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Cyclotron Resonance Measurements in Bismuth*†

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The derivative dR/dH of the surface resistance $R(H)$ versus H has been measured for H parallel to the three principal crystallographic axes in bismuth. The experiments were performed at liquid-helium temperatures using circularly polarized radiation of wavelength 1.25 cm. The sample formed one end of a cylindrical resonant cavity, the static magnetic field being normal to the sample surface. The results obtained at fields higher than 300 G are in general agreement with those of Galt *et al.* Part of the structure present for fields less than 300 G is interpreted as an Azbel'-Kaner type resonance for electrons having a zero average velocity component parallel to the magnetic field. We have also seen the electron spin resonance and combined cyclotron resonance–spin flip transitions. The electron cyclotron effective masses determined are in good agreement with other experiments. The electron g factors have been determined for the three crystallographic directions, and are consistent with the theoretical predictions of Blount and Cohen.

INTRODUCTION

THE use of circularly polarized microwaves in cyclotron resonance experiments permits a distinction between holes and electrons in both semiconductors[1] and metals.[2] For metals, when the classical skin effect theory is applicable, an inflection point in the magnetic field dependence of the power absorption is observed for each carrier when the condition

$$H=\omega m^*/e \qquad (1)$$

is approximately satisfied. This type of cyclotron resonance has been analyzed theoretically by Anderson[3] and by Lax *et al.*[4] and the results applied to experiments on bismuth[2] and antimony.[5] The use of circular polarization provides, in addition, the possibility of distinguishing between hole and electron spin resonance transitions and various types of combined spin and cyclotron resonance transitions.

On the basis of their magnetothermal experiments Boyle, Hsu, and Kunzler[6] have suggested that it should be possible to see a spin splitting of cyclotron resonance lines. This splitting has not been reported by either Aubrey and Chambers[7] or Aubrey[8] using H parallel to the surface, or by Galt *et al.*[2] using H normal to the surface in conjunction with circular polarization. Smith *et al.*[9] have reported the observation of the electron spin resonance and have seen evidence for transitions of the combined cyclotron resonance and spin flip types.

EXPERIMENTAL METHODS

A. Sample Preparation

In bismuth there is only about 10^{-5} conduction electron/atom, necessitating very pure materials. Single-crystal boules were prepared by a modified Bridgman technique starting with zone-refined material. This material was Tadanac Brand high-purity metals from the Consolidated Mining and Smelting Company of Canada Limited. The residual resistance ratio of samples prepared in this manner was $R(297°\text{K})/R(4.2°\text{K})=160$. Samples, characteristically $\frac{3}{4}$ in. square and $\frac{1}{8}$ in. thick, were cut from a boule, oriented using a Laue back-reflection camera, by either an acid string saw or spark cutter.[10] Acid-cut samples were polished flat chemically[11] while those cut by spark erosion were reoriented, spark planed flat, and finally chemically polished to produce a shiny, strainfree surface. Equally strainfree surfaces resulted but with the latter technique, misorientation could be reduced to less than 1°.

B. Microwave Details

The microwave spectrometer was very similar in design to those used in electron spin resonance measurements. The essential difference was in the use of a turnstile junction[12] and associated cylindrical components in place of the more conventional magic tee. The turnstile junction consists of five arms, four of rectangular waveguide and the fifth of cylindrical. This junction was used to produce circular polarization by placing shorts in two of the rectangular arms.[12] The only power coupled into the remaining rectangular arm was that reflected by the resonant cavity terminating the cylindrical arm. A ratio of power circularly polarized in one sense to that in the opposite sense in excess of 40:1

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[1] G. Dresselhaus, A. F. Kip, and C. Kittel, Phys. Rev. **98**, 368 (1955).

[2] J. K. Galt, W. A. Yager, F. R. Merritt, B. B. Celtin, and A. P. Brailsford, Phys. Rev. **114**, 1396 (1959).

[3] P. W. Anderson, Phys. Rev. **100**, 749 (1955).

[4] B. Lax, K. J. Button, H. J. Zeiger, and L. M. Roth, Phys. Rev. **102**, 715 (1956).

[5] W. R. Datars and R. N. Dexter, Phys. Rev. **124**, 75 (1961).

[6] W. S. Boyle, F. S. L. Hsu, and J. E. Kunzler, Phys. Rev. Letters **4**, 278 (1960).

[7] I. E. Aubrey and R. G. Chambers, J. Phys. Chem. Solids **3**, 128 (1957).

[8] I. E. Aubrey, J. Phys. Chem. Solids **19**, 321 (1961).

[9] G. E. Smith, J. K. Galt, and F. R. Merritt, Phys. Rev. Letters **4**, 276 (1960).

[10] Servomet Spark Machine, Metals Research Ltd., 91 King Street, Cambridge, England.

[11] L. C. Lovell and J. H. Wernick, J. Appl. Phys. **30**, 234 (1959).

[12] Massachusetts Institute of Technology Radiation Laboratory Series, Vol. 9, p. 375.

is possible only over a fairly narrow bandwidth necessitating some care in cavity design.

The sample is made to form one end of a right circular cylindrical cavity operating in a TE_{113} mode, Fig. 1(a). The cavity and sample are located in a vacuum jacket and this assembly suspended in a helium Dewar. In practice a small volume of helium was admitted to the vacuum space to ensure good thermal contact of the sample with the surrounding bath. The exclusion of liquid helium avoids noise from boiling at temperatures above the lambda point. Three factors dictated the cavity design. (1) To compensate for the cavities not being perfect right circular cylinders, two tuning stubs were provided in the side wall which could be adjusted with the sample in place at helium temperature. (2) Prefect circular polarization being possible only along the cavity axis, it was machined so that the sample represented only a fraction of the area of the cavity end. (3) To minimize strain and still maintain good electrical contact, the sample was held in place with a light spring against a choke groove machined in the end of the cavity. The field region of interest in this work is characteristically below 150 G. To avoid field distortion due to potentially superconducting and ferromagnetic materials, use was made of lead-free brass, 304 stainless steel, and nonsuperconducting solders.

C. Magnet Considerations

To avoid a bend in the cylindrical waveguide, a solenoid was used to provide the magnetic field. To keep the size and power consumption minimal, it was immersed in liquid nitrogen as shown in Fig. 1(b). The field of 35 G/A was uniform (to about 0.03%) over the sample volume. A second coil provided the 40-cps modulation field. A shunt in series with the solenoid was used to provide tha x-axis voltage for a Houston Instrument Company X-Y recorder.

D. Detection

The power reflected by the cavity was crystal detected and the resulting ac voltage amplified by a preamplifier, and a twin tee amplifier before being fed into a phase sensitive detector. The output, proportional to dR/dH, was recorded as the y-axis voltage on an X-Y recorder. To gaurantee measuring just dR/dH, the frequency of the klystron was locked to the resonant frequency of the sample cavity by a method similar to that of Kip.[13]

EXPERIMENTAL RESULTS

Figures 2 to 4 show the measured magnetic field dependence of the derivative of the surface resistance dR/dH for each of the principal axes, for both senses of polarization. In addition, the range of 0–175 G is shown on an expanded scale for the binary and bisectrix axes.

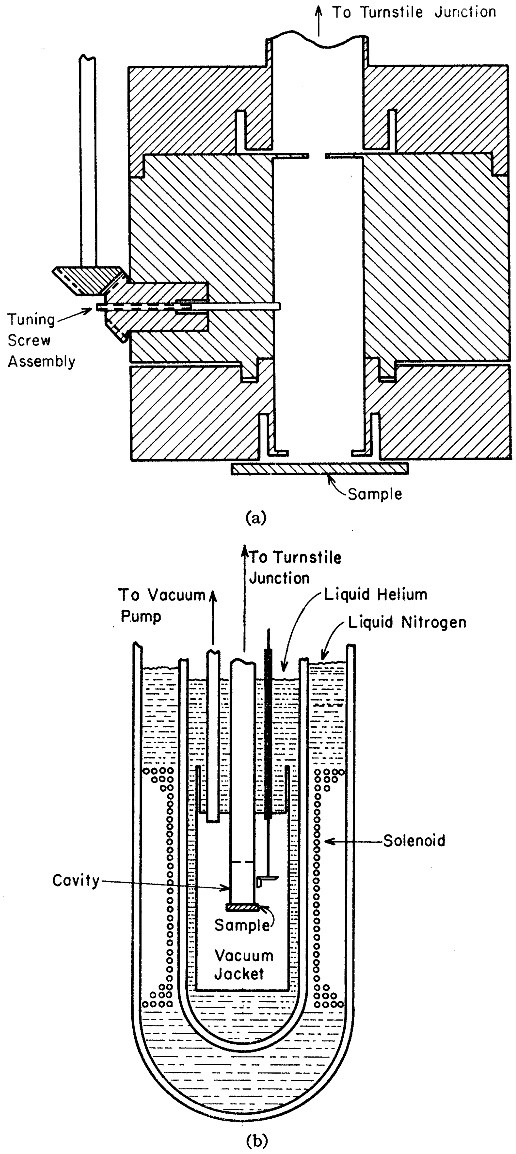

FIG. 1. (a) Sketch of the resonant cavity assembly. The sample is held in place by a spring-loaded plunger not shown in the drawing. (b) Sketch of solenoid and Dewar assembly.

These measurements were all made at 1.25°K and at 24.6 kM/sec. In general, the effect of lowering the temperature from 4.2 to 1.25°K was an increase in intensity of the derivative signal and a sharpening of some of the lines. The maximum field strength of 1400 G, was the practical operating limit of the solenoid.

For the sense of circular polarization sensitive to holes, zeros in dR/dH or maxima in $R(H)$ are present at about 800 G for the trigonal axis and at about 350 G for the binary axis. For the electron sense of polarization there is a maximum in $R(H)$ at about 350 G for the binary axis. Above 200 G for both senses of polarization, the dependence of dR/dH for the bisectrix axis is essentially monotonic. Above 200 G our results are in

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[13] A. F. Kip, Physica **20**, 813 (1954).

good qualitative agreement with those of Galt *et al.*[2] The peaks above 200 G are the singularities referred to as dielectric anomalies by Galt *et al.*[2] and will not be considered further. In the low-field region for the binary and bisectrix axes, there is a great deal of structure. For the binary axis-hole sense of polarization, Fig. 2(c), the peaks Nos. 4 through 9 are periodic in the reciprocal $1/H$ of the field and suggests an Azbel'-Kaner (abbreviated hereafter as A-K) type of cyclotron resonance phenomenon. For the electron sense of polarization the electron spin resonance is also present. In the next section the origin of the A-K type of behavior will be discussed. Our results will be interpreted on the basis of an A-K effect with the magnetic field normal to the sample surface, spin resonance transitions, and the combined Landau–spin flip transitions.

INTERPRETATION OF EXPERIMENTAL RESULTS

The crystal structure of bismuth is rhombohedral with two atoms per unit cell. A small overlapping of the valence with the conduction band results in its behavior as a semimetal with approximately 10^{-5} conduction electron/atom and an equal number of holes. The Fermi surface for the electrons, inferred by Shoenberg,[14] consists of three ellipsoids. One ellipsoid has the form

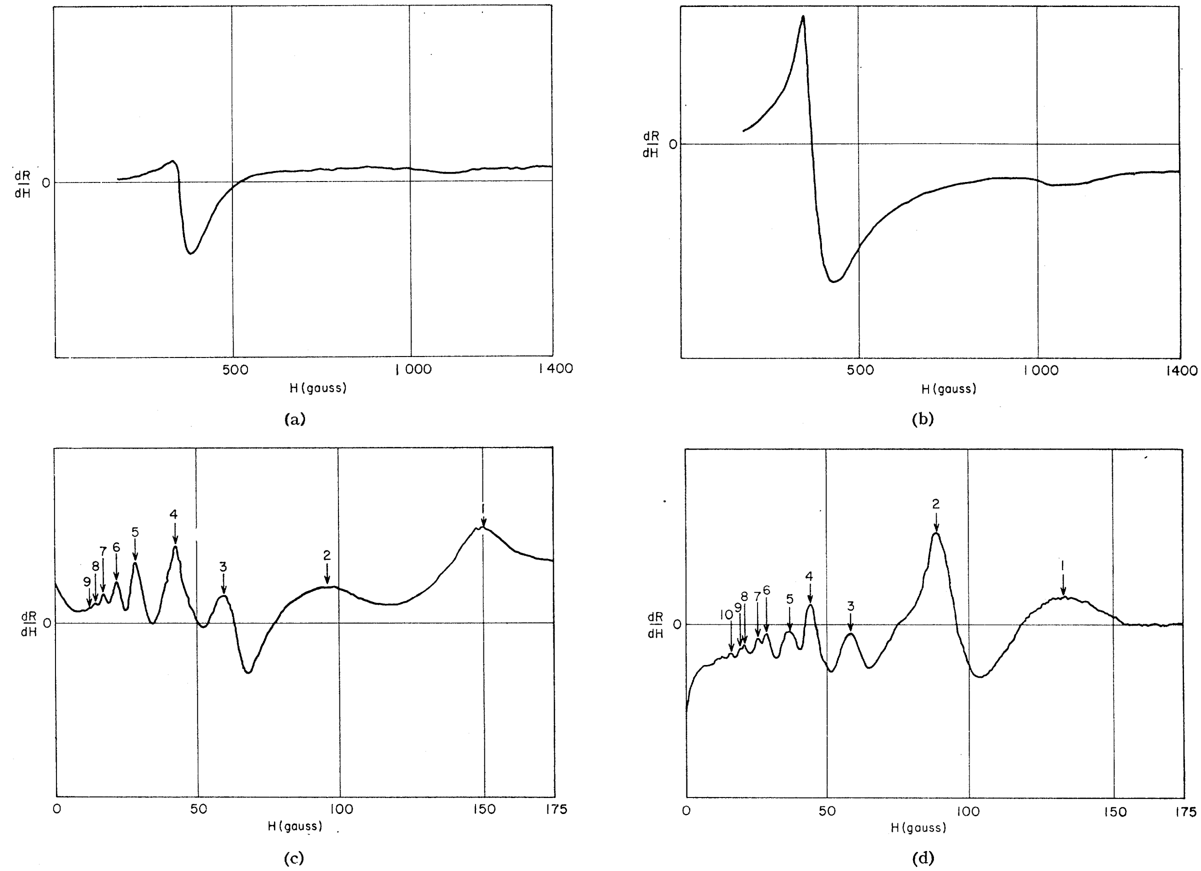
$$2m_0E_e=\alpha_1p_x^2+\alpha_2p_y^2+\alpha_3p_z^2+2\alpha_4p_yp_z, \tag{2}$$

where the momenta are referred to the bottom of the conduction band and the coordinates x, y, and z refer to the binary, bisectrix, and trigonal axes, respectively. The two additional ellipsoids are obtained by rotations of ±120° of this ellipsoid around the trigonal axis. Brandt[15] has proposed for the Fermi surface of the holes, an ellipsoid of revolution about the trigonal axis of the form

$$2m_0E_h=\beta_1(p_x^2+p_y^2)+\beta_2p_z^2. \tag{3}$$

The possibility of the existence of an additional band of heavy holes could not be investigated because of the low maximum fields attainable with the solenoid.

In their original work on cyclotron resonance for



(a) (b) (c) (d)

FIG. 2. The measured dependence of the derivative of the surface resistance dR/dH plotted vs the magnetic field H for H normal to the sample surface and parallel to a binary axis. This distinction between the two senses of incident circular polarization is given in the text. (a) Hole sense of polarization from 175 to 1400 G. (b) Electron sense of polarization from 175 to 1400 G. (c) Hole sense of polarization from 0 to 175 G. (d) Electron sense of polarization from 0 to 175 G.

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[14] D. Shoenberg, Proc. Roy. Soc. (London) **A170**, 341 (1939).

[15] N. B. Brandt, A. E. Dubrouskaya, and G. A. Kytin, Soviet Phys.—JETP. **10**, 405 (1960); N. B. Brandt, *ibid.* **11**, 975 (1960).

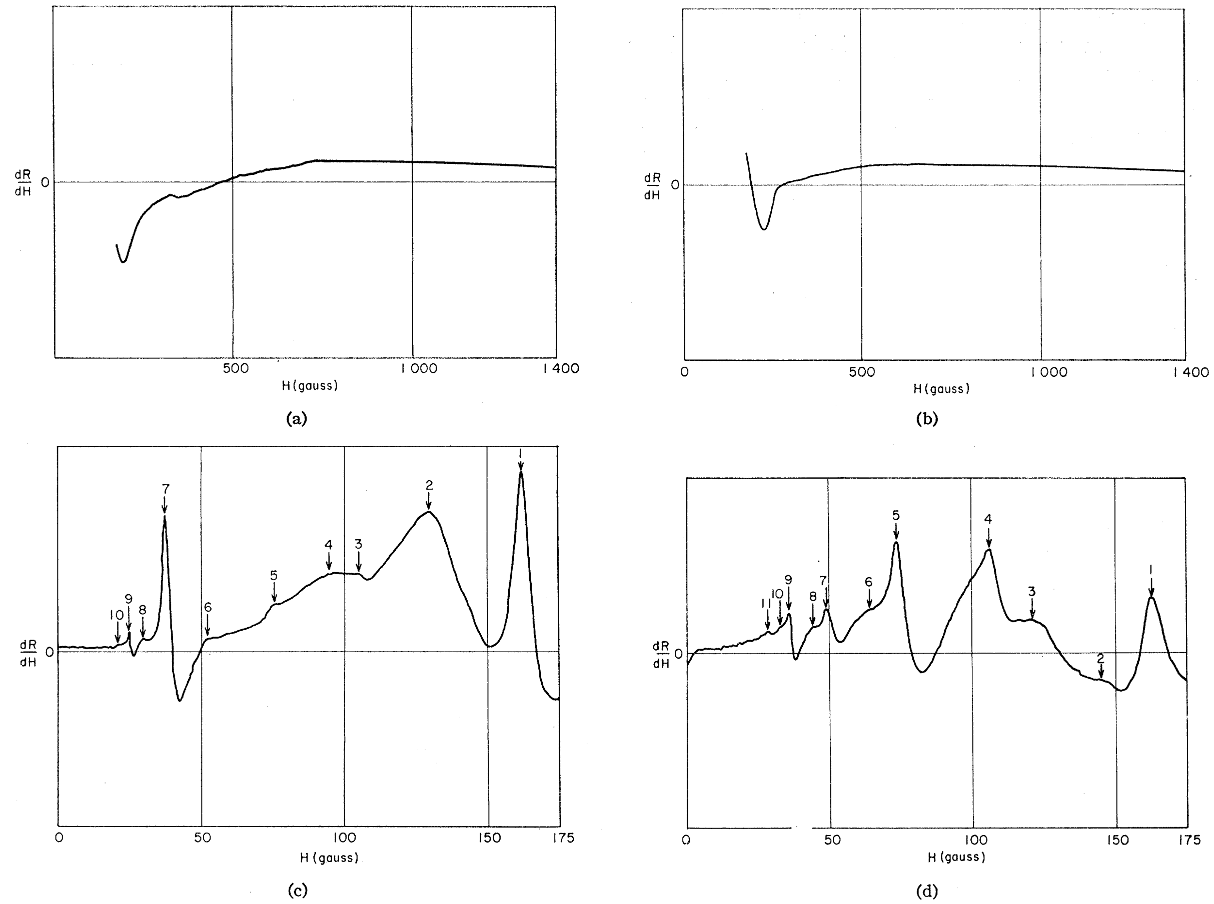

FIG. 3. The measured dependence of the derivative of the surface resistance dR/dH plotted vs the magnetic field H, for H normal to the sample surface and parallel to a bisectrix axis. The distinction between the two senses of incident circular polarization is given in the text. (a) Hole sense of polarization from 175 to 1400 G. (b) Electron sense of polarization from 175 to 1400 G. (c) Hole sense of polarization from 0 to 175 G. (d) Electron sense of polarization from 0 to 175 G.

metals, Azbel' and Kaner[16] predicted that the resonance at the cyclotron field H_c, and the subharmonics at $H=H_c/n$, should vanish for very small departures of the static magnetic field from strict parallelism with the sample surface. Subsequent experimental work has shown that the strength of the resonant series diminishes as the field is tipped but not as predicted.[17,18] This has led to the recognition of the fact that for those carriers in a small zone on the Fermi surface with an average drift velocity in the direction of the field, $\bar{v}_H$, approximately equal to zero, the orbits in real space are stationary.[19–21] The carriers with $\bar{v}_H \neq 0$ do not contribute to an Azbel'-Kaner type of cyclotron resonance because scattering occurs before multiple transits through the skin depth are completed as illustrated in Fig. 5. Harrison[22] has shown that the average drift velocity parallel to the field is given by

$$\bar{v}_H = (h/2\pi m^*)(\partial S/\partial k_H), \tag{4}$$

where S is the orbit area in wave number space and k_H is the projection of the wave vector in the direction of the field. For bismuth with ellipsoidal sections of Fermi surface, the condition for zero average drift velocity is $k_H=0$. If the magnetic field is along a principal axis for a particular ellipsoid, the orbits in real space corresponding to $k_H=0$ will lie in a plane which is parallel to the surface and thus can contribute to the normal diamagnetic resonance but not to a true cyclotron resonance.[16] For the magnetic field not along a principal ellipsoidal axis, those electrons on the central section, i.e., $k_H=0$, the motion in real space will be an ellipse but the orbit plane will make an angle with the sample

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[16] M. Ya. Azbel' and E. A. Kaner, Soviet Phys.—JETP. **5**, 730 (1957).

[17] A. F. Kip, D. N. Langenberg, B. Rosenblum, and G. Wagoner, Phys. Rev. **108**, 494 (1958).

[18] J. F. Koch and A. F. Kip, Phys. Rev. Letters **8**, 473 (1962) have reported observing an Azbel'-Kaner resonance in tin with the magnetic field normal to the sample surface.

[19] R. G. Chambers, Can. J. Phys. **34**, 1395 (1956).

[20] V. Heine, Phys. Rev. **107**, 431 (1957).

[21] J. C. Phillips, in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960), p. 154.

[22] W. A. Harrison, Phys. Rev. **118**, 1190 (1960).

surface, the sample surface being normal to the magnetic field direction. If this angle of tilt is large and the mean orbit radius is large compared to the skin depth, the electron will spend only a fractional part of a period in the skin depth. Under these conditions the electrons of the central section will undergo an acceleration in synchronism with the rf field. This gives rise to a series of absorption maxima that are periodic in $(1/H)$. Quantum mechanically, this can be described by transitions between the various Landau levels into which the electrons are quantized in the presence of a magnetic field. Following the suggestion of Cohen and Blount,[23] the effect of the spin is further to split the Landau levels.

For H parallel to the three principal crystallographic axes, H is, in each case, also parallel to a principal ellipsoidal axis of the holes. The stationary hole orbits being parallel to the sample surface excludes an A-K type behavior. The hole contribution to the surface resistance is an inflection point at their cyclotron field arising from the diamagnetic resonance. Our maximum field strength permits observation of the hole inflection point only for H parallel to the trigonal axis. For the electrons, because of the tilt of the ellipsoids, the static magnetic field cannot be along a principal ellipsoidal axis of more than one of the three ellipsoids for any crystallographic direction. For the binary axis, H is parallel to one, and for the bisectrix and trigonal axes, parallel to no principal ellipsoidal axis. The electrons of the central section have a sinusoidal velocity component parallel to the field and normal to the sample surface which can be expressed as

$$v_H = dr_H/dt, \tag{5}$$

where r_H is given by

$$r_H = r_H{}^0(H)\,\sin\omega t, \tag{6}$$

where ω_c is defined by Eq. (1). Using the value of the Fermi energy for the electrons determined by Shoenberg[14] and Aubrey's[8] determination of the effective mass parameters, in connection with the classical skin depth δ, the ratio $\mathcal{R}$, defined by

$$\mathcal{R} = 2r_H{}^0(H_c)/\delta, \tag{7}$$

has been calculated at the cyclotron field for the electrons of the three principal crystallographic axes. The ratio $\mathcal{R}$, analogous to the ratio of orbit diameter to skin depth, must satisfy the condition $\mathcal{R} \gg 1$ for an A-K resonance. For each principal axis, this condition is reasonably well satisfied for just one set of electrons. The dependence of the skin depth on magnetic field, calculated for the magnetic field normal to the surface and the metal anomalous,[24] gives a value greater than that calculated classically from zero field to the region around H_c. Thus, the ratio $\mathcal{R}$ at the cyclotron field can be considerably smaller than has been estimated.

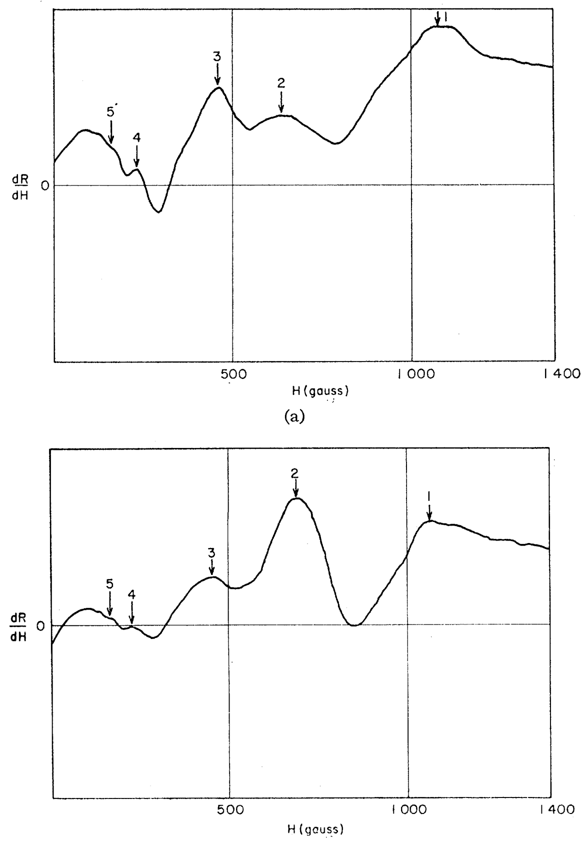

FIG. 4. The measured dependence of the derivative of the surface resistance dR/dH plotted vs the magnetic field H, for H normal to the sample surface and parallel to the trigonal axis. (a) Electron sense of polarization. (b) Hole sense of polarization.

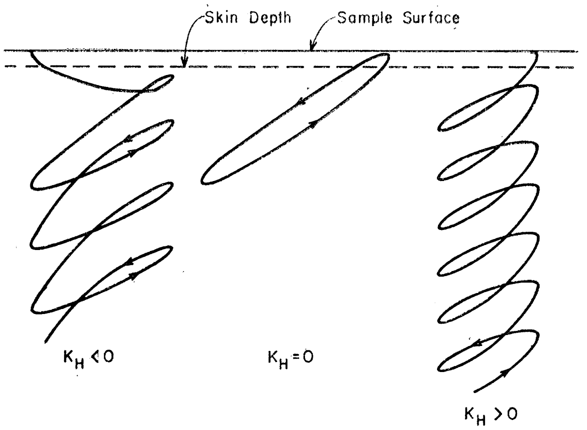

FIG. 5. The motion of electrons on an ellipsoidal Fermi surface when the magnetic field is normal to the sample surface and not parallel to a principal ellipsoidal axis. For $k_H \neq 0$, the nonzero drift velocity parallel to the field prevents the electrons from making multiple transits through the skin depth. For $k_H = 0$, the drift velocity parallel to the field is zero, and the orbit is stationary. These electrons can make multiple transits of the skin depth and absorb energy resonantly from the rf electric field.

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[23] E. I. Blount and M. H. Cohen, Phil. Mag. 5, 115 (1960).

[24] Piotr B. Miller and R. R. Haering (to be published).

In the limit of $\omega t \gg 1$, the maxima in the derivative dR/dH of the surface resistance occur at subharmonics of the cyclotron field.[25] From spin resonance theory[26] as modified to include the anomalous skin effect conditions,[27] the maximum in dR/dH occurs at the spin resonance field H_s in the limit of $\omega t_1 \gg 1$. The combined cyclotron resonance–spin flip transitions indicated in Fig. 6 have not been studied theoretically. The spin effective mass[23] m_s^* is given by $m_s^* = (2/g)m_0$. The ratio of the cyclotron to the spin effective mass, denoted by $\Delta = m_c^*/m_s^*$, can be shown theoretically to be less than or equal to one for bismuth.[28] In this case the fields for the combined cyclotron resonance–spin flip transitions are

$$H_n^3 = H_c/(n-\Delta), \tag{8}$$

$$H_n^4 = H_c/(n+\Delta), \tag{9}$$

where H_c is given by Eq. (1). The type 3 transitions correspond to cyclotron resonance minus a spin flip, type 4 to cyclotron resonance plus a spin flip, and type 2 to the spin resonance. Transitions 1, 3, and 4 plotted versus $1/H$ have the form

$$1/H_n = (n + a\Delta)/H_c, \quad a = 0, \ \pm 1, \tag{10}$$

where $a=0$ corresponds to type 1 and $a = \pm 1$ to type 4 and type 3 transitions, respectively. The A-K effect and spin resonance theories cannot be applied quantitatively to our results but are used as a qualitative guide. The A-K effect requires orbit diameters large compared with the skin depth, while spin resonance theory[26] requires that they be small, making it impossible to satisfy both conditions for the same carrier. For the types 3 and 4 transitions, we have assumed, by analogy with the A-K and spin resonance cases, that maxima in dR/dH will be related to the resonance fields.

X Axis

For the magnetic field parallel to the x axis there are two electron effective masses. For the heavier mass electrons, H is parallel to a principal ellipsoidal axis. The stationary orbits are parallel to the sample surface and do not lead to an A-K behavior, but can give rise to an inflection point in the surface resistance. For the lighter electrons the orbit planes are not parallel to the sample surface, the ratio $\mathcal{R}$ is $\mathcal{R} = 40$ and the condition $\mathcal{R} \gg 1$ is quite well satisfied.

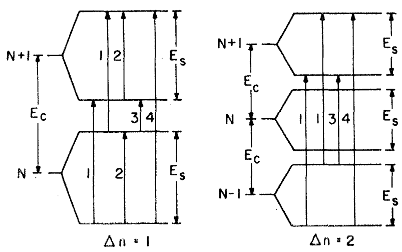
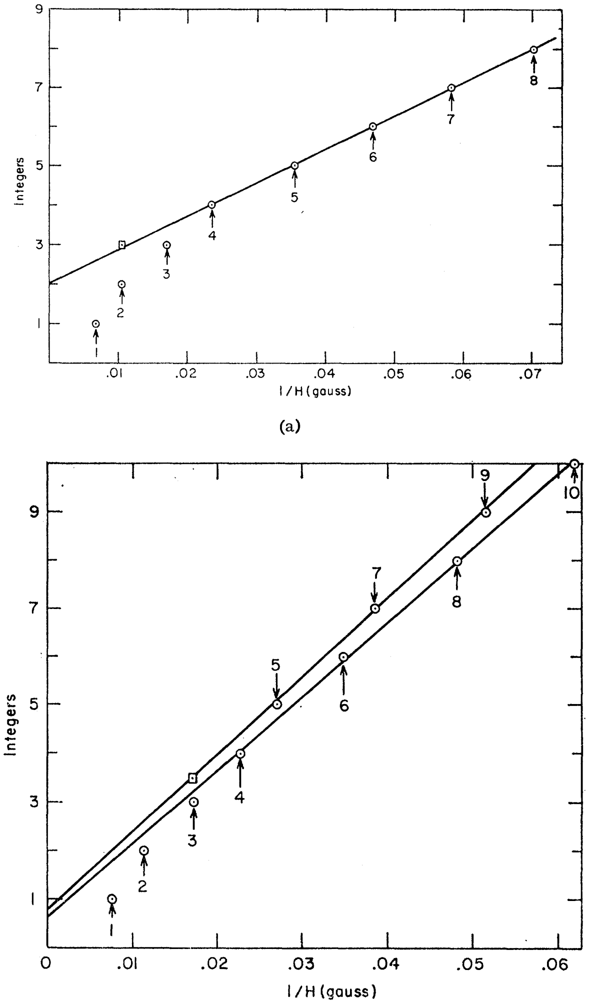


FIG. 6. Energy level diagrams illustrating the spin splitting of the Landau levels and transitions for the cases $\Delta n = 1$ and $\Delta n = 2$. The numbering of the transitions is that of Smith *et al.* (reference 9).



(a)

(b)

FIG. 7. Plot of the positions in the reciprocal of the field $1/H$ of maxima in the derivative of the surface resistance dR/dH, vs successive integers for H parallel to a binary axis. (a) Hole sense of polarization. (b) Electron sense of polarization.

In Figs. 7(a) and 7(b) the peak positions in $1/H$ are plotted versus successive integers for the hole and electron senses of polarization, respectively. For the hole sense of polarization, peaks Nos. 4 through 9 determine a straight line, a least-squares fit of which gives a cyclotron field of 86.0 G and an intercept which is zero to within the experimental error. This corresponds to an effective mass of $m^* = 0.00981$. Peaks Nos. 4 through 9, associated with the type 1 transitions, correspond to the second through seventh subharmonics. Peak No. 2, associated with the fundamental, falls approximately on this line if displaced upwards by one integer as indicated by the open square. The

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[25] M. Ya. Azbel' and I. M. Lifshitz, in *Progress in Low-Temperature Physics*, edited by J. C. Gorter (North-Holland Publishing Company, Amsterdam, 1961), Vol. 3, p. 302.

[26] F. J. Dyson, Phys. Rev. 98, 349 (1955).

[27] C. Kittel, reference 25, Sec. V.

[28] M. H. Cohen (private communication).

fundamental is very broad and shifted in position due to the A-K condition not being satisfied at this field, interference with the normal diamagnetic resonance, and possibly due to an interference with peak No. 1. The origin of peaks Nos. 1 and 3 is not understood, however, displacing peak No. 3 upwards by one half-integer places it very nearly on the straight line. It is tempting to associate this with the cyclotron resonance process but for a half integral value of n. The possible origin of such a process is not understood.

For the electron sense of polarization, the $1/H$ plot, Fig. 7(b), indicates two sets of peaks having approximately the same slope but different intercepts. The slopes have approximately the same value as that determined for the hole sense of polarization. The interference between successive peaks at low fields makes the determination of the slopes and intercepts uncertain. The peaks Nos. 4, 6, 8, and 10 correspond to integral values of n while peaks Nos. 5, 7, and 9 correspond to half-integral values. Peak No. 3 lies on the latter curve if displaced upwards by half an integer, indicated by the open square. Peak No. 2 is the electron spin resonance of the lighter mass electrons, the g factor being $|g|=200$. The ellipsoidal character of the Fermi surface should in principle, permit the observation of the spin resonance for both polarizations of the incident microwave power. This is not observed. The occurrence of the spin resonance for the electron sense of polarization only is puzzling, but is taken to indicate that the g factor is negative. The theoretical considerations[23] yield only the magnitude of the g factor. The ratio of the cyclotron to spin effective mass gives the value $\Delta=0.97$, and is in fair agreement with the value, $\Delta=0.92$, obtained by Kunzler *et al.*[6] An estimate of the spin relaxation time from the half-width of the line is $\omega\tau_s=10$. A correction for the relaxation time[26] places the resonant field about 4% higher and gives a value, $\Delta=0.94$, in much better agreement with the value of Kunzler *et al.*[6] The corrected value, $g=-192$, is in good agreement with the value of Smith *et al.*[9]

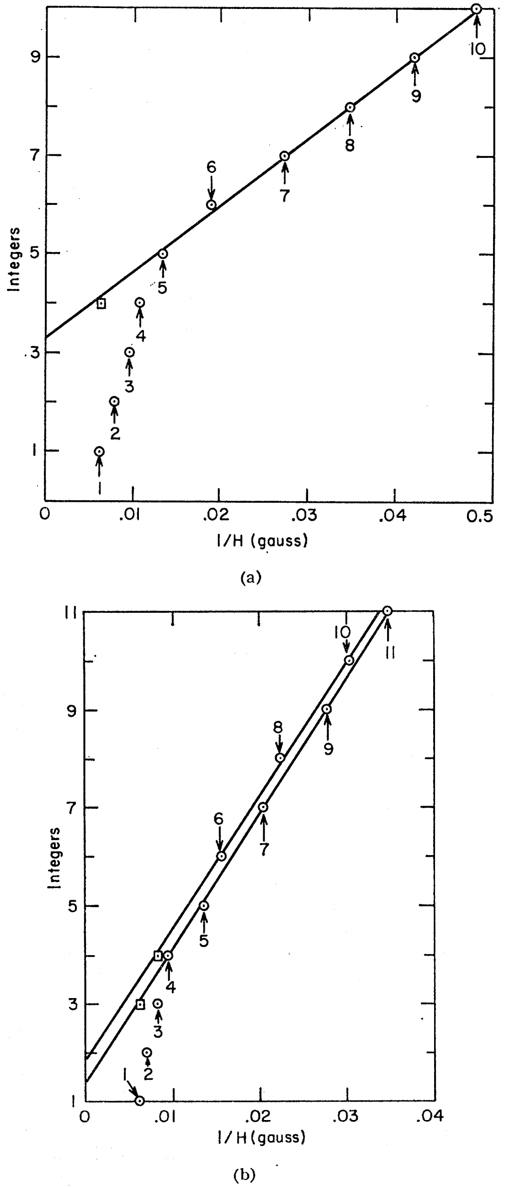

FIG. 8. Plot of the position in the reciprocal of the field $1/H$ of maxima in the derivative of the surface resistance dR/dH vs successive integers for H parallel to a bisectrix axis. (a) Hole sense of polarization. (b) Electron sense of polarization.

To draw any conclusions from the apparent nonzero intercepts obtained for the electron sense of polarization is unwarranted, because of the interference between the two curves causes poor resolution and probably phase shifts. By comparing peaks Nos. 4, 6, and 8 for the electron sense of polarization, Fig. 2(d), with peaks Nos. 4, 5, and 6 for the hole sense of polarization, Fig. 2(c), we conclude that these represent the same process, the type 1 or A-K transitions. The origin of the second set of peaks, occurring at half-integral values of the cyclotron field, is not understood. The value of $\Delta<1$ excludes the possibility of combined cyclotron resonance–spin flip transitions.

Y Axis

For the magnetic field parallel to the bisectrix axis there are two electron effective masses, the heavier being approximately twice the lighter. H is not parallel to a principal ellipsoidal axis for either set of electrons but is only 6° away for the lighter set. The tilt of the light electron orbit planes in real space with respect to the sample surface is small, the ratio $\mathcal{R}$ being $\mathcal{R}=4.9$. While the A-K condition for these carriers is not well satisfied, there are peaks present that could be associated with the second and third subharmonics. We will come back to this point. For the heavier electron, $\mathcal{R}=63$ and an A-K behavior should be present. An unambiguous interpretation of this data is made difficult by the factor of 2 difference in mass values expected.

For each set of electrons there is the possibility for any or all of the four types of transitions discussed in connection with the binary axis data. A final complication, aside from the fact that several of these transitions can occur at approximately the same magnetic field, is the polarization conversion that occurs in the reflection of the electromagnetic wave from the sample,[2] occurring also for the x axis. There is still, however, a marked difference for the two senses of polarization of the incident wave. We continue, for convenience, to use the expressions electron and hole senses of polarization to distinguish the different sets of data obtained.

Plotting peak positions in $1/H$ versus successive integers is shown in Figs. 8(a) and 8(b) for the two senses of polarization respectively. For the hole sense of polarization, peaks Nos. 5 through 10 determine a straight line. The slope, determined by a least-squares fit, gives a cyclotron resonance field of 135.2 G corresponding to an effective mass of $m^*=0.01536m_0$. Displacing peak No. 1 upwards by three units, as indicated by the open square, places it very nearly on this line. Peaks Nos. 2, 3, and 4 cannot be made to fall on this line by whole integer displacements. Referring to the actual data, Nos. 3 and 4 are poorly resolved; however, No. 3 can be made to fall on the straight line by displacing it $1\frac{1}{2}$ units. Peak No. 2 occurs at roughly the cyclotron field and is associated with the diamagnetic resonance, the shift in the peak position from the cyclotron field being a consequence of the finite relaxation time of these carriers.

The intercept is appreciably different from zero. The condition, $\Delta<1$, requires peak No. 5 to be associated with $n=1$. The value of $\Delta=0.72$, determined from the intercept, is quite uncertain due to possible relaxation time phase shifts. Peak No. 1 has to correspond to $n=0$ to satisfy the condition $\Delta<1$ and is identified as the spin resonance. From the ratio of the field at the maximum to the half-width of this peak, the relaxation time is $\omega\tau_s=30$. The peak position should be displaced by about 1% from the resonance field. Calculating the g factor from the position of the maximum only gives $|g|=108$. The spin resonance, occurring for both senses of polarization due to the ellipsoidal character of the Fermi surface, does not permit a determination of the sign of the g factor, the ratio of the cyclotron to spin effective mass Δ is $\Delta=0.837$. The peaks Nos. 5 through 10 are associated with the type 4 transitions, peak No. 5 corresponding to $n=1$. The occurrence of peak No. 3 at a half-integral value of n is not understood.

For the electron sense of polarization, Fig. 8(b), the situation is similar to that for the hole polarization except that two straight lines are determined, having, to within the experimental error, the same slope. The slope of the lower curve, determined by the well resolved odd numbered peaks Nos. 5 through 11, gives a cyclotron resonance field of 136.0 G corresponding to an effective mass of $m^*=0.01546m_0$. The upper curve, determined by the even numbered peaks Nos. 6, 8, and 10, is more uncertain, being related to shoulders rather than well-resolved maxima, but gives the same effective mass to within the uncertainty in the peak positions. Displacing peak No. 1 by two units and peak No. 3 by one unit as indicated by open squares, places them on the lower and upper curves, respectively. Peak No. 1 is is the spin resonance occurring for the electron sense of polarization. Peak No. 4 occurs exactly on the lower curve but corresponds to a half-integral value of n. It also appears, but very weakly, as peak No. 3 for the hole sense of polarization. For the lower curve the condition $\Delta<1$ can only be satisfied by identification as type 4 transitions with peak No. 5 corresponding to $n=1$. For the upper curve the intercept, uncertain for the same reasons discussed in connection with the slope, is about 0.1. These peaks are identified as being type 1 or A-K transitions, the nonzero intercept being associated with the difficulty in locating the actual maxima due to interference with adjacent peaks and finite relaxation time phase shifts. Peak No. 3 is associated with the type 1 fundamental transition but displaced and broadened. This results from: (1) the finite relaxation time of the electrons; (2) The A-K condition not being well satisfied at this field; and (3) interference with the diamagnetic resonance and peak No. 4.

The mass of the light electrons m_1 for H parallel to the bisectrix axis is related to the mass of the heavier electrons m_2 by the expression

$$2m_1=m_2[1+3(\alpha_1\alpha_2-\alpha_4^2)/\alpha_1\alpha_3]^{1/2}. \qquad (11)$$

From Shoenberg's determination of the α's, one obtains the value

$$(\alpha_1\alpha_2-\alpha_4^2)/\alpha_1\alpha_3\cong 0.004.$$

Thus to within an error of less than 1%, the mass of the lighter is just one half the mass of the heavier electrons. The mass of the lighter electrons is $m^*=0.0077m_0$. It would, therefore, be impossible, on the basis of peak positions only, to make an independent determination of the mass of the lighter electrons. In addition, for the lighter mass electrons, the A-K condition is not even approximately satisfied. The only transition expected for these electrons is the diamagnetic resonance. This is not distinguishable from an A-K transition of the heavier electrons. The spin resonance for the lighter electrons, expected from the theoretical considerations[23] to be in the region of 70 G, if present, would interfere with the type 4 transition of the heavier electrons. The large amplitude of peak No. 7 for the hole sense of polarization compared with the other peaks in this region indicates a constructive interference of two separate processes. An attempt to separate the two processes so as to determine the g factor of the lighter electrons will have to wait for an adequate theory of cyclotron and spin resonance under these experimental conditions.

Z Axis

In Figs. 4(a) and 4(b) is shown the derivative of the surface resistance dR/dH for the electron and hole senses of polarization, respectively. For H parallel to the trigonal axis there is just one electron effective mass. The value of $\mathcal{R}$ calculated from Eq. (3) of $\mathcal{R}=25$ indicates that an A-K type resonance should be possible. For this orientation, the cyclotron field for the light holes is within the field range studied. For these holes, H is parallel to a principal ellipsoidal axis, $\mathcal{R}=0$, and no A-K type behavior is possible. The normal diamagnetic resonance leading to an inflection point in $R(H)$ for this light hole is present. A determination of the hole effective mass based on the position of the inflection point has been given[2] and will not be repeated here.

In Figs. 4(a) and 4(b) Peak No. 1 represents the onset of the high-field limiting behavior of the surface resistance. Peak No. 2 for the hole sense of polarization characterizes the maximum slope in $R(H)$ preceding the dielectric anomaly.[2] Peaks Nos. 3 and 4 and the shoulder, No. 5 for both senses of circular polarization, are associated with an A-K behavior for the electrons. An average of the separations in $1/H$ gives a value for the cyclotron field and effective mass of

$$H_c=450 \text{ G}, \quad m^*=0.051m_0.$$

The remaining Peak No. 2 for the electron sense of polarization at 640 G is thought to be associated with either the electron spin resonance or the inflection point in $R(H)$ associated with the electrons. The assumption that this is the electron spin resonance gives a g factor of $g=-27.5$. This is to be compared with the value of $g=-30$ obtained by Smith *et al.*[9] The ratio of spin to the cyclotron effective mass determined for our data is

$$m_s^*/m_c^*=1.40.$$

This compares favorably with the ratio

$$m_s^*/m_c^*=\sqrt{2}$$

predicted theoretically.[23] The small change in slope at 350 G for the electron sense of polarization indicates that peaks 2 and 3 are superimposed on a more slowly varying contribution to $R(H)$. The possibility that this variation is associated with the maximum in dR/dH for the diamagnetic resonance inflection point in $R(H)$ supports the identification of the spin resonance. Samples have been chemically rather than electropolished to avoid the strain that would result from making mechanically the good electrical contact necessary for electropolishing. Low-melting-point solders that could provide the required electrical contact were ruled out to avoid the field distortion that would occur if they became superconducting. The development of etch pits which occurs for the trigonal plane in bismuth could be minimized but not completely eliminated with chemical polishing. Those remaining after a careful chemical polishing act as scattering centers leading to shorter relaxation times than characterize the bulk material. This would account for the broadness of the spin resonance line, the presence of only two subharmonics in the A-K behavior, and the absence of the types 3 and 4 transitions.

TABLE I. Comparison of the electron effective mass values determined by this experiment for the three principal crystallographic directions with those given by Aubrey[a] and by Galt *et al.*[b] No values for the hole effective masses were determined for reasons discussed in the text.

	This determination	Aubrey[a]	Galt *et al.*[b]
$H\parallel x$			
m_1^a	0.0098	0.0085	0.0105
m_1^b		0.119	0.13
$H\parallel y$			
m_2^a	0.0077	0.0078	0.0091
m_2^b	0.0155	0.0155	0.0180
$H\parallel z$			
m_3	0.051	0.0546	0.080

[a] See reference 8.
[b] See reference 2.

The effective mass values determined are given in Table I, the uncertainty being 6%. For comparison the results of Aubrey[8] and Galt *et al.*[2] are also tabulated. For reasons discussed earlier, we did not determine the mass of the heavier electron associated with the binary axis.

CONCLUSION

An A-K phenomenon has been observed for the magnetic field normal to the surface of bismuth single crystals, in addition to the spin resonance and combined Landau–spin flip transitions. We have determined the cyclotron effective masses and the g factors of the electrons for the three principal crystallographic directions. The cyclotron effective masses determined are tabulated in Table I along with the results of other experiments for purposes of comparison. The agreement is within our experimental error of 6%. The values of the g factor determined are

$$H\parallel x, \quad g=-192;$$
$$H\parallel y, \quad |g|=108;$$
$$H\parallel z, \quad g=-27.5.$$

For H parallel to the binary and the trigonal axis Smith has obtained the values of $g=-200$ and $g=-30$. The agreement between these two determinations is good. The ratio of cyclotron to spin effective mass is in good agreement with theoretical predictions.

For the A-K behavior with $\omega\tau\gg1$, the positions of the maxima in the derivative dR/dH of the surface resistance occur at the cyclotron field H_c and at the subharmonics H_c/n.[25] For the spin resonance, the maximum in dR/dH corresponds to the spin resonance field for $\omega\tau_s\gg1$. In each case the spin resonance has been determined from the position of its maximum. For the binary and trigonal axes, the cyclotron effective masses were determined from the average separations in $1/H$ of the derivative maxima. For the bisectrix axis the cyclotron effective masses were determined from the position of the combined Landau–spin flip transitions in conjunction with spin resonance transition. This procedure has the obvious advantage of being less sensitive to the effect of a finite relaxation time and the additional effects that the presence of other carriers can have on the position of the inflection point. The A-K behavior with the field normal to the surface and circular polarization does not permit a discrimination between holes and electrons. For this one still has to rely on the location of an inflection point for the two senses of polarization.

The origin of the unexplained structure associated with the binary and bisectrix axes is not understood. Aubrey[8] has seen, in addition to the holes observed by Brandt[15] and Galt *et al.*,[2] peaks which he attributes to a very light hole band. An examination of our data for the presence of these light holes is inconclusive. They do not correspond to our unexplained structure. We have inspected the binary axis data for possible subharmonics of the heavier mass electron. Such peaks, which would be related to the departure of the conduction from parabolicity, have not been found.

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Many-Particle Theory of Impurity States in Polar Crystals

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An attempt is made to generalize to polar semiconductors, Kohn's many-particle approach to the theory of shallow impurity states in nonpolar crystals. Nuclear coordinates are included as dynamic variables. The impurity state is described as a linear combination of exact many-particle eigenfunctions that correspond to the motion of a polaron through the impurity-free crystal. The resulting effective dielectric constant is likewise identified as the usual static constant, by considering the interaction between an electron bound by an infinitesimal impurity charge and a small classical charge fixed at a large displacement from the impurity. Corrections to the resulting hydrogenic equation arise from the need to include real phonon states. These corrections are estimated for substances with weak electron-lattice coupling only. The corrections are found small for most III–V semiconductors. They are rather more serious for substances such as $CdAs_2$ and CdS, that have somewhat stronger coupling, suggesting a limitation to the applicability of the theory. In an Appendix an interpretation of the new formal contribution to the effective dielectric constant is given in terms of the motion of the ion cores.

1. INTRODUCTION

IN a well-known paper Kohn has given a many-particle theory of impurity states in nonpolar crystals, which gives a rigorous basis to the customary effective-mass treatment of the problem.[1] Recently, impurity states in polar crystals have become of wide experimental interest.[2–4] The theoretical analysis of the polar problem has likewise already received attention.[5,6] The present paper attempts to show that a generalization of Kohn's theory to polar crystals is possible, at any rate for crystals in which the coupling between conduction electrons and phonons is weak.

A number of measurements have been made via electrical properties of the impurity activation energy in substances with relatively weak electron phonon coupling: in indium-doped cadmium sulphide (CdS), for example, by Piper and Halsted,[2] and in $CdAs_2$ by Fischler and Koenig.[3] In both materials investigators have found rough agreement with the hydrogenic ionization energies providing that the static rather than the high-frequency dielectric constant was used.[7] The

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