Bi samples investigated by us exceeded the average mobility in Zitter's samples[12] by approximately two times, the agreement between the calculated and measured values of the Nernst coefficient becomes good.

In n-type and p-type bismuth samples, Q also goes through a maximum with decreasing T, but the Nernst coefficient at the maximum is in this case 3–4 orders of magnitude smaller than in pure bismuth. This is connected, primarily, with the decrease of the mobility. The decrease of the partial thermal emf of the electrons and holes also comes into play.

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