or perhaps less. Finally

$$f_{p\sigma}\sim 1\times 10^{-2}, \tag{62}$$

or perhaps less. The $\psi_d\phi_x$ and $\psi_d\phi_s$ cross terms in (59) make a very small contribution.

This is to be compared to the experimental values of Eq. (18). It is seen to be much too large, although the uncertainty in the experimental values makes definite conclusion unwise. The discrepancy could be caused by (1) a non-negligible value of $f_{p\pi}$; (2) underestimate of the size of the cross terms.

We note that, regardless of the signs of S or λ, Eqs. (55) and (59) predict a paramagnetic shift, i.e., ΔH positive. However, the ψ_1 electron must exist in the transition metal ion for the theory to apply. In the case of CrF_3, where this electron is expected to be absent, the nuclear resonance is found to be unshifted.[20]

ACKNOWLEDGMENTS

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[20] Jaccarino, Shulman, and Stout, Phys. Rev. **106**, 602 (1957).

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Anomalous Skin Effect in Bismuth*†

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High-frequency (23.5-kMc/sec) surface resistance measurements have been made on plane surfaces of single-crystal bismuth at 2°K as a function of orientation. It has been ascertained that extreme anomalous skin effect conditions prevail, allowing details of the Fermi surface to be deduced from Pippard's theory. In Shoenberg's model of the electron band, components of the inverse effective-mass tensor divided by the Fermi energy are found to be $\alpha_1/E_e=9.10$, $\alpha_2/E_e=0.088$, $\alpha_3/E_e=4.7$, and $\alpha_4/E_e=0.38$ (in units of 10^3/ev). These results are in essential agreement with values obtained from de Haas–van Alphen experiments and cyclotron resonance. The number of ellipses is definitely established to be six and the number of electrons found to be $N=5.5\times 10^{17}/\text{cm}^3$. The parameters for the two hole ellipsoids are found to be $\beta_1/E_h=\beta_2/E_h=1.5$ and $\beta_3/E_h=0.12$. Assuming Shoenberg's value $E_e=0.0177$ ev, we calculate $E_h=0.00112$ ev from specific heat data. It is also found that the reflection of carriers from the surface of the sample is predominantly specular in contrast to diffuse reflection found in other metals.

1. INTRODUCTION

IT has been shown[1,2] that measurements of the high-frequency surface resistance of pure single-crystal metals can yield valuable information about the Fermi surface when so-called extreme anomalous conditions are achieved. This requires that the mean free path l be much greater than the skin depth δ, and that $\omega\tau$ be small enough to prevent relaxation effects, where ω is the frequency and τ the relaxation time.

For a plane surface, the surface resistance will have the form

$$R=R_x\cos^2\theta+R_y\sin^2\theta, \tag{1}$$

where x and y are principal axes of the surface, and θ the angle between the current direction and the x axis. Pippard,[1] assuming that only those electrons traveling nearly parallel to the surface are effective in absorbing energy, derives the expression

$$R_x=b\frac{\sqrt{3}}{2}\left[\frac{\pi\omega^2\hbar^3}{e^2c^4\int|\rho_y|\,dy}\right]^{\frac{1}{3}}, \tag{2}$$

where ρ_y is the radius of curvature of the Fermi surface in a plane normal to the y axis at the point where the normal to the Fermi surface is parallel to the surface of the metal. The quantities ρ_y and y are expressed in units of momentum. The integration must include summing over all sheets of the Fermi surface when it is not simply connected. A similar expression holds for R_y. The constant b is equal to 8/9 for specular reflection of electrons from the surface of the metal and equal to 1 for diffuse reflection. The choice of b for the interpretation of the present experiment will be discussed in Sec. 5. It will be noted that R is independent of the relaxation time and depends only on the geometrical shape of the Fermi surface. It is further evident that a deduction of the Fermi surface from the measured

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[1] A. B. Pippard, Proc. Roy. Soc. (London) **A224**, 273 (1954).
[2] E. H. Sondheimer, Proc. Roy. Soc. (London) **A224**, 260 (1954).

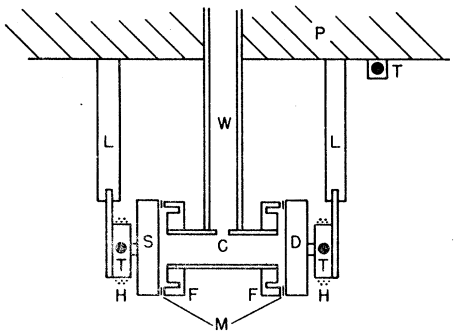

FIG. 1. Schematic drawing of the apparatus.

dependence of R on orientation may admit more than one solution so that its value lies primarily in fixing details once a general shape is known from other considerations.

The band structure of bismuth has been studied extensively, and it has been found that the uppermost filled band overlaps slightly with the next highest band. This causes a small number of electrons to "spill over" and leaves an equal number of holes behind. The Fermi surface has been studied experimentally by the de Haas–van Alphen,[3] cyclotron resonance,[4–6] and galvanomagnetic[7] effects so that a reasonably well-established model exists for the interpretation of anomalous skin effect data. The model consists of either three or six electron ellipses and one or two hole ellipses, and various values for effective masses and Fermi energies exist in the literature. The possibility of greater accuracy for the electron band, the relative lack of data concerning the hole band, and the possibility of ascertaining the actual number of ellipses instigated the present investigation.

2. EXPERIMENTAL METHOD

To obtain a large mean free path and small skin depth, the experiment was carried out at 23.5 kMc/sec and 2.1°K on samples of bismuth highly purified by zone refining. Since the skin depth is approximately 0.5 micron, it is necessary that the surface be smooth on this scale and free of strain in order to approximate the bulk material. This was accomplished by cutting $\frac{1}{8}$-in. slabs of desired orientation with a 280-grit alundum wheel and sandblasting them into $\frac{5}{8}$-in. diameter disks. One surface was then electropolished by passing a current of about 1 ampere through a solution of 35 g KI, 1 g I, and 10 cc HCl in 200 cc of water, and a rinse of $\frac{1}{2}$ HCl and $\frac{1}{2}$ alcohol was used to remove a chemical film which accumulates. This was done for about 10 cycles of 60 seconds each during which approximately 0.015 in. of material was removed. Microscopic examination indicated that the resulting surfaces were flat on the scale of 1 micron and x-ray examination indicated that they were free of strain.

The experimental technique was essentially the calorimetric one used by Fawcett[8] in measuring the microwave surface resistance of tin and is shown schematically in Fig. 1. A rectangular microwave cavity C which terminates the end of a stainless steel rectangular line W is enclosed in a vacuum space with a brass plate P serving as contact to the helium bath. The sample S is lightly spring loaded against one end of the cavity and a dummy sample of brass D at the other. Both are thermally isolated from the cavity by means of 0.003-in. mica spacers M and connected to the helium bath through heat leaks of stainless steel tubing L. The pressure is lowered to 10^{-6} mm of mercury in order to prevent heat conduction by gas. Standard choke plate flanges F on the ends of the cavity prevent microwave power from being coupled into the vacuum space. Carbon resistance thermometers T are placed on the sample, on the dummy, and on the contact to the helium bath, and form arms of a dc bridge. The microwave frequency is adjusted to the resonant frequency of the cavity, causing a temperature rise in the samples due to the microwave power absorbed, and the ratios of sample to bath and dummy to bath resistances are separately measured. With the microwave power off, dc heaters H on both sample and dummy are adjusted to give the same ratios and the dc powers measured. Since sample, heater, and thermometer are in good thermal contact compared to the heat leak, this gives an absolute measure of the microwave power absorbed. The surface resistance R of the sample is given by $R=KP_s/P_d$, where P_s and P_d are the powers absorbed in the sample and dummy, and K depends upon geometry and the dummy surface resistance, both of which are kept constant throughout the course of the experiment. This constant K is found by measuring an alloy for which the surface resistance can be computed from its dc resistivity ρ using the classical formula

$$R=(2\pi\omega\rho/c^2)^{\frac{1}{2}}. \quad (3)$$

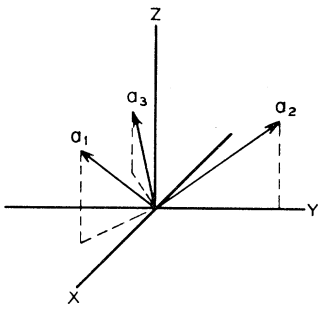

FIG. 2. The relationship between lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ of the rhombohedral unit cell and the Cartesian coordinate system in which the Fermi surface is expressed.

[3] D. Shoenberg, Proc. Roy. Soc. (London) **A170**, 341 (1939); Trans. Roy. Soc. (London) **A245**, 1 (1952). J. S. Dhillon and D. Shoenberg, Trans. Roy. Soc. (London) **A248**, 1 (1955).
[4] J. E. Aubrey and R. G. Chambers, J. Phys. Chem. Solids **3**, 128 (1957).
[5] J. E. Aubrey (private communication).
[6] Galt, Yager, Merritt, Cetlin, and Brailsford, Phys. Rev. **114**, 1396 (1959).
[7] B. Abeles and S. Meiboom, Phys. Rev. **101**, 544 (1956).
[8] E. Fawcett, Proc. Roy. Soc. (London) **A232**, 519 (1955).

The resistance of the carbon thermometers at 2.1°K was 5000 ohms and changed 15% with 10 microwatts of power being absorbed by the sample, corresponding to a temperature rise of approximately 0.1 degree. This change and the dc power could be measured to better than 0.1%. The main source of error in the power measurement came from drifts in the incident microwave power so successive readings of the two ratios were made and averages taken. Repeated measurements of P_s/P_d show less than 1% scatter. The heat leak across the mica spacers was measured and found to be negligible compared to the stainless steel tubing. A separate carbon resistor not in contact with the sample or cavity was placed near the side of the sample to determine the leakage of microwave power past the choke plate. Errors from this source are estimated to be less than 1%.

3. RESULTS

Bismuth has a crystal structure which can be described by a rhombohedral unit cell containing two

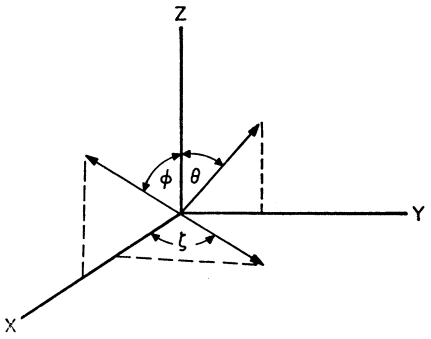

FIG. 3. Angles used to specify the directions of surface normals in the XYZ coordinate system.

atoms. A Cartesian coordinate system XYZ is chosen in which the trigonal axis lies along Z and a binary axis along X. The relationship of the unit cell vectors in this system are given in Fig. 2. Another coordinate system xyz is defined for each sample in which z is normal to the surface and y perpendicular to the trigonal axis. From symmetry considerations, this results in x and y being principal axes of the surface as defined by (1).

To investigate the dependence of surface resistance upon relaxation time, samples of two different purities were studied. One was a spectroscopic grade purchased from Cerro de Pasco from which crystals were grown by pulling from a melt. The residual resistivity ratio for current flow perpendicular to the trigonal axis was 104. The other was the same material which had been further purified by zone-refining in this laboratory§ and samples cut from large grains in the resulting ingot. The residual resistivity ratio for the same current direction was 220.

§ The author is indebted to D. H. Reneker for supplying the zone refined material.

TABLE I. Experimental values of the surface resistance and values calculated from the deduced mass parameters assuming specular reflection.

Sample	P_s/P_d	Measured R (10^{-2} ohm)	Calculated R (10^{-2} ohm)
Spectroscopic grade			
$R_x(X)$	1.333	7.50	7.24
$R_y(X)$	1.617	9.10	9.01
$R_x(Y)$	1.058	5.96	6.01
$R_y(Y)$	0.741	4.17	4.47
$R(Z)$	0.961	5.41	5.38
Zone-refined			
$R_x(X)$	1.320	7.43	7.24
$R_y(X)$	1.521	8.56	9.01
$R_x(Y)$	1.012	5.70	6.01
$R_y(Y)$	0.776	4.37	4.47
$R_x(\theta=135°)$	1.512	8.51	8.35
$R_y(\theta=135°)$	1.170	6.59	6.29
$R_x(\theta=75°)$	1.541	8.68	8.76
$R_y(\theta=75°)$	1.147	6.46	5.81
$R_x(\theta=105°)$	1.125	6.33	7.67
$R_y(\theta=105°)$	0.716	4.03	5.04

The measured values of P_s/P_d and the corresponding values of surface resistance $R=KP_s/P_d$ for each orientation measured are shown in Table I. The symbol in brackets to the right of R indicates the direction of the surface normal in the coordinate system of Fig. 3. For the alloys, P_s/P_d, their measured dc resistivities, and the computed value of K are shown in Table II. Both the brass and bronze were found to be homogeneous by metallographic inspection and were chosen largely because their surface could be given a smooth polish. The similar values of ρ are merely fortuitous. The scatter in K indicates that the absolute calibration is accurate to 2%. The largest discrepancy between spectroscopic grade and zone-refined samples is 6% and the average error for the four where comparison is made is 4%. It is felt that these discrepancies result largely from surface preparation and misorientation errors. The average error in orientation is estimated to be $1\frac{1}{2}°$ and the maximum error estimated to be 3°. This can be shown to give at most a few percent error in R for all orientations except $\theta=75°$ and $\theta=105°$. These orientations will be discussed further below.

4. DEDUCTION OF THE FERMI SURFACE

Following the model proposed by Shoenberg,[3] the electron band is assumed to consist of six ellipsoids, one of which is given by

$$2m_0E_e=\alpha_1p_x^2+\alpha_2p_y^2+\alpha_3p_z^2+2\alpha_4p_yp_z, \qquad (4)$$

TABLE II. Absolute calibration data.

Sample	ρ (10^{-6} ohm cm)	R (ohms)	P_s/P_d	$K=R/(P_s/P_d)$
Brass No. 1	3.74	0.0587	1.025	0.0573
Brass No. 2	3.74	0.0587	1.039	0.0564
Bronze	3.71	0.0586	1.061	0.0553
				$K_{Av}=0.0563$

TABLE III. Values of α_i/E_e and β_i/E_h in units of 10^8/ev for the cases of specular and diffuse reflection of carriers from the surface. Shoenberg's original data and the data as modified by cyclotron resonance is presented for comparison. The number of electrons N is calculated from α_i/E_e using Eq. (6).

Source	α_1/E_e	α_2/E_e	α_3/E_e	α_4/E_e	β_1/E_h	β_3/E_h	$10^{-17}\times N$ (cm^{-3})
Anomalous skin effect (specular)	9.10	0.088	4.7	0.38	1.52	0.118	5.5
Anomalous skin effect (diffuse)	6.40	0.062	3.3	0.27	1.07	0.083	9.4
de Haas–van Alphen effect[a]	24.0	0.045	2.3	0.23			8.2
de Haas–van Alphen effect modified by cyclotron resonance[b]	9.5	0.113	5.6	0.56			4.8
de Haas–van Alphen effect modified by cyclotron resonance[c]	11.5	0.094	4.7	0.47			5.5

[a] See reference 3.
[b] See reference 4.
[c] See reference 5.

where p_x, p_y, and p_z are momenta along the XYZ axes shown in Fig. 2. The other five are generated by rotations of 120° about the Z axis and inversion through the origin. The six minima coalesce into three only if they happen to lie at the centers of zone faces.[9] The hole band is assumed to consist of two ellipsoids of revolution about the Z axis given by

$$2m_0E_h=\beta_1(p_x^2+p_y^2)+\beta_3p_z^2. \tag{5}$$

Abeles and Meiboom,[7] in their interpretation of galvanomagnetic effects in bismuth, propose one such ellipsoid, but since it is allowed by inversion symmetry, and to obtain somewhat closer agreement with the present data, two are assumed here. A drawing of the proposed Fermi surface is shown in Fig. 4.

Using the above model, the integration (2) was carried out (see Appendix I) for each orientation leaving the α's and β's as variables and a numerical iteration used to determine the best fit to the data. In doing the calculation, we assumed that the number of electrons N_e, and the number of holes N_h, were equal. Expressing the number of carriers by $2/h^3$ times the volume enclosed by the Fermi surface in momentum space,

$$N_e=6\frac{8\pi}{3h^3}\frac{(2m_0E_e)^{\frac{3}{2}}}{[\alpha_1(\alpha_2\alpha_3-\alpha_4^2)]^{\frac{1}{2}}}, \tag{6}$$

and

$$N_h=2\frac{8\pi}{3h^3}\frac{(2m_0E_h)^{\frac{3}{2}}}{(\beta_1^2\beta_3)^{\frac{1}{2}}}. \tag{7}$$

As noted previously, it is a Fermi momentum which is measured or essentially ratios of α_i/E_e and β_i/E_h so that $N_e=N_h=N$ may be used to eliminate one ratio. This condition of charge neutrality shows that the momenta are comparable, and hence electrons and holes will, on the average, contribute equally to $\int|\rho_y|dy$. Because of the high anisotropy, however, at certain orientations the resistance is largely determined by electron conduction and at others, largely by hole conduction.

The effect of the "tilt" of the ellipses (i.e., α_4) is largest for the orientations $\theta=75°$ and $\theta=105°$ and the fact that the ratios $R_x(\theta=75°)/R_x(105°)=1.37$ and $R_y(75°)/R_y(105°)=1.60$ are greater rather than less than one show that α_4 is positive. This can be seen from the equations in Appendix I. However, since the actual values of R change very rapidly with orientation in this region, and are hence more subject to misorientation error, these samples were used largely to fix the sign of α_4 and not weighted greatly in the calculation of quantitative values. The resulting values for α_i/E_e and β_i/E_h, and the computed number of electrons N are given in Table III for the cases of both specular and diffuse reflection of carriers from the surface. Shoenberg's values for electrons are presented for comparison since the de Haas–van Alphen effect is the one other experiment in which an observed quantity is determined directly by suitable combinations of α_i/E_e. No de Haas–van Alphen effect for holes has been reported. The most accurate quantities which he measures are of the form $\alpha_i\alpha_1/E_e^2$, and, as pointed out by Aubrey and Chambers, α_1/E_e may be individually changed as

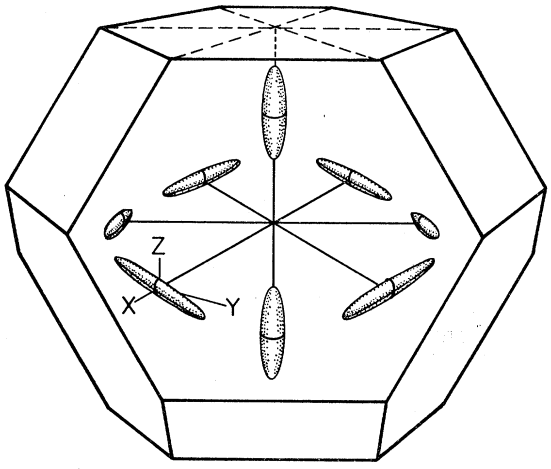

FIG. 4. A drawing of the proposed Fermi surface and its relationship to the Brillouin zone. The XYZ coordinate system is drawn on one electron ellipse to show the direction of tilt and the other five electron ellipses tilt alternately in opposite directions. The two hole ellipsoids lie with their principal axis along the Z direction.

[9] M. Cohen and E. I. Blount, Scientific Paper 6-94760-2-P19, Westinghouse Research Laboratories, 1958 (unpublished).

TABLE IV. Absolute values of the mass parameters and their ratios to one another. An electron energy of $E_e=17.7\times10^{-3}$ ev and a hole energy of $E_h=1.2\times10^{-3}$ ev are assumed. Other data are presented for comparison. No tilt to the electron ellipses was assumed in the galvanomagnetic data.

Source	α_1	α_2	α_3	α_4	β_1	β_3	$\alpha_1:\alpha_2:\alpha_3:\alpha_4$	$\beta_1:\beta_3$
Anomalous skin effect (specular)	160	1.56	83	6.7	1.7	0.13	103:1:53:4.4	12.8:1
Anomalous skin effect (diffuse)	113	1.10	58	4.9	2.0	0.16	103:1:53:4.4	12.8:1
de Haas–van Alphen effect[a]	420	0.8	40	4.0			500:1:50:5.0	
Cyclotron resonance ∥ field[b]	168	2.0	100	10			84:1:50:5.0	
Cyclotron resonance ∥ field[c]	202	1.67	83.3	8.33			122:1:50:5.0	
Cyclotron resonance ⊥ field[d]	114	1.39	108	9.47	14.7	1.07	82:1:78:6.8	13.7:1
Galvanomagnetic effects[e]							40:1:24:	3.7:1
Sound attenuation[f]	178	1.1	84.5	7.2			162:1:76:6.5	

[a] See reference 3.
[b] See reference 4.
[c] See reference 5.
[d] See reference 6.
[e] See reference 7.
[f] D. H. Reneker, Phys. Rev. **115**, 303 (1959).

long as their product is kept constant. Such a reinterpretation of Shoenberg's data based on cyclotron resonance data has been carried out by Aubrey and Chambers and later by Aubrey. Their results are also included in Table III. It should be pointed out here that if three rather than six electron ellipses were assumed, the values of α_i/E_e derived from the present work would be a factor of two smaller, and be in disagreement with Shoenberg's data. This result is in accord with the symmetry argument presented previously.

To separate the above ratios, Shoenberg's value for the electron Fermi energy, $E_e=17.7\times10^{-3}$ ev, is assumed. The electronic contribution to the specific heat $\gamma=(1.6\pm0.1)\times10^{-5}$ cal/deg^2-gram atom as measured by Kalinkina and Strekov[10] has been used to obtain a Fermi energy for the holes. This can be expressed as

$$\gamma=\tfrac{1}{2}\pi^2k^2(N/E_e+N/E_h), \tag{8}$$

where k is the Boltzmann constant. Inserting the value of N from the present work and Shoenberg's electron Fermi energy results in a Fermi energy for holes of $E_h=1.12\times10^{-3}$ ev. The resulting mass parameters are shown in Table IV together with values obtained from other experiments. It will be noted that α_4 has been made positive in all cases to agree with the coordinate system used here. The sign of α_4 would change if the XYZ coordinate system in Fig. 2 were rotated 180° about the Z axis with the lattice vectors fixed.[11]

5. DISCUSSION

Table III has been computed for the cases of both specular and diffuse reflection of carriers from the surface of the sample; the difference between them being that the computed α_i/E_e and β_i/E_h are larger in the specular case by a constant factor $(9/8)^3=1.42$. Because the results following from the assumption of specular reflection are in much better agreement with the modified de Haas–van Alphen effect data, we believe that specular reflection does indeed take place. On the other hand, it has been shown experimentally that the reflection of electrons from the surface of metals previously studied[12] (Cu, Ag, Au, Pb, Sn, Cd, Al) is diffuse. This is reasonable on the basis that the electron wavelength for these metals is of the order of the distance between atoms, thus roughness on an atomic scale would give rise to diffuse reflection. In the semimetal bismuth, however, the wavelength is of the order of 100 atomic separations; hence surface roughness on an atomic scale is probably unimportant. From this point of view, the better agreement with specular reflection is not surprising.

There are restrictions on the magnitudes of the relaxation times and Fermi momenta which must be met to insure the validity of (2). For a single isotropic carrier, the condition is that

$$\tfrac{3}{2}(l/\delta)^2\gg(1+\omega^2\tau^2)^{\frac{3}{2}}, \tag{9}$$

where l is the mean free path and δ the skin depth as calculated from the classical formula

$$\delta=c/(2\pi\omega\sigma)^{\frac{1}{2}}, \tag{10}$$

and where σ is the dc conductivity. For two carriers, the skin depth is determined by the total conductivity and the inequality (9) is required to hold for each carrier. The condition (9) can be checked if the electron and hole mobilities are known. However, mobility estimates based on existing magnetoresistance and Hall-effect data may be unreliable because the magnetic fields used did not satisfy the low-field condition $\omega_c\tau\ll1$, where ω_c is the cyclotron frequency. Nonetheless, as a guide, electron and hole mobilities obtained from galvanomagnetic measurements[13] at

[10] I. N. Kalinkina and P. G. Strekov, J. Exptl. Theoret. Phys. U.S.S.R. **34**, 616 (1958) [translation: Soviet Phys. JETP **34**(7), 426 (1958)].

[11] In connection with the sign of α_4, we note that the relation between α_4 and m_4 in Shoenberg's 1952 paper contains an error in sign.

[12] R. G. Chambers, Proc. Roy. Soc. (London) **A215**, 481 (1952).

[13] A. L. Jain, Phys. Rev. **114**, 1518 (1959).

4.2°K and the measured dc conductivity of our zone-refined samples, $\sigma=2.0\times10^6$ (ohm-cm)$^{-1}$, have been used to obtain mean free paths for electrons and holes of $l_e=0.18$ cm and $l_h=0.06$ cm and relaxation times of $\tau_e=3\times10^{-10}$ sec and $\tau_h=3\times10^{-9}$ sec. The inequality is seen to be satisfied by a factor of 10^3 for the electrons, but for the holes it is not satisfied by a factor of 10^2 because of the large $\omega\tau_h=370$.

The above result led to an investigation of the effect of a large hole relaxation time upon surface resistance. Dingle[14] has presented tables which show the variation of surface resistance with relaxation time for a single isotropic carrier. They exhibit the feature that when $l/\delta\gg1$, as τ increases, one goes from the anomalous skin effect region into a transition region which is dependent upon τ, and finally into a so-called extreme anomalous relaxation region. This last region, for diffuse reflection, is again independent of τ, and, for specular reflection, reverts to the τ-dependent classical ($l/\delta\ll1$) result. The above estimates indicate that the electrons are in the anomalous skin effect region and the holes in the extreme relaxation region. Therefore, an exact calculation of surface resistance for the case of two carriers was initiated, the details of which are presented in Appendix II. An isotropic model was assumed by transforming the ellipses into spheres of the same volume and, in the above limit, it was found that for both types of scattering from the surface, the hole contribution to the surface resistance was completely negligible. Assuming electrons alone, however, leads to mass parameters which are radically different from those obtained by other methods. Measurements on the four orientations $R_x(X)$, $R_y(X)$, $R_x(Y)$, and $R_y(Y)$ were made using both zone-refined and spectroscopic-grade samples and, as seen in Table I, were found to agree within experimental error. Since the relaxation time of the zone-refined bismuth is a factor of two larger than that of the spectroscopic grade, as shown by the residual resistivity ratios, this independence of surface resistance upon τ allows us to assume that the holes are not in some intermediate region. No quantitative calculations were made, however, to find an expected variation of R with τ, because of the complexity of the problem. The results of these considerations leads one to believe that the hole relaxation time calculated from the mobilities derived from galvanomagnetic experiments is either incorrect or not directly applicable to this problem. It is felt that τ_h should instead be a factor of ten lower, justifying the use of Eq. (2) in interpreting the experimental data. In connection with this supposition we note that Galt *et al.* find that the shape of the absorption curves in their cyclotron resonance experiments are best fitted assuming an $\omega\tau$ for holes of approximately 10.

The rms error between the observed and calculated values of R is found to be 4% so that adding the calibration error of 2% and recalling that α/E is proportional to $1/R^3$, the resulting error in α_i/E_e and β_i/E_h is approximately 20%. Comparison with the de Haas–van Alphen effect data as modified by cyclotron resonance data shows that the electron data (assuming specular reflection) is in essential agreement. There are no existing data for a direct comparison of β_i/E_h but it will be seen from Table IV that the ratio β_1/β_3 agrees well with that obtained by Galt *et al.* The discrepancy with mobility ratios might be accounted for by an anisotropic relaxation time. There is, however, a factor of 10 disagreement in absolute magnitude between Galt's β_i and the β_i obtained from this experiment in conjunction with the specific heat data.

A possible explanation of the discrepancy would be a division of the holes into a heavy-mass band and a light-mass band. If both hole bands have the same symmetry and mass ratio, it would be impossible to distinguish between them from the anomalous skin effect data. However, the specific heat data places a restriction on the possible numbers of light and heavy holes. As an example, we can assume Galt *et al.*'s average hole mass of $m_h=0.16m_0$ for the light band and $m_h=2m_0$ for the heavy band; then the ratio of the number of light holes to the number of heavy holes must be no more than $\frac{1}{2}$. In connection with this supposition, Jain has suggested that an anomaly in the low-temperature resistivity of bismuth-antimony alloys may be explained by the existence of a third set of carriers.

APPENDIX I

The integral in Eq. (2) has been carried out as a function of orientation for the relatively simple cases of the surface normal being parallel to the XY, XZ, and YZ planes shown in Figs. 2 and 3. The directions of the surface normals are specified here by the angles shown in Fig. 3. Since the total integral includes summing over ellipses, the contribution of each ellipse is presented separately. A contribution from an ellipse obtained by inversion is the same as that of the original ellipse.

For the electrons, ellipse No. 1 is that given by Eq. (4), and ellipses No. 2 and No. 3 are those obtained by rotations of $\pm120°$. Because of their similarity except for signs, ellipses No. 2 and No. 3 will be presented as a single expression with the upper sign referring to No. 2 and the lower to No. 3. Letting $a_i=\alpha_i/2m_0E_e$, we find that

$$\int|\rho_y|\,dy=(\pi/2)I_y/[a_1(a_2a_3-a_4^2)]^{\frac{1}{2}},$$
$$\int|\rho_x|\,dx=(\pi/2)I_x/[a_1(a_2a_3-a_4^2)]^{\frac{1}{2}}. \tag{11}$$

The I's for the various ellipses and orientations are given below.

[14] R. B. Dingle, Physica **19**, 311 (1953).

ZY Plane

No. 1: $I_x=2a_1/(a_2\sin^2\theta+a_3\cos^2\theta+2a_4\sin\theta\cos\theta)^{\frac{1}{2}}$,

$$I_y=2(a_2a_3-a_4^2)/(a_2\sin^2\theta+a_3\cos^2\theta+2a_4\sin\theta\cos\theta)^{\frac{3}{2}}.$$

No. 2 and No. 3:

$$I_x=4\{4a_1a_2\sin^2\theta+[a_3(a_1+3a_2)-3a_4^2]\cos^2\theta-4a_1a_4\sin\theta\cos\theta\}[(3a_1+a_2)\sin^2\theta+4a_3\cos^2\theta-4a_4\sin\theta\cos\theta]^{-\frac{3}{2}},$$

$$I_y=4[a_3(3a_1+a_2)-a_4^2]/[(3a_1+a_2)\sin^2\theta+4a_3\cos^2\theta-4a_4\sin\theta\cos\theta]^{\frac{3}{2}}.$$

XZ Plane

No. 1: $I_x=2[a_2(a_1\sin^2\phi+a_3\cos^2\phi)-a_4^2\cos^2\phi]/[a_1\sin^2\phi+a_3\cos^2\phi]^{\frac{3}{2}}$,

$$I_y=2a_1a_3/(a_1\sin^2\phi+a_3\cos^2\phi)^{\frac{3}{2}}.$$

No. 2 and No. 3:

$$I_x=4\{4a_1a_2\sin^2\phi+[a_3(3a_1+a_2)-a_4^2]\cos^2\phi\mp4\sqrt{3}a_1a_4\sin\phi\cos\phi\}[(a_1+3a_2)\sin^2\phi+4a_3\cos^2\phi\mp4\sqrt{3}a_4\sin\phi\cos\phi]^{-\frac{3}{2}},$$

$$I_y=4(a_1a_3+3a_2a_3-3a_4^2)/[(a_1+3a_2)\sin^2\phi+4a_3\cos^2\phi\mp4\sqrt{3}a_4\sin\phi\cos\phi]^{\frac{3}{2}}.$$

XY Plane

No. 1: $I_x=2a_1a_2/(a_1\cos^2\zeta+a_2\sin^2\zeta)^{\frac{3}{2}}$,

$$I_y=2[a_3(\sin^2\zeta a_2+a_1\cos^2\zeta)-a_4^2\sin^2\zeta]/(a_2\sin^2\zeta+a_1\cos^2\zeta)^{\frac{3}{2}}.$$

No. 2 and No. 3:

$$I_x=16a_1a_2/[(3a_1+a_2)\sin^2\zeta+(a_1+3a_2)\cos^2\zeta\pm2\sqrt{3}(a_2-a_1)\sin\zeta\cos\zeta]^{\frac{3}{2}},$$

$$I_y=4\{a_3[(3a_1+a_2)\sin^2\zeta+(a_1+3a_2)\cos^2\zeta\pm2\sqrt{3}(a_2-a_1)\sin\zeta\cos\zeta]-a_4^2(\sin\zeta\pm\sqrt{3}\cos\zeta)^2\}[(3a_1+a_2)\sin^2\zeta+(a_1+3a_2)\times\cos^2\zeta\pm2\sqrt{3}(a_2-a_1)\sin\zeta\cos\zeta]^{-\frac{3}{2}}.$$

The hole band, given by Eq. (5), is much simpler and its full orientational dependence can be described by the single angle θ. Any rotation of a surface normal about the Z axis leaves the surface resistance unchanged. The integral in (2) for a single ellipse is given below.

$$\int|\rho_x|\,dx=\pi2m_0E_h/\beta_3^{\frac{1}{2}}(\beta_1\sin^2\theta+\beta_3\cos^2\theta)^{\frac{1}{2}},$$

$$\int|\rho_y|\,dy=\pi2m_0E_h\beta_3^{\frac{1}{2}}/(\beta_1\sin^2\theta+\beta_3\cos^2\theta)^{\frac{3}{2}}.$$

APPENDIX II

We shall use the following symbols:

$j=e$ refers to electron parameters,

$j=h$ refers to hole parameters,

$p_j=$ Fermi momentum,

$m_j=$ effective mass,

$l_j=$ mean free path,

$l_0=(l_e+l_h)/2$,

$L_j=l_j/l_0$,

$A_j=8\pi^2e^2\omega p_j^2l_0^3/c^2h^3$,

$\gamma_j=L_j/(1+\omega\tau_j)$,

$\mathfrak{A}_j=i\gamma_jA_j$,

$s_j=t\gamma_j$,

$B=\omega^2l_0^2/c^2=$ displacement current term,

$Z=$ complex surface impedance.

A calculation of the surface impedance from the Boltzmann equation has been carried out for the case of two spherical bands of the form $E_e=p_e^2/2m_e$ and $E_h=p_h^2/2m_h$. The derivation closely follows Reuter and Sondheimer's[15] calculation for the case of a single carrier and need not be repeated here. We first consider the case of diffuse scattering from the surface. Utilizing Dingle's[14] suggestion for simplifying Eq. (A36) of Reuter and Sondheimer, the admittance $Y=1/Z$ is given by

$$Y=c^2\nu/4\pi i\omega l_0, \tag{12}$$

where

$$\nu=(1/\pi)\int_0^\infty dt\,\ln\{1+[\mathfrak{A}_eK(s_e)+\mathfrak{A}_hK(s_h)-B]/t^2. \tag{13}$$

Partial integration of (13) puts it in the form

$$\nu=(2/\pi)\int_0^\infty dt\frac{\mathfrak{A}_e\mathcal{K}(s_e)+\mathfrak{A}_h\mathcal{K}(s_h)}{\mathfrak{A}_eK(s_e)+\mathfrak{A}_hK(s_h)+t^2-B}, \tag{14}$$

where

$$\mathcal{K}(s)=(1/s^3)[-5s+(3s^2+5)\tan^{-1}s],$$

and

$$K(s)=(2/s^3)[-s+(s^2+1)\tan^{-1}s].$$

The surface impedance for the case of specular reflection, similar to Reuter and Sondheimer's equations (21) and (29), is found to be

$$Z=(4\pi i\omega l_0/c^2)\mu,$$

where

$$\mu=(2/\pi)\int_0^\infty dt[\mathfrak{A}_eK(s_e)+\mathfrak{A}_hK(s_h)+t^2-B]^{-1}. \tag{15}$$

The functions $K(s)$ and $\mathcal{K}(s)$ are similar and, to a high

[15] G. E. H. Reuter and E. H. Sondheimer, Proc. Roy. Soc. (London) **A195**, 336 (1948).

degree of accuracy, exhibit the behavior of being constant for $s<1$ and going smoothly into a $1/s$ dependence for $s>10$. The estimates presented in 5 show that, in the present notation, the inequality (9) becomes for the electrons, $|A_e||\gamma_e|^3\gg 1$, and for the holes, $|A_h||\gamma_h|^3\ll 1$. Since A_e and A_h are of the same order of magnitude, this implies that $|\gamma_e|\gg|\gamma_h|$. In this limit, it can be seen that one may replace $K_e(s_e)$ by its asymptotic value π/s_e, $\mathcal{K}(s_e)$ by $3\pi/2s_e$, and $K(s_h)$ and $\mathcal{K}(s_h)$ by their value for $s=0$ which is $\frac{4}{3}$. Equations (14) and (15) now become

$$\nu=(2/\pi)\int_0^\infty dt(C'+Dt)/(C+Dt+t^3), \qquad (16)$$

and

$$\mu=(2/\pi)\int_0^\infty dt(C+Dt+t^3)^{-1}, \qquad (17)$$

where $C=\pi\mathfrak{A}_e/\gamma_e$, $D=4\mathfrak{A}_h/3$, and $C'=3C/2$. Equations (16) and (17) can be easily integrated and the result is that one obtains a value for the surface resistance which is, to an accuracy of better than 0.1%, the same as the anomalous skin effect value for the electrons alone. This is not surprising when one considers that the electron term is $C\approx 10^8$ and the hole term is $D\approx 10^4$.

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Zeeman Splittings of Paramagnetic Atoms in Crystalline Fields

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The paper deals with the energy levels as a function of magnetic field of paramagnetic ions in crystalline surroundings. The necessary information is given to write down the Hamiltonian matrix for ions in common crystalline fields. The method has been previously developed and it consists of determining the Hamiltonian matrix of $\beta\mathbf{H}\cdot(\mathbf{L}+2\mathbf{S})$ for the lowest states of an ion by the methods of group theory and time inversion considerations. The Hamiltonian matrix contains a certain number of undetermined constants which may be evaluated if the wave functions of the ions are known or the constants may be determined from experiment. In general, the number of available constants is larger than found in the conventional spin Hamiltonian formalism. The present method may be applied in cases where the conventional spin Hamiltonian formalism is inadequate to describe experimental results or where greater accuracy is required.

I. INTRODUCTION

In a previous paper[1] the authors developed a method of treating Zeeman splittings of paramagnetic atoms. The method was based on symmetry arguments and thus was very general in its results. In particular, it contained more terms and available constants than the generally used effective spin Hamiltonian.[2,3] It has been demonstrated by the wide use of the spin Hamiltonian that the additional terms of the new method in general do not represent a sizable contribution to the energy. However, as more precise measurements covering a large range in frequencies become available, the theoretical treatment of reference 1 may be useful in fitting the experimental data.

In order to apply this new method to the various crystalline symmetries and the various paramagnetic ions certain matrices have to be evaluated. In reference 1 the method has been demonstrated for a ^6S state in a crystalline field of cubic symmetry. In this paper we shall give the necessary information to write down the Hamiltonian matrix for ions in some common[4] point groups of crystal lattices.

For coherence it will be necessary to repeat here briefly some of the results of reference 1.

In the method of reference 1, it is assumed that the wave functions of the ion in the crystalline field are

[1] G. F. Koster and H. Statz, Phys. Rev. **113**, 445 (1959).
[2] B. Bleaney and K. W. H. Stevens, Repts. Progr. in Phys. **16**, 108 (1953).
[3] K. D. Bowers and J. Owen, Repts. Progr. in Phys. **18**, 304 (1955).

[4] The complete tables may be obtained by writing to the authors. They have also been deposited as Document No. 6059 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $6.25 for photoprints or $2.50 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.