Electron velocities in bismuth and antimony

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Fermi velocities of the current carriers in bismuth and antimony in three crystallographic planes are determined by measuring the angular dependence of longitudinal sound attenuation at 500 and 825 MHz in an inclined magnetic field. The experimental Fermi velocity values for bismuth are in good agreement with those calculated with assumption of a parabolic energy band and are consistent with other data. Velocities on the electron Fermi surface of antimony can be satisfactorily described by an empirical model based on de Haas–van Alphen and cyclotron-resonance data. The experimental velocity distribution on the antimony electron Fermi surface is used to estimate the density of states, $v(\epsilon) = 0.112 \times 10^{-33}$ cm^{-3} erg^{-1}.

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Many studies have been made of the energy spectrum of carriers in bismuth and antimony. The most detailed information has been obtained by means of the de Haas-van Alphen effect,[1-4] cyclotron resonance,[5,6] radio-frequency size effect,[7] and magnetoacoustic measurements.[8-10] Data from these investigations have permitted determination of the extremal diameters and the areas of the extremal sections of portions of the Fermi surface, the cyclotron masses of the carriers, and the Fermi energy ϵ_F. However, up to the present time there have been no direct experimental measurements of the Fermi velocities of carriers in bismuth and antimony over a wide range of directions. Since the electron velocity on the Fermi surface $v_F = \partial\epsilon/\partial p$ is a local function of momentum extremely sensitive to the shape of the Fermi surface, study of the anisotropy in the velocities is of considerable interest.

The Fermi velocity of current carriers can be determined directly from experiments on damping of magnetoplasma waves and from the tilt effect. The latter was first observed by Reneker,[11] who noted a rapid rise of the sound absorption coefficient on deviation of the magnetic field vector **H** by a small angle from the direction $\mathbf{q} \cdot \mathbf{H} = 0$ (**q** is the sound wave vector). This phenomenon, also known as the fork effect, is due to absorption of sound by electrons from the vicinity of the elliptical inflection point and permits determination of the electron velocities at this point.[12] At some critical deviation angle

$$\varphi_{cr} = \arcsin(s/v_{H\ max}) \tag{1}$$

a group of carriers from the vicinity of the inflection point on the Fermi surface appears which is moving with the maximum velocity $v_{H\ max}$ in phase with the wave and which efficiently absorbs the energy of the wave (s is the velocity of sound). Observation of the effect is possible for the conditions $qR \ll 1$, $\omega\tau \gg 1$ (R is the cyclotron radius of the electron orbit, τ is the relaxation time). It is possible to measure v_F experimentally only for metals with a small Fermi energy and also for anomalously small groups of carriers in ordinary metals.

In the present work we report measurements of the Fermi velocities of the carriers in bismuth and antimony.

METHOD OF MEASUREMENT

The samples for the measurements were cut with a spark cutter from single crystals obtained by zone re-fining. The initial material was characterized by a resistivity ratio $R_{300}/R_{4.2} = 300$ for bismuth and $R_{300}/R_{4.2} = (5-6) \times 10^3$ for antimony.[1] The direction of the crystallographic axes was determined by means of an optical goniometer with an accuracy of 1°. Finishing of the samples to the required plane parallel shape within 1' of arc was accomplished by fine abrasives; in this process this surface layer was disturbed to a depth of about 0.1 mm, which amounted to less than 20% of the sample thickness. The experiments were carried out at a temperature of 1.6 K at longitudinal sound frequencies of 500 and 825 MHz. Plate transducers of LiNbO$_3$ with a fundamental frequency of 165 MHz were used to excite the oscillations. Curves of $\partial\Gamma(\varphi)/\partial\varphi$ were recorded symmetrically relative to the direction $\mathbf{q} \cdot \mathbf{H} = 0$, which avoided errors due to inaccurate adjustment of the sample in the cryostat. Where the wave vector of the sound deviated from the rotation axis of the main magnetic field when the condition $\mathbf{q} \cdot \mathbf{H} = 0$ was satisfied, a compensating field **h** directed along the principal rotation axis was introduced:

$$h = \pm H \, \text{tg} \, \theta \cos \psi. \tag{2}$$

where θ is the angle between **q** and the magnetic field rotation axis, and ψ is the angle of rotation of the principal magnetic field relative to the projection of **q** on the plane of rotation of the field.

The experimental apparatus has been described in detail previously.[13]

EXPERIMENTAL RESULTS

The experimental method used permits determination of the angular position of the inflection point on the curve of the absorption coefficient Γ as a function of the angle of inclination of the magnetic field **H** with respect to the sound wave vector. As shown by us previously,[14] for $\omega\tau \gg 1$ the angular position of the inflection point φ_0 on the curve $\Gamma(\varphi)$ coincides to a high degree of accuracy with the value φ_{cr}.

Measurement of the angles φ_0 was carried out for three orientations of the sound wave vector relative to the crystallographic axes of bismuth and antimony. Here and subsequently X, Y, and Z are respectively the binary, bisector, and trigonal axes of the crystal.

1. $\mathbf{q} \parallel X$. Here the projection of the Fermi velocities of the carriers on the plane YZ was obtained.

2. $\mathbf{q} \parallel Y$. This orientation permits determination of the projection of the velocities on the plane XZ.
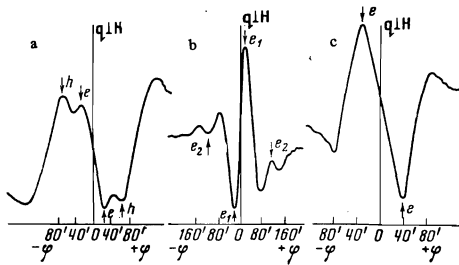
FIG. 1. Examples of recordings of the derivative of the sound absorption coefficient as a function of the angle of inclination of the magnetic field for three crystallographic directions in antimony: a) q∥Z, H∥X; b) q∥Y, H∥X; c) q∥X, H∥Z. The indices e and h respectively mark resonance peaks due to sound absorption by electrons and holes.
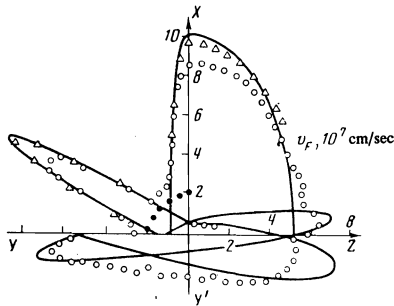

FIG. 2. Anisotropy of Fermi velocities of carriers in bismuth in three crystallographic planes. Points—experiment: ○—electrons, ●—holes, △—velocity values with correction for finite value of $\omega\tau$; curve—calculation in the quadratic approximation of the dispersion law.

3. $q \parallel Z$. In this case the projection of the velocities on the XY plane is measured.

The characteristic appearance of the function $\partial\Gamma(\varphi)/\partial\varphi$ for bismuth in three crystallographic planes is shown in Fig. 1. In Figs. 1a and b, two peaks are observed in the function $\partial\Gamma(\varphi)/\partial\varphi$ which correspond to the resonance absorption of sound by two groups of carriers with different velocities in different portions of the bismuth Fermi surface. In Fig. 1c the difference of the velocities is insignificant and it is not possible to separate the contribution from the different carrier groups in the $\partial\Gamma(\varphi)/\partial\varphi$ curve. The shape of the experimental curves of $\partial\Gamma(\varphi)/\partial\varphi$ in antimony has a similar appearance. In the case $q \parallel X$ in bismuth and $q \parallel Z$ in antimony the projections of the velocities from the different portions of the many-valleyed Fermi surface apparently differ by no more than a factor of two for a given magnetic field direction, and therefore the observed function $\Gamma(\varphi)$ represents a certain averaging over the valleys.

In Figs. 2 and 3 we have shown polar diagrams of the measured Fermi velocities of the carriers in bismuth and antimony. Values of the velocity of sound for determination of v_F from Eq. (1) were taken from refs. 9 and 15 and are given in Table I.

DISCUSSION OF RESULTS

Let us compare the results obtained with existing models of the energy spectrum of bismuth. In the quadratic approximation of the dispersion law

$$\varepsilon = \frac{1}{2m_0}\left[\mathbf{p} \times \frac{1}{m}\mathbf{p}\right] \tag{3}$$

the electron velocity at the elliptical inflection point of

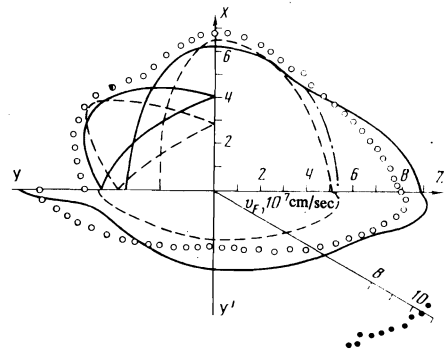FIG. 3. Anisotropy of Fermi velocities of carriers in antimony in three crystallographic planes. Points—experiment: ○—electrons, ●—holes; the solid curve is a calculation with the empirical model, the dashed curve is the quadratic approximation, and the dot-dash curve shows possible values of the velocities from the second inflection point of the electron Fermi surface.

TABLE I

	s, 10^5 cm/sec	
	Bi [15]	Sb [9]
s_X	2.62	3.85
s_Y	2.70	4.08
s_Z	2.02	2.58

the Fermi surface has the following form:

$$v_F = \left[\frac{2\varepsilon_F}{m_0}\left(\hat{n}\frac{1}{m}\hat{n}\right)\right]^{1/2}, \tag{4}$$

where m is the effective mass tensor and $\hat{n} = \mathbf{H}/|\mathbf{H}|$.

The velocity values calculated from Eq. (4) have been plotted in Fig. 2 as the smooth curves. The spectral constants for the calculations were taken from refs. 5 and 17.

A characteristic feature of the experimental data for bismuth is the systematic error in determination of the maximum velocity values in comparison with the theory and with the experimental results given elsewhere.[18-20] This can be explained as follows. As can be seen from Eq. (25) of ref. 14,

$$\frac{\Gamma}{\Gamma_\Lambda^{(0)}} = \frac{s}{v_F\sin\varphi}\Phi, \tag{5}$$

$$\Phi = \operatorname{arctg}\left[\omega\tau\left(\frac{v_F\sin\varphi}{s}-1\right)\right] + \operatorname{arctg}\left[\omega\tau\left(\frac{v_F\sin\varphi}{s}+1\right)\right],$$

for the condition $\omega\tau \gg 1$ the location of the inflection point on the $\Gamma(\varphi)$ curve practically coincides with the value $\varphi_{cr} = \arcsin(s/v_F)$. In our experiments, as shown by estimates made from the oscillations of the geometrical resonance, from the shape of the $\Gamma(\varphi)$ curve for the tilt effect, and also from measurements of the dispersion of the velocity of sound in an inclined field, the value of the parameter $\omega\tau \simeq 1.5$. A numerical calculation with Eq. (5) showed that this leads to a reduction in the values of the measured velocities by 15%. In the case where the function $\Gamma(\varphi)$ is a superposition of several curves, a correction of this type is difficult to make. We should also note the effect of averaging of the velocities over the belt on the Fermi surface for small $\omega\tau$, which becomes particularly important in the case of maximal velocities from the portions of the Fermi surface with small curvature. The values of the velocities with inclusion of a correction for the finite value of $\omega\tau$ are given in Fig. 2 by the triangles. Since the discrepancy between the experimentally measured velocities and the calculated values when the correction

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is included do not exceed the experimental error, we shall limit ourselves to the quadratic approximation of the dispersion law. Evidently for $\omega\tau > 10$ a velocity measurement with an accuracy 2—3% would permit a more detailed comparison with the real Fermi surface of bismuth.

For the orientation $\mathbf{q} \parallel \mathbf{Z}$, absorption peaks from the hole Fermi surface of bismuth are present in the $\partial\Gamma(\varphi)/\partial\varphi$ curve over the entire range of angles in the basal plane. The hole velocities in the basal plane are isotropic and according to the experimental data are $v_F^h = 2.1 \times 10^7$ cm/sec.

A theoretical calculation of the antimony energy spectrum[21] and also the data of several experiments[3,4,7] indicate a very substantial departure of the carrier spectrum from quadratic. Therefore for comparison of our experimental results with the data of other authors we attempted to use an empirical model based on the experimental data on anisotropy of the extremal areas[4] or diameters of the Fermi surface,[7,10] and also on measurements of the cyclotron mass in antimony.[6] The construction of this model was based on the conclusions of the Lifshitz-Pogorelov theorem[22] that it is possible to establish the energy spectrum of metals from the de Haas-van Alphen effect under the following conditions. The Fermi surface (or individual regions of the Fermi surface) must be closed, must possess an inversion center and a radius vector passing through the inversion center, and must cross it only once. The Fermi surface of antimony considered by us satisfies these requirements. For equal-energy surfaces having these properties, the extremal cross section is central. According to ref. 22 the area $A(\mathbf{H})$ of the extremal section of the Fermi surface with a plane perpendicular to the magnetic field is

$$A(\mathbf{H}) = \tfrac{1}{2}\int \rho^2(\mathbf{l})\delta(\mathbf{lH})d\Omega_l, \qquad (6)$$

where $\rho(\mathbf{l})$ is the length of the radius vector drawn from the inversion center in the direction $\mathbf{l}$, $\delta(x)$ is the Dirac δ function, and $d\Omega_l$ is the element of area of the unit sphere.

Mueller[23] proposed to use as an approximation the expansion of the square of the radius of the Fermi surface $\rho^2(\theta, \varphi)$ and of the area of the extremal cross sections $A(\theta, \varphi)$ in real spherical harmonics:

$$\rho^2(\theta,\varphi) = \sum_{l,m} [\gamma_{l,m}^g C_{l,m}^g(\theta,\varphi) + \gamma_{l,m}^u C_{l,m}^u(\theta,\varphi)],$$

$$A(\theta,\varphi) = \sum_{l,m} [\beta_{l,m}^g C_{l,m}^g(\theta,\varphi) + \beta_{l,m}^u C_{l,m}^u(\theta,\varphi)]. \qquad (7)$$

In these expressions the superscripts g and u refer respectively to symmetric and antisymmetric harmonics relative to the substitution $\varphi \to -\varphi$. Substitution of the system of equations (7) into (6) leads to a simple relation between the expansion coefficients $\beta_{l,m} = \pi P_l(0)\gamma_{l,m}$, which greatly facilitates the calculation for a limited number of experimental data ($P_l(0)$ is the Legendre polynomial of order l).

For a Fermi surface whose shape is close to ellipsoidal, one uses as the first approximation the ellipsoid[24]

$$P_x^2/P_{x0}^2 + P_y^2/P_{y0}^2 + P_z^2/P_{z0}^2 = 1. \qquad (8)$$

Here the orientation of the principal axes of the ellip-

TABLE II

l	m	$\gamma_{l},$ m· 10^{-42} g²-cm²-sec⁻²	$\beta_{l},$ m· 10^{-42} g²-cm²-sec⁻²	$\frac{\partial\gamma_{l},\text{m}}{\partial\varepsilon}\cdot 10^{-21}$ g
0	0	66.691	210.641	0.596
2	0	−0.557	0.875	−0.0168
2	2g	−3.104	4.876	0.00412
2	2u	−10.109	15.879	−0.0289
4	0	−0.573	−0.696	0.00883
4	2g	−0.242	−0.294	−0.0626
4	2u	4.621	5.617	0.00266
4	4g	−0.788	−0.958	−0.00659
4	4u	4.935	5.999	−0.0368

soid (8) P_{x0}, P_{y0}, and P_{z0} was chosen in accordance with ref. 24. The approximation by the functions (7) is carried out in a coordinate system transformed by the relations

$$P_x' = P_{y0}P_x/P_{x0}, \quad P_y' = P_y, \quad P_z' = P_{y0}P_z/P_{z0}. \qquad (9)$$

Here the areas of the central cross sections of the Fermi surface $A(\theta, \varphi)$ are related to the areas of the corresponding cross sections in the transformed coordinate system $A(\theta', \varphi')$ as follows:

$$A(\theta, \varphi) = T(\theta, \varphi \to \theta', \varphi')A(\theta', \varphi'),$$
$$T(\theta, \varphi \to \theta', \varphi') = \alpha\gamma[\sin^2\theta(\sin^2\varphi + \alpha^{-2}\cos^2\varphi) + \gamma^{-2}\cos^2\theta]^{1/2}, \qquad (10)$$
$$\alpha = P_{y0}/P_{x0}, \quad \gamma = P_{y0}/P_{z0}.$$

The velocity of electrons at the boundary surface is determined by the equality $\mathbf{v}_F = \nabla_p\varepsilon$, or in spherical coordinates

$$\mathbf{v}_F = \left(\frac{\partial\varepsilon}{\partial\rho}\right)_{\theta,\varphi}\hat{\rho} + \frac{1}{\rho}\left(\frac{\partial\varepsilon}{\partial\theta}\right)_{\rho,\varphi}\hat{\theta} + \frac{1}{\rho\sin\theta}\left(\frac{\partial\varepsilon}{\partial\varphi}\right)_{\rho,\theta}\hat{\varphi}. \qquad (11)$$

Using the relation $m^* = (2\pi)^{-1}\partial A/\partial\varepsilon$, we can find the derivatives of the parameters with respect to energy $\partial P_{x0}/\partial\varepsilon = 8.171 \times 10^{-9}$ sec-cm⁻¹, $\partial P_{y0}/\partial\varepsilon = 3.907 \times 10^{-9}$ sec-cm⁻¹, $\partial P_{z0}/\partial\varepsilon = 3.353 \times 10^{-9}$ sec-cm⁻¹, $\partial\alpha/\partial\varepsilon = 2.184 \times 10^{10}$ sec²-g⁻¹-cm⁻², $\partial\gamma/\partial\varepsilon = 4.928 \times 10^{10}$ sec²-g⁻¹-cm⁻². The values of the coefficients $\gamma_{l,m}$, $\beta_{l,m}$, and $\partial\gamma_{l,m}/\partial\varepsilon$ are given in Table II. For the calculations we used values of $m^*(\theta, \varphi)$ from cyclotron resonance in antimony[6] and areas of the extremal cross sections were obtained from the model used in ref. 24. In selecting the parameters by the method of least squares, we varied all coefficients including the first to reduce the rms error of the approximation. From the known parameters and also their derivatives with respect to energy and with use of the relations of ref. 25, we determined all components of the velocity in (11), and then the total velocity. The numerical value of the modulus of the velocity is invariant with respect to the transformation (9), and the direction of the velocity vector at a given point of the Fermi surface coincides with the normal to the surface and is calculated from the well known dependence $\rho(\theta, \varphi)$.

The calculated values of v_F are plotted in Fig. 3 as the solid line, and the dashed line shows values of the Fermi velocities in the quadratic approximation with use of the spectrum parameters from refs. 3 and 6. It is evident from the discussion that the velocity vectors obtained by means of the empirical model are in good agreement with the data of the present work and also with the results of ref. 26. According to the calculation, for certain directions of the electron Fermi surface of antimony it is possible to observe the effect simultaneously from two inflection points of the Fermi surface, but the small value of $\omega\tau$ apparently does not permit this possibility to be realized. The velocity values for a number of directions are given in Table III. The error in approximation of the experimental data on the

TABLE III

Direction; v, 10^7 cm/sec					Sources
v_X	v_Y	v_Z	v *	v **	
Electrons					
6.80	2.70	7.90	7.55	–	Present work
6.20	3.71	8.80	7.18	–	Empirical model
6.54	2.50	5.26	5.20	–	Quadratic approximation***
6.43			7.10	–	[26]
Holes					
–	–	–	–	10.5	Present work
–	–	–	–	9.72	Quadratic approximation***
–	–	–	–	11.66	[26]

*The direction forms an angle 5° with the Z axis in the ZY plane.
**The direction forms an angle 35° with the Z axis in the ZY plane.
***In the quadratic approximation the spectrum parameters from refs. 3 and 6 were used.

areas of the extremal cross sections[4,24] and the cyclotron masses[6] with inclusion of the experimental errors amounted to 5%, which determined the accuracy of the calculated velocity values. The value of $\omega\tau$ at a sound frequency of 825 MHz was 4, and in this case the experimental error amounted to 5%.

In the region of angles from 30° to 50° from the Z axis in the ZY plane we experimentally observed second peaks which were assigned to the main hole ellipsoid of the antimony Fermi surface. The velocity values obtained $v_F^h = 10.5 \times 10^7$ cm/sec agree satisfactorily with the data of ref. 26, but since the hole Fermi surface of antimony does not satisfy the conditions of the Lifshitz-Pogorelov theorem, comparison of the results with the experimental measurements of extremal areas and cyclotron masses is impossible.

Using data on the shape of the electron Fermi surface of antimony and the distribution of velocities on it, we can determine the density of states on the Fermi surface,

$$\nu_s(\varepsilon) = \int_{\varepsilon = \varepsilon_F} \frac{ds}{|v_F|}. \tag{12}$$

The density of states per ellipsoid, calculated from the experimentally measured velocity distribution on the electron Fermi surface of antimony, is $\nu^e(\varepsilon)$ = 0.112×10^{-33} cm^{-3}-erg^{-1}. Use in Eq. (12) of velocity values calculated from the empirical formula gives $\nu^e(\varepsilon) = 0.117 \times 10^{-33}$ cm^{-3}-erg^{-1}, and the same quantity in the quadratic approximation is $\nu^e(\varepsilon) = 0.132 \times 10^{-33}$ cm^{-3}-erg^{-1}. The absence of complete information on the velocity distribution on the hole Fermi surface of antimony does not permit determination of the density of hole states or comparison with experimental results on the electronic thermal conductivity of antimony or with data obtained from the Nernst-Ettinghausen effect.

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