TEMPERATURE DEPENDENCE OF THE ELECTRON AND HOLE MEAN FREE PATHS IN ANTIMONY

V. F. GANTMAKHER and V. T. DOLGOPOLOV

Institute of Solid State Physics of the U.S.S.R. Academy of Sciences

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The temperature dependences of the mean free paths for electrons and holes in antimony are measured separately on the basis of the amplitudes of the radio frequency size effect lines. In both cases the temperature-dependent part of the path was found to be proportional to $T^{-2}$, the proportionality coefficient for holes being three times greater than that for electrons. It is shown that if the Fermi surface resembles a long, narrow cylinder, the term quadratic with respect to temperature in the carrier scattering probability may be ascribed to interaction between electrons and phonons and that it is precisely this case which is encountered in bismuth and antimony. The magnitudes of the deformation potentials in antimony are estimated for both electrons and holes.

So far there is rather little information concerning the connection between the cross section for scattering of electrons in a metal and their position on the Fermi surface. Kinetic processes widely used for the investigation of electron relaxation times, such as electric or thermal conductivity, are determined by quantities averaged over the entire Fermi surface. At the same time, there already exist methods for separating and investigating individual groups of carriers in a metal. Such methods include, in particular, the measurement of the amplitude of the lines of the radio frequency size effect (SE). The SE line is formed by electrons located in the vicinity of a definite extremal section of the Fermi surface. Therefore the line amplitude is determined by the probability of scattering of precisely these electrons.

The purpose of the experiments described here was to compare the cross sections for the scattering of the carriers of both types by phonons, using one sample of antimony (in one experiment), by measuring the temperature dependence of the amplitude of the SE lines from the electronic and hole parts of the Fermi surface.

EXPERIMENT

An antimony sample in the form of a disk of thickness $d = 0.32$ mm and diameter 10 mm was grown from the melt in a dismountable quartz mold. The initial material was antimony with a resistance ratio $R_{	ext{room}}/R_{4.2}$ $\approx 2700$. The angles between the normal to the plane of the sample and the axes $C_1$ and $C_2$ were $46^\circ10'$ and $44^\circ20'$. The experiments were performed in the temperature range from 1.1 to 4.2 $\text{K}$. The amplitudes of the SE lines were measured on the plots of the derivatives, with respect to the magnetic field, of the imaginary part of the surface impedance, $\delta X/\delta H$ or $\delta^2 X/\delta H^2$, at a frequency 12.5 MHz. We used the usual modulation procedure for the measurements—see, for example, (1). To record the second derivative, the detecting part of the apparatus was tuned to a frequency equal to double the modulation frequency.

A considerable line width ($\Delta H/H \approx \delta/d \approx 15\%$; $\delta =$

FIG. 1. Sample plots of SE lines for antimony. The left line in the lower plots pertains to the hole ellipsoid, for which $\psi = 30^\circ$, and the right one to the electronic ellipsoid, which lies in the plane of the sample ($\xi = 37^\circ$). The arrows show the value chosen for the line amplitude in this plot.

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urements of the free paths, we used a quadratic model with the following values of the principal semiaxes of the ellipsoids and cyclotron masses at the minimal cross sections (\(k\) is in \(\text{cm}^{-1}\)):

\[
\begin{array}{cccc}
\text{Holes:} & 10^{-7} k_1 & 10^{-7} k_2 & 10^{-7} k_3 \\
\text{Electrons:} & 0.22 & 0.45 & 1.4 \\
\end{array}
\]

Since the electron can, generally speaking, execute several revolutions on the trajectory, it is more accurate to write in place of (1) the sum

\[
A(T) = C \sum_{\text{val}} e^{-\eta T} = C(e^{\eta T} - 1) = C[\eta \exp(\pi d T^2/2\beta) - 1]^{-1},
\]

where \(C = A(0) (\eta = 1)\) and \(\eta = \exp(\pi d/2l_0)\). From (3) we obtain the expression

\[
\ln \left(\frac{C}{A(T)} + 1\right) = \frac{\pi d}{2l_0} + \frac{\pi d}{2\beta^{-1} T},
\]

in which, unlike in (1), the logarithm contains the parameter \(C\), defined by the value of \(l_0\). A reduction of the experimental data by means of formula (4), even with \(C\) corresponding to \(l_0 = 0.3\ \text{mm}\), did not lead to a change of the exponent \(n\). The coefficient \(\beta\) increased at this value of \(C\) by 15%. Larger values of \(l_0\) have low probability, since no SE was observed on samples 0.5 mm thick, made of the same material, down to the lowest temperatures.

**DISCUSSION**

Since the experimentally obtained degree \(T^2\) is characteristic of the contribution of electron-electron scattering, we first make some estimates of the probability of the electron-electron collision.

To this end we use the formula for the differential cross section for the scattering of an electron from the state \(k\) to the state \(k'\) by a screened potential in the form \(U(r) = (e^{2r/\kappa}) \exp -gr\) (\(\kappa\) is the static dielectric constant and \(g^{-1}\) the Debye radius; see [41] Ch. 6):

\[
d\sigma = \frac{2\pi m^2}{\hbar^2} \left(\|k - k'\|^2 + g^2\right)^{-1}.
\]

If it is recognized that the Fermi wave vector is \(k_F \approx g\) both for an ordinary metal (\(k_F \approx g \approx 1/a\), where \(a\) is the interatomic distance) and for a semimetal (in bismuth \(k_F \approx g \approx 100/a\), and in antimony \(k_F \approx g \approx 10/a\)), then the total scattering cross section at \(k = k_F\) is expressed in terms of the Fermi energy \(\epsilon_F\):

\[
\sigma = 10\pi \left(\frac{m^2}{\hbar^2}\right) \left(g(4g^2 + g^2)^{-1} \approx \left(\frac{\epsilon_F}{\kappa \epsilon_F}\right)^2
\]

Multiplying by the number of scatterers, taking into account the limitations imposed by the Pauli principle on the possible collisions in the electron gas, we obtain for the free path \(l_{ee}\)

\[
l_{ee} \approx \sigma \frac{4}{N_e} \left(\frac{\partial N_e}{\partial \epsilon}\right)^2 (k_B T)^{\frac{3}{2}}, \quad l_{ee} \approx \frac{N_e}{\hbar \epsilon_F} \left(\frac{\partial N_e}{\partial \epsilon}\right)^{\frac{3}{2}} (k_B T)^{\frac{3}{2}},
\]

\(N_e\) is the total number of electrons per unit volume and \(k_B\) is Boltzmann's constant).

For antimony, \(N_e = 10^{20}\ \text{cm}^{-3}\), \(\partial N_e/\partial \epsilon \approx 10^{38}\ \text{erg}^{-1}\ \text{cm}^{-3}\), \(k_B \approx 100\) [65] and \(l_{ee} \approx 10/T^2\). We see therefore that the coefficient of \(T^2\) exceeds by 10 times the corresponding value from our measurements of \(l_T\). Furthermore, as is known from calculations for sodium, the estimate obtained for \(l_{ee}\) from (6) is underestimated by several times because of numerical factors. The entire further discussion will therefore be devoted to electron-phonon interaction.

For an isotropic electron dispersion law, the value of \(l_T\) measured with the aid of the SE and determined...
by the scattering of the electrons by the phonons should be proportional to
\[ l_r \propto T^{-1} \text{ for } q_r / k_r \ll 1, \]
\[ l_r \propto T^{-1} \text{ for } \delta / d \ll q_r / k_r \ll 1 \]
(8)

\[(q_T = k_B T / h), s \text{ is the speed of sound; depending on the type of the SE, the inequalities (7) and (8) may contain other expressions in lieu of } \delta / d \text{--for details see }^{(22)}, \]
\[ l_r \propto T^{-1} \text{ for } q_r / k_r \gg 1 \]

(the high-temperature case; under these conditions, however, the SE is no longer observed).

In (8) and (9), the measured value of \( l_T \) is the true path length traversed by the electron between two collisions with phonons (\( l_T = l_{e, ph} \)). Of course, the experimentally obtained relation \( l_T \propto T^{-2} \) can be regarded as a transition from (8) to (9), since at 4° K \( q_T \approx 0.3 \times 10^7 \text{ cm}^{-1} \) in antimony (compare with the values of \( k_T \) listed in the table above). However, as indicated in \(^{(19)}\), in the case of a sharply anisotropic electron dispersion law the relation \( l_T \propto T^{-2} \) should be obtained in a definite rather broad temperature interval.

Indeed, we shall use a model in which the probability of scattering of an electron with a wave vector \( K \) is given by the expression
\[ \frac{v}{l_{sa}} = \frac{\Delta^2}{8\pi^2 N M_s} \left\{ \left( n_q \frac{(1 - f_{q, 0})}{(1 - f_{q, 0})} \Delta (\epsilon_q + h q_s - \epsilon_{q, 0})ight) + (n_q + 1) (1 - f_{q, 0}) \Delta (\epsilon_q - h q_s - \epsilon_{q, 0}) \right\} dq. \]

(10)

Here \( \Delta \) is the deformation potential, \( M \) the mass of the lattice ions, \( N \) the number of atoms per unit volume, \( v \) the electron velocity, and \( n_q \) and \( f_{K+q} \) are the occupation numbers for the phonons and electrons; the two terms in the square brackets take into account respectively the absorption and production of the phonon, the integration is carried out over all wave vectors \( q \), and the \( \delta \) function ensures satisfaction of the conservation laws (see \(^{(4)}\), Ch. 5). The deformation potential, generally speaking, is a tensor quantity: \( \Delta_{ij}(K) \). In our experiments, however, we measured the total scattering of the electrons by phonons of all polarizations, and the effect of the action of different phonons was automatically averaged. It is therefore natural to regard \( \Delta \) as a scalar quantity and to take it outside the integral sign in (10). The averaging of \( \Delta \) over \( K \) occurs along the orbit of the electron in \( k \)-space, and therefore, naturally, \( \Delta^{se} \neq \Delta^0 \).

Let the Fermi surface be an infinite circular cylinder of radius \( K \) and, as always at low temperatures, let the conditions \( \langle K \rangle \gg h q_s \) and \( V_F \gg s \) hold. Owing to the conditions of inequality, the distance \( \Delta k \) between two equipotential surfaces \( \epsilon \) and \( \epsilon + h q_s \) in \( k \)-space is \( \Delta k = q_s / v \ll q_s \), and it can be assumed that the electron remains after scattering on the same surface. The region of integration in \( q \)-space in (10) reduces to a cylinder of the same radius \( K \), passing through the origin, with an axis parallel to the Fermi-cylinder axis. Indeed, the argument of the \( \delta \) functions is
\[ \epsilon_q \pm h q_s - \epsilon_{q, 0} = \pm h q_s - \frac{h^2}{2m} \left( \frac{q_s}{2K} \pm 2K \varphi \cos \varphi \right) \]
\[ \approx \frac{h^2 K_t}{m} \left( \frac{q_s}{2K} \pm \cos \varphi \right), \]
where \( q_s \) is that component of the vector \( q \) which is perpendicular to the cylinder axis, and \( \varphi \) is the angle between \( K \) and \( q_s \). Equating the expression in the parentheses in (11) to zero, we obtain precisely the equation of a cylinder.

Expression (10) in terms of the function \( f_K \pm q \) depends on the energy of the scattered electron, so that this expression must be averaged over the initial values of the electron energy along the normal to the Fermi surface. It is necessary to bear in mind here that the SE lines are formed only by the nonequilibrium electrons determined by the increment \( \Delta \) to the equilibrium distribution function \( f^{(0)} \). The value of \( \Delta \) is proportional, as is well known, to the derivative \( \partial f^{(0)} / \partial \epsilon \); the proportionality coefficient, which can be regarded as a constant near the Fermi surface during the course of integration along the normal to this surface, drops out upon normalization, so that it is necessary to make in (10) the substitution
\[ 1 - f_{q, 0} \rightarrow - \int \frac{\partial f^{(0)}}{\partial \epsilon} (1 - f_{q, 0}) dq. \]

The expression in the square brackets in (10) then goes over into
\[ [n_q (1 - f_{q, 0}) + (n_q + 1) (1 - f_{q, 0})] \rightarrow x^e (e^e - 1)^2, \]
\[ x = h q_s / k_B T, \]
and (10) is transformed into
\[ \frac{v}{l_{sa}} = \frac{\pi^2}{2\pi^2 N M_s h^2} \left( \frac{k_B T}{h^2} \right)^2 \int_0^\infty dy \int_0^\infty \frac{x^e dx}{(1 - y^2/x^2)^2}, \]
\[ y^2 = 2Q / T, \]
where \( Q = h K s / k_B \) is the characteristic temperature, which replaces in this problem the Debye temperature \( \Theta \).

If the cylinder is sufficiently thin so that
\[ T \gg Q, \]
then we obtain from (12)
\[ \frac{v}{l_{sa}} = \pi \Delta^2 \left( \frac{K}{q_s} \right) \left( \frac{T}{\Theta} \right)^2 = \frac{\pi \Delta^2 K^2}{6 \hbar^2 MN} \left( \frac{T}{Q} \right)^2, \]
(14)

(\( \Delta^2 = 6 \pi^2 N \) is the Debye wave vector). It is precisely this case which is realized in bismuth for electrons.\(^{(18)}\)

In the opposite limiting case \( T \ll Q \), we obtain the same formula as for the Fermi sphere:
\[ \frac{v}{l_{sa}} = \frac{9\pi}{20} \frac{\Delta^2}{h^2 M_s} \left( \frac{q_s}{q_s} \right)^2 \left( \frac{T}{\Theta} \right)^2 = \frac{3\pi}{20} \frac{\Delta^2 K^2}{h^2 M N} \left( \frac{T}{Q} \right)^2, \]
\[ \zeta(3) = 1.20. \]

(15)

For the intermediate region of temperatures, the integral in (12) was evaluated with a computer (see Fig. 3).

Antimony falls precisely in the intermediate region. In order for the experimental points to fall in the region \( l \propto T^{-2} \) on the curve of Fig. 3 (the right-hand side of the curve, corresponding to \( T/Q > 1 \)), it would be necessary to assume that the average sound velocity is \( s \approx 10^8 \text{ cm/sec} \). This contradicts the experimental data.\(^{(19)}\) It is more correct to assume the average value to be \( s \approx 2 \times 10^8 \text{ cm/sec} \). In this connection, we can note the following.

In the region \( T \approx Q \), a change takes place in the char-
I = /f{ir << lo. This can probably explain why in such temperatures the scattering by phonons prevails over the experimental results on semimetals as the de Haas–van Alphen impurity scattering, and the resultant mean free path it follows that near the points $k_{lmax}$ at helium temperatures.

The quantities $l_{e,ph}$ measured by us make it possible to calculate the constant $\Delta$. Putting in (14) $M_N = 6.7 g/cm^3$, $s = 2 \times 10^6 cm/sec$, $v^e_l = 5.8 \times 10^7 cm/sec$, $v^h = 6.7 \times 10^7 cm/sec$, and $K = 4.4 \times 10^6 cm^{-1}$, we obtain

$$|\Delta^e| = 2.9 eV, \quad |\Delta^h| = 1.9 eV.$$  

(16)

These values can be compared, first, with measurements of the deformation potential as determined from the amplitude of the quantum oscillations of sound absorption: $\Delta^e$ by averaging the squares of the diagonal elements of the tensor $\Delta_{ij}$, we obtain for electrons $\Delta \approx 4.1 eV$, while all that is known for holes is that the components of the tensor are smaller than those for electrons. Second, we note that the deformation potential obtained under the assumption $|\Delta^e| = |\Delta^h| = \Delta$ from measurements of the thermal conductivity of antimony amounts to 1.8 eV.\(^{(13)}\)

Violation of condition (13) makes it necessary to consider the experimental values (16) as approximate. However, in view of the fact that for electrons and holes in antimony the transverse dimensions of the ellipsoids are practically the same, and the difference between the dimensions of the long semiaxes in the investigated temperature interval is negligible, since $kT/hv \ll k_B$, the "geometric factor" connected with the integration is the same for electrons and holes. Therefore the inaccuracy of formula (14) and the uncertainty in the choice of $s$ should not affect the ratio $|\Delta^e|/|\Delta^h| = 1.5$.

This ratio permits another comparison with an independent experiment. According to\(^{(14,1)}\), hydrostatic compression increases the number of carriers: $\Delta N_e/N_e \approx 1\%$ per kbar. Assuming for estimating purposes

$$\frac{\Delta N_e}{N_e} = \frac{2}{B} \frac{\Delta^h - \Delta^e}{E},$$

where $E$ is the band overlap and $B$ is the bulk modulus of elasticity ($B \approx 400$ kbar), we obtain either $\Delta^e = -0.3 eV$ and $\Delta^h = 0.2 eV$ (the extrema shift in opposite directions at decreasing specific volume), or $\Delta^e = -1.6 eV$ and $\Delta^h = -1.0 eV$ (both extrema shift downward). The second assumption agrees much better with (16).

A similar analysis can also be carried out with respect to the results of\(^{(6)}\) for bismuth. Although the $l_{ee}$ calculated from (6) differs much less from the mean free path $l_T$ measured in\(^{(6)}\) for electrons, there is every reason for assuming that in bismuth the temperature independence of the temperature-dependent part of the resistivity of semimetals in the corresponding temperature range. Indeed, in\(^{(10,11)}\) a quadratic dependence into the region of low temperatures.

Inasmuch as under the condition $T \geq Q$ each act of scattering by a phonon leads to a change of the electron momentum by a large angle, formula (14) can be used directly to calculate the quantity $l_T$ which enters in the electric resistivity of semimetals in the corresponding temperature range. Indeed, in\(^{(10,11)}\) a quadratic dependence of the temperature-dependent part of the electric resistivity of antimony on $T$ was observed in the region from $1.5 K$ to hydrogen temperatures.

Let us note one peculiarity of electron-phonon scattering. As seen from formulas (12), (14), and (15), $l_{e,ph}$ $\propto v^2$. Since the velocity along the principal directions of the ellipsoid is $v^2 = v^l_1 \approx k^2$, the mean free path $l_{e,ph}$ for electrons located near the major semiaxes turns out to be much smaller than near the minor ones. For electrons in bismuth, for example, where $k_{max}/k_{min} \approx 14$, the ratio $l_{e,ph}^{max}/l_{e,ph}^{min}$ reaches 200. In antimony this ratio is approximately 30 for electrons and 10 for holes. (These, of course, are only estimates, since no account was taken of either the anisotropy of the phonon spectrum or of the dependence of the integration region in (12) on $k$.) The values of $l_{e,ph}$ measured by us for antimony, and also in\(^{(6)}\) for electrons in bismuth, pertain to carriers with minimum values of the momentum within the limits of the given ellipsoid, i.e., close to $l_{e,ph}^{max}$.

Little is known concerning the anisotropy of $l_0$. From numerical estimates for the averaged value of $l_0$ it follows that near the points $|k| = k_{max}$ at helium temperatures the scattering by phonons prevails over the impurity scattering, and the resultant mean free path $l \approx l_{e,ph}^{min} < l_0$. This can probably explain why in such experiments on semi metals as the de Haas–van Alphen

FIG. 3. The double integral $I$ in expression (12) as a function of the parameter $T/Q$. The vertical dashed lines show the measurement regions for antimony and bismuth, respectively. The scale corresponds for antimony to the sound velocity $s = 2 \times 10^6 cm/sec$, and for bismuth to $s = 1.5 \times 10^5 cm/sec$. Effect, cyclotron resonance, or the size effect it is very difficult to observe the sections that pass through the major semiaxes of the Fermi ellipsoids.

Thus, it is quite probable that at helium temperatures $l_0 < l_{e,ph}$ for some carriers and $l_0 > l_{e,ph}$ for others. Under these conditions, strictly speaking, the electric resistivity cannot be subdivided into residual and ideal components, since the Matthiessen rule does not hold. It is therefore very difficult to compare our coefficients in (2) with the results of measurements of the electric resistance, and no great significance should be attached to the rather good agreement between our coefficients in (2) and the coefficient obtained from the data of\(^{(10,11)}\) from the quadratic term $\rho_T$ in the resistance in accordance with the formula $\rho_T = hK/N_e e^\omega \rho_T$.
Electron and hole mean free paths in antimony

Electron and hole mean free paths in antimony is determined by electron-phonon collisions. This is confirmed, in particular, by the character of the dependence of the coefficient of the temperature-dependent part of the electric resistivity on the carrier density in bismuth-antimony alloys. The data of reduced in accordance with formula (14) lead to \( \Delta_{\text{el}}^B = 2.6 \text{ eV} \), whereas the diagonal elements of the tensor \( \Delta_{ij} \) for bismuth yield \( \Delta_{B1} = 3.8 \text{ eV} \).

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