Electric conductivity and transport lengths of electrons in bismuth at low temperatures

I. N. Zhilyaev and L. P. Mezhov-Deglin

Institute of Solid State Physics, USSR Academy of Sciences
(Submitted December 27, 1974; resubmitted October 11, 1975)
Zh. Eksp. Teor. Fiz. 70, 971–982 (March 1976)

The experimentally-observed singularities in the temperature and size effect dependences of the electric conductivity σ of bismuth samples can be attributed to changes that occur with decreasing temperature, in the relations between the characteristic transport lengths of the electrons in intravalley (l_{intra}) and intervalley (l_{inter}) volume scattering and the sample thickness d, and to manifestation of the diffusion size effect in the electric conductivity. From a cycle of measurements performed on a perfect bulky single crystal, the thickness of which was gradually decreased from experiment to experiment, it was possible to extract three sets of data: the $\sigma(T)$ dependence at various d, the dependence of the transverse electric field that arises at $T \leq 7$°K on T and d, and the size dependences of $\sigma(d)$ at different T. Each of the sets can yield in principle an independent estimate of the relations between l_{intra} and l_{inter}, and the last two sets can be used also to estimate the probability w of the intervalley recombination on the surface. Judging from the results of our measurements, at helium temperatures we have $l_{\text{intra}} \approx 1.9\,T^{-2}$ [cm], $l_{\text{inter}} \approx 4.3 \times 10^{-4} e^{35/T}$ [cm], and $w \leq 0.1$.

PACS numbers: 72.15.Qm, 72.15.Eb

1. INTRODUCTION

Singularities in the dependence of the electric conductivity of bismuth $\sigma(d)$ on the dimensions at 4.2 °K were observed many times[1–6] (Fig. 1). The only acceptable explanation of the step that appears on the $\sigma(d)$ curve is obtained by resorting to the theory of the diffusion size effect (DSE), developed by Rashba and Kravchenko.[7] In a multivalley semiconductor or semimetal, it is possible to introduce two characteristic times corresponding to intravalley (τ_{intra}) and intervalley (τ_{inter}) scattering of the carriers in the volume. At sufficiently low temperatures, the probability of intravalley scattering is much larger than the probability of the intervalley scattering, $\tau_{\text{inter}} \gg \tau_{\text{intra}}$; Zitter[8] estimated $\tau_{\text{inter}}/\tau_{\text{intra}} = 30$ in bismuth at $T = 4.2$ °K. At these temperatures near the surface of the plate, in a layer on the order of the diffusion length $L = v_F\,(\tau_{\text{inter}}\tau_{\text{intra}})^{1/2} \equiv (l_{\text{inter}} l_{\text{intra}})^{1/2}$ (v_F is the Fermi velocity) there can exist transverse density gradients of carriers belonging to different valleys. The conductivity theory of the layer is several times lower than the bulk conductivity of the metal. As a result, the electric conductivity of bulky samples can depend strongly on their characteristic dimensions even at $d \gg l_{\text{intra}}$. When the plate thickness d is decreased, two flat regions can be observed on the $\sigma(d)$ curves, the first at $d \gg L$ and the second at $l_{\text{intra}} \ll d \ll L$, where the conductivity of the sample is determined completely by the conductivity of the layer.

As follows from the theory, in the region of the second plateau, i.e., at thicknesses where the transverse concentration gradients of the carriers belonging to different valleys exist in the sample, a transverse electric field comparable in magnitude with the applied longitudinal field can be observed if a direct current is made to flow through the sample. When the ratio of L and d is changed, for example by decreasing the temperature or by decreasing the sample (at a fixed temperature), a dependence of the transverse field on the sample thickness or the temperature should be observed (in the region $d \gtrsim L$, inasmuch as at $d \gg L$ the transverse field is negligibly small).

The presence of two transport lengths l_{intra} and l_{inter}, the magnitudes and temperature dependences of which can differ significantly, should manifest itself also in a change of the slope of the $\sigma(T)$ curve plotted in a wide temperature interval, in the temperature region where l_{inter} becomes comparable with l_{intra}.

Thus, by investigating simultaneously the dependence of the electric conductivity and of the transverse electric field on the temperature and on the dimensions of the sample of a wide range of temperatures it is possible, in principle, to estimate the ratio of the intervalley and intravalley ranges of the carriers and the rate of the intervalley recombination on the surface of a bismuth crystal.[7]

This problem was not raised before, and the temperature and size dependences $\sigma(d)$ and $\sigma(T)$ cited in the literature pertain to samples of different quality and orientation, making comparison of results of different workers difficult. We have therefore carried out a cycle of measurements of the electric conductivity and of the

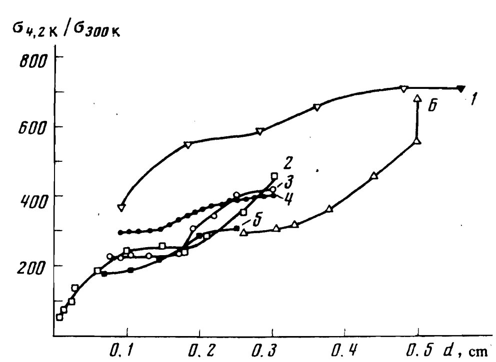

FIG. 1. Dependence of the electric conductivity of bismuth samples of the thickness at $T = 4.2$°K: 1—present work, 2—results of[1], 3—[2], 4—[3], 5—[4], 6—[5].

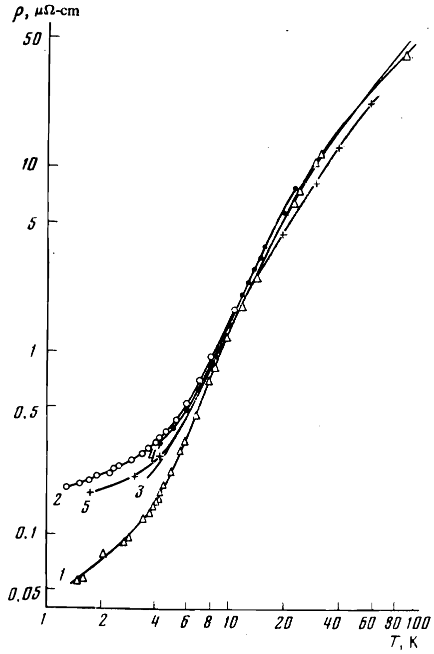

FIG. 2. Temperature dependence of the resistivity of bismuth samples in the interval 1—80 °K: 1, 2—present work, sample thickness, $d = 0.56$ and 0.59 cm, respectively; 3—from[11], 4—from the data of[12], 5—data of[13].

transverse electric field in the temperature interval from 1.3 to 70 °K, using the most perfect single crystals available at present, (resistivity ratio $\rho_{300\,K}/\rho_{4.2\,K} \geqslant 700$), where thickness was gradually changed by etching from ~6 to 1 mm.

The sample preparation procedure is similar to that described earlier,[5,9] but in contrast to[5] the oval samples were etched with nitric acid prior to the start of the cycle until natural faceting appeared[1)] and the potential contacts were placed pairwise of opposite faces of the crystal so that it was possible not only to measure the conductivity but also to observe the appearance of the transverse electric field as the temperature was lowered.[10] It is important to note that preliminary deep etching makes it possible to investigate the influence of the size on the properties of the sample, at a fixed orientation, at fixed quality of its crystal structure, and fixed surface properties. Inasmuch as the faceting of the crystal is preserved in the subsequent etching (only the ratio of the width of the sample to the thickness d changes as a result of the different rates of etching of the different faces), the transverse potential contacts were attached to the same opposite faces after each such etching.

The external magnetic field was cancelled out accurate to 0.05 Oe, and the magnetic field of the direct current flowing through the sample did not exceed 0.01 Oe. The accuracy with which the longitudinal and the transverse potential differences were made by a null-method manovoltmeter (F118/1) not was worse than 4% in the entire working interval.

The temperature was measured with a carbon thermometer calibrated against the saturated vapor pressure of liquid helium and against a standard platinum resistance thermometer. The accuracy with which the temperature was determined in the entire temperature interval was not worse than 2%.

2. TEMPERATURE DEPENDENCE OF THE RESISTIVITY

Figure 2 shows the measured resistivities ρ of various samples as functions of the temperature. The cross section of our sample was a parallelogram with an acute angle ~45°. The ratio of the sample thickness to the width at the start of the measurement cycle was 4 : 5, and decreased to 1 : 3 with further etching. The sample orientation was not set during the course of its manufacture, and the crystal grew without a primer; the C_3 and C_2 axes made angles ~56° and 40° with the longitudinal axis of the sample.

Above 10 °K, the values of ρ given by different authors are close to one another. At lower temperatures, the values of ρ differ, owing to differences in the quality and dimensions of the samples. The temperature dependences of $\rho(T)$ agreed qualitatively, however, in the entire interval from 1.3 to 70 °K. A power-law approximation of $\rho(T)$ turns out to be close to linear above 30 °K and closer to quadratic below 20 °K down to 1.3 °K. When plotted in the form $\rho = f(T^2)$, the temperature dependence of ρ can be approximated by two straight lines intersecting near 5–7 °K. The coefficient of T^2 decreases to approximately one-half at a temperature below 5 °K.

The conductivity of the bismuth is determined mainly by the electrons, the mobility of which is approximately four times larger than the hole mobility.[11,12] The quadratic $\rho(T)$ dependence at low temperatures can be attributed either to electron-phonon or to electron-electron scattering. Measurements in which impurities are introduced and altered the electron density[13,14] have shown that electron-electron scattering is small in comparison with the electron-phonon scattering. Calculations of the intervalley-phonon scattering in bismuth are complicated and none have been published so far, but from the geometry of the electron energy spectrum it follows that at helium temperatures the dependence of the characteristic mean free path l_{inter} on the temperature is close to exponential, $l_{\text{inter}} \sim e^{40/T}$.[15]

The quadratic $\rho(T)$ dependence at $T \leqslant 4$ °K can be attributed to intravalley electron-phonon scattering: calculations of τ_{intra}[16] and l_{intra}[17] agree well with the experimental estimates. Above 4–5 °K, according to[16,17], in the presence of intravalley scattering only, the quadratic $l_{\text{intra}}(T)$ dependence and accordingly that of $\tau_{\text{intra}}(T)$ should give way to a linear dependence. The dashed curve in Fig. 3 shows the temperature dependence of the resistivity as predicted by calculations[17] for intravalley scattering of electrons. Within the framework of the model developed by us, the steeper growth of the resistivity at $T > 6$ °K is due to turning on the intervalley bulk electron scattering mechanism with increasing temperature.

Assuming that the contributions of the different bulk scattering mechanisms are additive, i.e., $\rho = \rho_0 + \rho_{\text{intra}}$

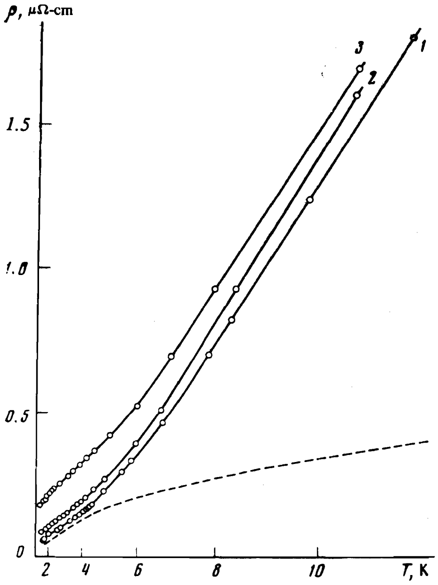

FIG. 3. Plot of $\rho(T^2)$: 1—at $d=0.56$ cm, 2—$d=0.28$, 3—$d=0.09$ cm. The dashed curve shows the resistivity variation due to the intravalley electron-phonon scattering in accordance with the calculations performed in[16,17].

$+\rho_{inter}$ (ρ_0 is the residual resistivity, ρ_{intra} and ρ_{inter} are the contributions of the intravalley and intervalley scattering mechanisms), we can calculate ρ_{inter}, and consequently also l_{inter}, from the measured ρ for the thickest sample (the influence of boundary effects is minimal for this sample) and from the temperature dependence of l_{intra} (corresponding to ρ_{intra}), which is known from calculations.[17] The value of ρ_0 is estimated by extrapolating the experimental curves to $T=0$.

The coefficient for the conversion from ρ to l can be estimated by using the experimental data on the resistance of the thinnest samples at the lowest (~ 1.3 °K) temperature, assuming for them[2] $\rho_0 = A/d$.[2)] For our sample $A = 1.4\times 10^{-2}$ $\mu\Omega\text{-cm}^2$. Assuming further that at $T\leqslant 4$ °K the $\rho(T)$ temperature dependence is due mainly to intravalley scattering of electrons in the interior of the sample, and writing $\rho-\rho_0=\rho_{intra}=A/l_{intra}$, we obtain $l_{intra}\approx(1.9\pm 0.2)T^{-2}$ [cm]. This estimate is close to the temperature-dependent length obtained in[19] from the temperature dependence of the amplitude of the radio-frequency size effect, and to the estimates given in[16,17,20]. For convenience in the subsequent calculations we approximate the $l_{intra}(T)$ dependence by a quadratic curve for $T\leqslant 4$ °K, and assume also that in the thickest sample ($d=5.6$ mm), at $T>4$ °K, the diffusion effects are small and have little influence on its electric conductivity. Assuming that the calculated value of $l_{intra}(T)$ from[17] should coincide at $T=4.2$ °K with our estimate of the mean free path, we can obtain the course of $l_{intra}(T)$, and consequently of $\rho_{intra}(T)$ of a bulky crystal at higher temperatures (dashed curve in Fig. 3). Neglect of the influence of DSE[3)] and the contribution of holes introduces, naturally, an error in the calculations, but the usually cited numerical estimates of the free path do not claim an accuracy higher than ± 50%.

Figure 4 shows the results of the calculations of l_{inter} (curve 2) as well as a plot of $l_{intra}(T)$ (curve 1). The obtained transport length $l_{inter}(T)$ at $T=5$–20 °K is close to the length in electron-hole recombination, l_{eh}, calculated from the measurements of the acousto-magnetoelectric effect[15] (curve 3). From the plot of $l_{inter}(T)$ we can estimate the argument of the exponential $l_{inter}\approx 4.3\times 10^{-4}e^{35/T}$ [cm], which agrees with the estimates $l_{inter}\sim l_{eh}\sim e^{40/T}$ given by Lopez[15] for the interval $T\leqslant 20$ °K. Above 20 °K, the $l_{inter}(T)$ and $l_{eh}(T)$ curves intersect and have different temperature dependences, possibly as a result of differences of the determination of the effective mean free path: as already noted in[15], the cited quantity l_{eh} is in fact not the transport length. It is also clear that the length l_{inter} which enters in the electric conductivity is determined not only by the electron-hole but also by the electron-electron intervalley transfer, but it is impossible to distinguish between the scattering mechanisms on the basis of the $l_{inter}(T)$ temperature dependence.

The effective electron mean free path in the volume for intervalley scattering becomes comparable with the intravalley value at $T\sim 7$ °K, and then increases rapidly with decreasing temperature, i.e., the diffusion effects in pure single crystals of bismuth can be observed only at $T\leqslant 7$ °K. Since at $T\leqslant 4$ °K the mean free path is $l_{inter}\geqslant 1$ cm, the possibility of intervalley scattering by defects (impurity atoms, vacancies, dislocations) must also be taken into account under these conditions. For example, the maximum values of l_{eh} decrease in[15] with decreasing resistivity ratio $\rho_{300}/\rho_{4.2}$ of the investigated constant-thickness samples.

3. TRANSVERSE FIELD

The potential contacts placed on opposite faces of the sample made it possible to measure simultaneously the longitudinal ($U_\parallel$) and transverse ($U_\perp$) potential difference[10] when current was made to flow along the sample. The ratio of the actually measured potential differences $U_\perp/U_\parallel$ is connected with the ratio of the transverse ($E_\perp$) and applied longitudinal ($E_\parallel$) electric fields by the expression

$$\frac{E_\perp}{E_\parallel}=\frac{U_\perp}{U_\parallel}\frac{h}{d}=\frac{E_\perp^{\text{size}}}{E_\parallel}+\frac{E_\perp^{\text{bulk}}}{E_\parallel}+\frac{\delta}{d},$$

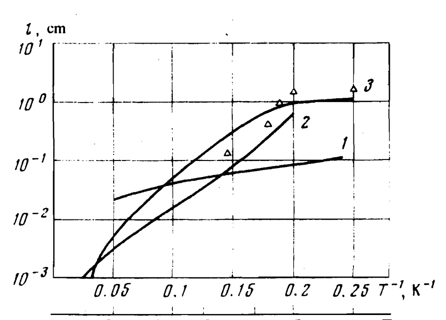

FIG. 4. Dependence of the effective electron mean free paths on the temperature: curve 1—l_{intra} according to the data of[17], normalized to $T=4.2$ °K; 2—l_{inter} calculated from the resistivity $\rho(T)$; 3—l_{eh} calculated from measurements of the acousto-magnetoelectric effect.[15] Points—estimates of l_{inter} from measurements of the transverse electric field (see Sec. 3).

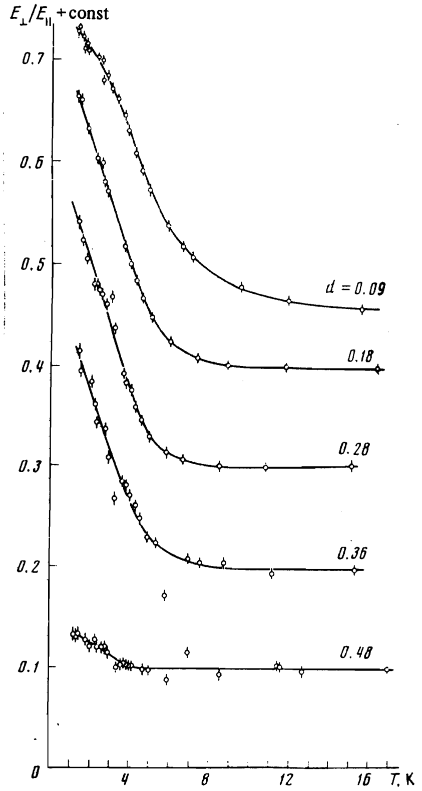

FIG. 5. Temperature dependence of the ratio $E_\perp/E_\parallel$ for different sample thicknesses.

where $h = 2$ cm is the distance between two pairs of transverse contacts, d is the sample thickness, δ is the misalignment of the transverse contacts mounted on opposite faces ($\delta < 0.1$ cm), E^{size} is the sought transverse field, and E^{bulk} does not depend on the dimensions and describes the anisotropy of the bulk conductivity.

According to the data of Friedman[11] and Hartman,[12] the ratios of the electron mobilities measured along different axes do not depend on the temperature at $T > 7$ °K; the bulk resistivity of bismuth at $T > 7$ °K is independent of the orientation within 10%, i.e., the second term in the given expression is small and is independent of temperature. The third term is also obviously independent of temperature.

The result of the measurements of $E_\perp/E_\parallel$ as a function of the temperature for different d are given in Fig. 5. For convenience, the experimental curves are displaced relative to one another along the ordinate axis, since we are not interested in the values of the constants, which are governed by the second and the third terms. The experimentally observed $E_\perp/E_\parallel$ dependence agrees qualitatively with that predicted in the introduction: at high temperatures, when the principal role in the resistance is played by intervalley scattering, $E_\perp/E_\parallel$ is practically independent of the temperature; at $T < 7$ °K, where $l_{\text{intra}} < l_{\text{inter}}$, the value of $E_\perp/E_\parallel$ increases with decreasing temperature and tends to saturation at small d at the lowest temperatures.

The observed increase of $E_\perp/E_\parallel$ with decreasing T can not be attributed to a change of only the relation between l_{intra} and d: Gorkun and Rashba[21] have shown that, neglecting intervalley scattering and at a fixed orientation of the sample, the value of $E_\perp/E_\parallel$ does not depend on the ratio of l_{intra} and d. The growth of the transverse field with decreasing temperature is not a manifestation of the DSE. Assuming that the transverse field becomes noticeable when the diffusion length $L = (l_{\text{intra}} l_{\text{inter}})^{1/2}$ becomes comparable with d, we can estimate l_{inter} by assuming that the temperature at which the horizontal section and the continuation of the inclined linear section of the plot of $E_\perp/E_\parallel$ against T intersects corresponds to $L = d$. The values of l_{inter} calculated for each of the dimensions are represented by the points in Fig. 4.

The values of l_{inter} obtained by us differ somewhat from our estimates given in[10], since l_{intra} is taken here to be the calculated $l_{\text{intra}}(T)$ curve of the recent study[17], normalized to 4.2 °K. As seen from the figure, the numerical values of l_{inter} obtained by different methods are in good agreement (it is obvious that the calculation of l_{inter} from the intersection of the $E_\perp/E_\parallel = f(T)$ curves should contain a numerical factor of the order of unity, which can easily be taken into account in the derivation of the appropriate theory).

4. SINGULARITIES IN THE SIZE-EFFECT DEPENDENCES OF THE ELECTRIC CONDUCTIVITY

Size-effect dependences of the electric conductivity on the transverse field at various temperatures are shown in Fig. 6. The clearly pronounced steps on the $\sigma(d)$ curves appear at $T < 7$ °K, in agreement with the estimates given above for l_{inter} and l_{intra}. A dimension-dependent transverse electric field appears at the very same temperatures.

The DSE theory developed in[7] is valid under the assumption that $l_{\text{intra}} \ll d$ and $l_{\text{intra}}/l_{\text{inter}} \ll 0.1$, and that the intervalley from the surface is small in comparison with the intervalley scattering in the volume. In the simplest case, the theoretical predicted dependence of the plate

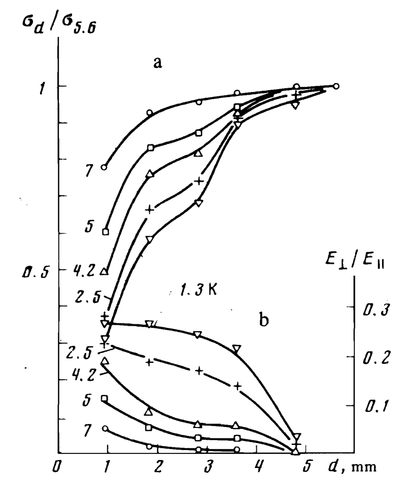

FIG. 6. Size-effect plots of the conductivity (a) and of $E_\perp/E_\parallel$ (b) at different temperatures. For convenience, the conductivity of a sample 5.6 cm thick is taken to be unity in each case; the $\sigma_T/\sigma_{300\,°\text{K}}$ ratios for this thickness correspond to 215, 490, 720, 1400, and 2200 for $T = 7, 5, 4.2, 2.5$, and 1.3 °K, respectively. The numbers of the curves represent the temperatures in °K.

conductivity on the thickness can be written in the form

$$\sigma=\sigma_\infty\left(1-k\frac{\operatorname{th}(d/L)}{d/L}\right),$$

and accordingly

$$\frac{E_\perp}{E_\parallel}\sim\frac{\operatorname{th}(d/L)}{d/L},$$

where $\sigma_\infty=ne^2 l_{\text{intra}}/p_F$ is the conductivity of an infinitely thick sample, k is a factor on the order of unity that depends on the sample orientation (according to the latest estimates of V. Ya. Kravchenko, $k\leq 0.6$), and p_F is the average Fermi momentum. It is seen from the formula that in the general case the conductivity of the sample can decrease with decreasing dimension, owing to the presence of the DSE, by a factor $1/(1-k)$ (by a maximum factor 2.5 in accordance with the estimate given above).

However, such simple formulas can not be used to describe the properties of perfect bismuth crystals of thickness less than one centimeter, inasmuch as at helium temperatures $l_{\text{intra}}\sim d$, and at higher temperatures l_{intra} and l_{inter} become close in value. Comparison of the theory with experiment calls for an exact computer calculation, similar to that performed by Gorkun.[22] Unfortunately, he does not take into account the presence of a third electron ellipsoid and of the hole surface, which, for example, can overestimate by an order of magnitude the maximum attainable ratio of the conductivities of the bismuth sample on the upper and lower plateau of the $\sigma(d)$ curve; no theoretical calculations of the behavior of the transverse field as a function of T and d were performed at all. It is clear from general considerations that with decreasing T the position of the step caused by the appearance of the DSE should shift on the $\sigma(d)$ curve towards larger thicknesses (larger mean free paths). Experiment has shown (Fig. 6) that the position of the step does not change when the temperature decreases from 4.2 to 1.3 °K. It is possible that with decreasing temperature there will appear, besides the DSE due to electrons, also a DSE due to holes, since the intravalley mean free path of the holes at 1.3 °K is estimated at ~1 mm[17] and l_{intra} of the electrons exceeds the maximum sample thickness.

From Gorkun's calculations[22] it follows that the step and the second plateau on the $\sigma(d)$ can certainly not be observed in the case when the probability of intervalley scattering from the surface becomes comparable with the probability of the intervalley scattering of the electrons in the volume; the shapes of the $\sigma(d)$ curves of many-valley and single-metals[23] are similar. This provides an upper-bound estimate of the probability w of the intervalley scattering from the surfaces of the investigated samples. Inasmuch as in all the cited experiments[1-6,10] and in our investigations the second plateau is observed at $d\approx 2.5$ mm, it follows from the foregoing arguments that at $T=4.2$ °K the probability of the intervalley scattering by the surface is $w\leq 0.1$: the recombination of the carriers on the surface can be neglected if $l_{\text{inter}}\ll d/w$. Assuming as an estimate $d/w\geq 3l_{\text{inter}}$, we obtain $w\leq 2.5/3l_{\text{inter}}=2.5/3\times 10\approx 0.1$ (estimates in other papers give $w=0.3$[6] and $w=0.01$[4]).

The diffusion effect can influence not only the plot of $\sigma(d)$ at a constant temperature, but also the temperature dependence of the resistivity of the samples below 7 °K, inasmuch as the ratios $l_{\text{inter}}/l_{\text{intra}}$ and L/d increase with decreasing temperature. As already noted, the conductivity of bismuth is decreased by the DSE at most by a factor 2.5. If the temperature dependence of $\rho(T)$ in the interval $1.3\leq T\leq 4.2$ °K is assumed to be quadratic throughout, i.e., if we write $\rho(T)=bT^2$, then the coefficient b can be charged with decreasing d, as a result of the DSE, but at most a factor of 2.5. For the described sample, the ratio of the resistivities on the plateau at $T=4.2$ °K is ~1.3, i.e., the expected change of the coefficient b with changing dimension is also 1.3, in agreement with experiment; when the thickness d changes by a factor of six b increases from 0.0067 to 0.0086 $\mu\Omega$-cm/°K^2.

The manifestation of the diffusion effect in the resistivity at helium temperatures can be described also by another method, assuming that the change in the ratios of the lengths and the thicknesses is accompanied by change of not the coefficient b but of the exponent, i.e., by writing $\rho(T)=bT^n$. In the interval 1–5 °K, allowance for the DSE leads to a change of n by at most from 2 to 1.4 times, and for the described sample from 2 to 1.8 times. This explains why, in spite of the existence of size effects, the temperature dependence of the resistivity of samples of various grades and dimensions are close at helium temperatures—in fact, the DSE manifests itself in the electric conductivity of bismuth as a small increment to the usual size-effect dependence.[23]

5. CONCLUSION

Introduction of the effective intravalley (l_{intra}) and intervalley (l_{inter}) mean free paths of the electrons, which differ at helium temperatures, makes it thus possible to explain from a unified point of view the temperature dependence of the electric conductivity of bismuth in a wide temperature interval, the singularities observed at helium temperatures in the size-effect dependences of the electric conductivity of bismuth samples with thickness on the order of 0.1–0.6 cm, as well as the appearance of a size-dependent transverse electric field at helium temperatures.

Simultaneous measurements of the temperature and size-effect dependences of the electric conductivity and of the transverse field on one and the same single crystal provide in principle three independent sets of data which make it possible to calculate the bulk electron transport lengths and the probability of intervalley scattering from the sample surface. Exact numerical estimates call for computer calculations, inasmuch as in a perfect bismuth crystal at $T<5$ °K the value of l_{intra} is comparable with the thickness of the actually investigated sample. However, as shown by our experiment, a number of results can be obtained even with a qualitative approach. This is all the more of interest, since the effective bulk electron transport length of intervalley electron-phonon scattering could not be theoretically calculated or directly measured to this day. According to estimates, the probability of the intervalley scattering of the electrons from the surface of an etched crystal at $T=4.2\,^\circ$K is small, $w<0.1$. It is clear that the probabilities of the intervalley and intravalley scattering can also differ strongly in carrier scattering by point defects (impurity atoms, vacancies) or line defects (dislocations). We have attempted to study the size-effect dependences of the electric conductivity of perfect crystals deformed by flexure, but it turned out that when these crystals are heated to room temperature they become partially annealed, and this makes it impossible to obtain reproducible results. It is of interest to carry out a similar cycle of measurements of the electric conductivity of weakly-doped bismuth crystals, since, as in the case of electron-phonon scattering, no theoretical calculations of the probability ratios of the intervalley and intravalley scattering by defects have been published as yet.

The authors thank É. I. Rashba for numerous discussions of the presented material and for useful remarks, V. N. Kopylov, V. Ya. Kravchenko, and V. F. Gantmakher for help and their useful discussions, and A. N. Lokhov and V. N. Khlopinskiĭ for technical help.

APPENDIX

Knowing the values of the transport lengths l_{intra} and l_{inter} we can, in principle, determine the matrix elements corresponding to the intravalley and intervalley scattering of electrons. The probability of the scattering of an electron by phonons, i.e., the collision frequency, (see, e.g., [24], formulas (6) and (38)) can be expressed in the form

$$\nu(k)=\frac{1}{(2\pi)^2\hbar}\int\frac{dS_q}{(\nabla E)_{k'}}M^2(k,q)\,\Phi\left(\frac{E}{T},\frac{\varepsilon}{T}\right), \tag{1}$$

where M is the matrix element of the probability of the electron scattering by a phonon; E, ε, and k, q are the energies and wave vectors of the electron and phonon; dS_q is an area element in q-space. In the simplest case, the square of the matrix element ([24], formula (5)), is

$$M^2(k,\ q)=\hbar q\Delta^2/2\mu s, \tag{2}$$

where Δ is the deformation potential, s is the average speed of sound, and μ is the mass per unit volume. Using the fact that in bismuth at $T\gtrsim 1\,^\circ$K the total cross section for the scattering of electrons by phonons coincides with the transport cross section, i.e., $l_{\text{inter}}/l_{\text{intra}}=\nu_{\text{intra}}/\nu_{\text{inter}}$, we estimate the ratio of the deformation potentials Δ_{intra} and Δ_{inter} for the intra- and intervalley scattering.

As shown by Gantmakher in[24] (formula (40)), at helium temperatures the probability of the intravalley electron-phonon scattering in bismuth is

$$\nu_{\text{intra}}\approx\frac{\pi}{3}\frac{m_c\Delta_s{}^2_{\text{intra}}(kT)^3}{\mu\hbar^4 s^3}\,. \tag{3}$$

The probability of intervalley scattering at the same temperatures can be written in the form

$$\nu_{\text{inter}}=\frac{2\pi}{\hbar}\frac{dn}{d\varepsilon}\frac{\hbar q(\theta_1)\Delta^2_{\text{inter}}}{2\mu s}\frac{\theta_1}{T}\cdot 2\exp\left(-\frac{\theta_1}{T}\right) \tag{4}$$

(formula (41) in[24], in which $\int ds_q/(\nabla E)_k$ is replaced by the density of states on the Fermi surface estimated from the specific heat[25]: $\int dS_q/(\nabla E)_k=4\pi^2 dn/d\varepsilon$, $dn/d\varepsilon=10^{20}$ eV^{-1} cm^{-3}). In these formulas m_c is the cyclotron mass in the section perpendicular to the direction of the largest momentum of electron ellipsoid, $q(\theta_1)$ is the wave vector of the phonon participating in the intervalley transfer, $\theta_1\approx 35\,^\circ$K in accordance with the estimates of l_{inter} and ν_{inter} (formula (4)). At $T=4\,^\circ$K, the ratio is

$$\frac{\nu_{\text{intra}}}{\nu_{\text{inter}}}=\frac{l_{\text{inter}}}{l_{\text{intra}}}=\frac{4.3\cdot 10^{-4}e^{35/4}}{1.9/16}\approx 23.$$

Substituting in (3) and (4) the numerical values, we obtain $\Delta_{\text{inter}}/\Delta_{\text{intra}}\approx 3$. Assuming that at helium temperatures in intravalley scattering the energies of the phonons interacting with the electrons are $\sim 1\,^\circ$K, we obtain

$$\frac{M_{\text{inter}}}{M_{\text{intra}}}\approx\frac{\Delta_{\text{inter}}}{\Delta_{\text{intra}}}\left(\frac{q(35K)}{q(1K)}\right)^{1/2}\approx 18.$$

1) The initial crystal was also changed. The samples were prepared of Bi-000 manufactured by the Chimkent lead plant.

2) It is assumed here that the intravalley scattering of the electrons by the surface of the etched (matte) sample is practically diffuse. According to estimates in[5,18], the coefficient of specular reflection from a mirror-smooth surface of the initial crystal after zone melting in deep vacuum exceeds 0.3 for intravalley electron scattering.

3) As will be shown later on, the influence of the diffusion size effect on the temperature dependence of the resistivity is small even at helium temperatures and is practically insignificant at higher temperatures when the lengths l_{intra} and l_{inter} become comparable in magnitude.

1. N. Garcia and Yi Kao, Phys. Lett. **26A**, 373 (1968).
2. J. E. Aubrey and C. J. Creasey, J. Phys. C **2**, 824 (1969).
3. A. N. Friedman and D. H. Koenig, IBM J. Res. Dev. **4**, 158 (1960).
4. T. Hattori, J. Phys. Soc. Jap. **23**, 19 (1967).
5. V. N. Kopylov and L. P. Mazhov-Deglin, Zh. Eksp. Teor. Fiz. **65**, 720 (1973) [Sov. Phys. JETP **38**, 357 (1974)].
6. Yu. A. Bogod and V. B. Krasovitskiĭ, Fizika kondensirovannogo sostoyaniya, FTINT AN USSR, 1974, vyp. XXX, p. 11.
7. E. I. Rashba, Zh. Eksp. Teor. Fiz. 48, 1427 (1965) [Sov. Phys. JETP **21**, 954 (1965)]; V. Ya. Kravchenko and É. I. Rashba, *ibid.* **56**, 1713 (1969) [**29**, 918 (1969)].
8. R. N. Zitter, Phys. Rev. Lett. **14**, 14 (1965).
9. L. P. Mezhov-Deglin and V. N. Kopylov, Prib. Tekh. Eksp. **1**, 230 (1975).
10. I. N. Zhilyaev and L. P. Mezhov-Deglin, Pis'ma Zh. Eksp. Teor. Fiz. **19**, 461 (1974) [JETP Lett. **19**, 248 (1974)].
11. A. N. Friedman, Phys. Rev. **159**, 533 (1967).
12. R. Hartman, Phys. Rev. **181**, 1070 (1969).
13. V. Chorpa, R. K. Ray, and S. M. Bhagat, Techn. Report Univ. Maryland, 1970.
14. E. W. Fenton, J. P. Karlsson, and R. Singler, Phys. Rev. **184**, 663 (1969).
15. A. A. Lopez, Phys. Rev. **175**, 923 (1968).
16. S. M. Cheremisin, Zh. Eksp. Teor. Fiz. **65**, 1564 (1973)

[Sov. Phys. JETP 38, 779 (1974)].
[17]E. S. Medvedev, V. N. Kopylov, and L. P. Mezhov-Deglin, Fiz. Nizkikh Temp. 1, 1192 (1975) [Sov. J. Low Temp. Phys. 1, 572].
[18]V. S. Tsoĭ, Zh. Eksp. Teor. Fiz. 68, 1849 (1975) [Sov. Phys. JETP 41, 927 (1975)].
[19]V. F. Gantmakher and Yu. S. Leonov, Pis'ma Zh. Eksp. Teor. Fiz. 8, 264 (1968) [JETP Lett. 8, 162 (1968)].
[20]V. S. Édel'man, Doctoral dissertation, Inst. of Semicond. Phys., 1975.
[21]Yu. I. Gorkun and E. I. Rashba, Fiz. Tverd. Tela 10, 3053 (1968) [Sov. Phys. Solid State 10, 2406 (1969)].
[22]Yu. I. Gorkun, Ukr. Fiz. Zh. 16, 657, 1609 (1971); 18, 742 (1973).
[23]K. Fuchs, Proc. Cambridge Phil. Soc. 34, 100 (1938).
[24]V. F. Gantmakher, Rep. Prog. Phys. 37, 317 (1974).
[25]H. K. Collan, M. Krusius, and G. R. Pickett, Phys. Rev. [B] 7, 2888 (1970).

Translated by J. G. Adashko

Nonlinear relaxation effects in paramagnetic substances

V. V. Isaev-Ivanov, V. A. Ryzhov, and V. N. Fomichev

Nuclear Physics Institute, USSR Academy of Sciences, Leningrad
(Submitted June 24, 1975)
Zh. Eksp. Teor. Fiz. 70, 983–991 (March 1976)

An analysis is made of the possibility of using nonlinear effects in the magnetization of paramagnets for investigating paramagnetic centers. The existence of new nonlinear effects is postulated: these are due to the known dependence of the relaxation time on the external magnetic field. An analysis of the case of two parallel magnetic fields shows that the magnitude of the effect (ratio of the magnetizations at the doubled and fundamental frequencies) may reach 20% even in fields of the order of 100 Oe. A description is given of apparatus constructed for detection and measurement of these nonlinear effects. The experiments carried out using this apparatus demonstrated the existence of strong nonlinear effects in weak magnetic fields and confirmed the assumption of a high sensitivity of the nonlinear effect method in investigations of paramagnetic substances.

PACS numbers: 75.20.–g

INTRODUCTION

It is well known that there are quite a few experimental situations in which fundamental and technical difficulties make it impossible to realize fully the high sensitivity and information potential of the ESR method. Other methods for investigating paramagnetic substances such as measurements of the magnetic susceptibility[1] and the Gorter method[2] suffer from a low sensitivity and, therefore, their usefulness is limited.

It follows from this statement that it would be extremely useful to develop new methods for investigating paramagnetic substances, particularly those that would give information unattainable by the ESR method and would have a sensitivity comparable with that of ESR spectroscopy, at least in some situations. The solution may lie in the adoption of methods based on various nonlinear effects in paramagnetic substances. It can be shown[3] that if the nonlinearity coefficient in the magnetization of a paramagnet in a harmonic rf field of amplitude $H_1 = 50$–100 Oe reaches 10%, the sensitivity of the method of measuring higher harmonics of the magnetization becomes equal to the sensitivity of the ESR method in which the ESR absorption line width is ~10 Oe.

We shall now review briefly possible nonlinear effects.

1. The nonlinear effects due to the nonlinearity of the magnetization curve of paramagnets are strong only in high fields at low temperatures or if optical pumping is used.[4]

2. The nonlinear effects resulting from saturation of paramagnetic resonance transitions[5] appear when not only allowed but also forbidden transitions become saturated.[3]

3. There are also nonlinear adiabatic effects observed on adiabatic magnetization of substances with high concentrations of paramagnetic particles.[3,6]

4. The nonlinear relaxation effects[3] should exist if the well-known dependence of the relaxation times T_1 and T_2 on the intensity of an external static magnetic field applies also to the instantaneous amplitude of an external alternating field.

In the case of a paramagnetic particle of spin $S=\frac{1}{2}$ in a liquid whose Hamiltonian is

$$\hat{\mathcal{H}}=\beta H(t)\,[\,(\Delta g\cos^2\theta+g_\perp)\hat{S}_z+\Delta g\cos\theta\sin\theta\cdot{}^1\!/_2(\hat{S}_+e^{-i\varphi}+\hat{S}_-e^{i\varphi})\,], \quad (1)$$

the application of nonstationary perturbation theory and the assumption that

$$\Delta g=g_\parallel-g_\perp\ll g_\perp,\quad H(t)=H_0+H_1\sin\omega t,$$
$$g_\perp\beta/\hbar=\gamma,\quad \gamma H_1/\omega<1$$

and that the stationary correlation function is $G(\tau)=G(0)\exp(-|\tau|/\tau_c)$, gives,[3] in the first order of smallness of $1/T_1$:

$$\frac{1}{T_1(t)}=\frac{4\beta^2\Delta g^2\tau_c G(0)}{\hbar^2}\left\{\frac{H_0^2}{1+(\gamma H_0\tau_c)^2}\right.$$