Cyclotron Resonance in Sodium and Potassium*

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Azbel'-Kaner cyclotron resonance has been observed in oriented single crystals of sodium and potassium. The data are isotropic in both metals and yield for the ratio of cyclotron effective mass to free electron mass the values 1.24±0.02 and 1.21±0.02 for sodium and potassium, respectively. The isotropy of the data for potassium indicates that its Fermi surface is very nearly spherical with the anisotropy in k_F probably less than 1%. The interpretation of the data for sodium is complicated by the existence of a low-temperature phase transformation.

I. INTRODUCTION

THE purpose of this paper is to present the results of a series of Azbel'-Kaner type cyclotron resonance experiments on sodium and potassium. In addition to giving the cyclotron mass, these experiments yield information on the topology of the Fermi surface. Furthermore, since the Fermi surface is found to be spherical, use of available data on the dimensions of the Fermi sphere in potassium allows accurate evaluation of the Fermi velocity of electrons in potassium. For potassium we find that the cyclotron mass, m_c, is isotropic, with the mass ratio $m_c/m = 1.21 \pm 0.02$, where m is the free-electron mass. (We have recently been informed by Shoenberg and Stiles of their new de Haas–van Alphen results in potassium, which give an effective mass ratio of 1.2, in excellent agreement with our result. They have measured, with an accuracy of a few percent, departures from a spherical Fermi surface which amount to about 1 part in 1000.) For sodium we observe an isotropic cyclotron mass having the mass ratio $m_c/m = 1.24 \pm 0.02$, but an evaluation of the significance of the data in sodium is complicated by the existence of a low-temperature phase transition.

Sodium and potassium are both thought to have nearly spherical Fermi surfaces so the cyclotron resonance curves (plots of dR/dH versus H, where dR/dH is the derivative of the real part of the surface impedance with respect to the magnetic field) should resemble the theoretical curves for a degenerate free-electron gas. In this investigation we found that the experimental curves closely resemble the theoretical curves when H is parallel to the surface of the alkali metal specimen, but when H is inclined at a small angle to the specimen surface the resonance peaks of the experimental curves show a splitting not predicted by the theories of cyclotron resonance.[1-5]

The arrangement of this paper is as follows: In Sec. II the experimental apparatus is described, and the experimental techniques and procedures are discussed. In Sec. III the experimental results are presented with our interpretation of the data. Section IV presents a summary of the experimental results and the conclusions drawn from the results.

II. EXPERIMENTAL APPARATUS AND TECHNIQUES

A. Apparatus

In the cyclotron resonance experiments the alkali metal specimen forms one wall of a resonant microwave cavity at liquid-helium temperatures. A microwave spectrometer operating at a frequency near 68 Gc/sec is employed to detect changes in the Q of the cavity as the magnetic field is varied. The spectrometer is similar to the lower frequency spectrometer used in cyclotron resonance in copper,[6] but employs a three-port circulator in place of the magic tee bridge, using a variable coupling cavity similar to that described by Gordon.[7] Magnetic field modulation is employed in conjunction with a phase sensitive detection system so the experimentally observed quantity is dR/dH. The value of dR/dH is recorded continuously as H is swept from -1 to $+20$ kOe.

The cylindrical microwave cavity is resonant in the TE_{111} mode. The rf currents excited in the sample by this mode are not perfectly rectilinear. A rough estimate indicates that approximately 85% of the current density lies with $\pm 10°$ of the direction of maximum current density. The symmetry of the cavity is destroyed by a small indentation in the cavity wall. The cavity is then resonant in two orthogonal modes separated in frequency by approximately 200 Mc/sec or 10 cavity resonance half-widths. The cavity orien-

[1] M. Ya. Azbel' and E. A. Kaner, Zh. Eksperim. i Teor. Fiz. **32**, 896 (1957) [translation: Soviet Phys.—JETP **5**, 730 (1957)];

M. Ya. Azbel' and E. A. Kaner, J. Phys. Chem. Solids **6**, 113 (1958).

[2] D. C. Mattis and G. Dresselhaus, Phys. Rev. **111**, 403 (1958).

[3] S. Rodriguez, Phys. Rev. **112**, 1616 (1958).

[4] E. A. Kaner, Zh. Eksperim. i Teor. Fiz. **33**, 1472 (1957) [translation: Soviet Phys.—JETP **6**, 1135 (1958)].

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

[6] A. F. Kip, D. N. Langenberg, and T. W. Moore, Phys. Rev. **124**, 359 (1961).

[7] J. P. Gordon, Rev. Sci. Instr. **32**, 658 (1961).

tation relative to the waveguide is such that the coupling to the two orthogonal modes is approximately equal. By tuning the klystron frequency from one mode to the other, the rf polarization is rotated 90° relative to the sample.

The mounting of the cyclotron resonance specimen must be such that the electrical losses in the joint between the cavity wall and the specimen are minimized, the specimen must not be strained, and the assembly must be rigid enough to avoid shaking due to interaction of the static magnetic field with the eddy currents induced by the field modulation. A high-Q cavity to which the sample could be clamped was prepared by machining from brass a TE_{111} cavity with a choke flange on the open end. The cavity was then plated with approximately 10^{-4} cm of silver. This thickness of plating is chosen because it is large compared with a microwave skin depth, but much smaller than the skin depth at the modulation frequency. By this means a high Q can be achieved without seriously attenuating the amplitude of the modulation field inside the cavity.

Specimens of sodium and potassium cannot be clamped tightly enough at room temperature to prevent shaking of the sample in the modulation field. If clamped tightly enough to avoid shaking, the specimens are partially extruded into the cavity and are ruined. This problem was solved by clamping the specimen very lightly at room temperature, cooling to helium temperature, and then clamping it securely to the cavity. This procedure is based on the observation that sodium and potassium harden as they are cooled to liquid-helium temperatures.[8] The specimen clamping arrangement had the additional advantage that the resonant frequency of the cavity could be varied over a narrow range by adjusting the pressure on the specimen. The ability to tune the cavity simplified identification of the cavity resonance in the presence of spurious reflections.

In some of the experiments the effects of tipping the magnetic field relative to the specimen surface were studied by mounting the cavity and specimen in the vertical plane. Rotation of the electromagnet about a vertical axis then corresponded to tipping **H** out of the plane of the specimen surface.

B. Specimen Preparation

The major impediment to performing a successful cyclotron resonance experiment is the difficulty of preparing an adequate specimen. The softness and extreme reactivity of the alkali metals made it necessary to devise special techniques for the preparation and handling of single-crystal specimens. The details of the procedures used in preparing the samples have recently

been described by Grimes.[9] Only a brief description will be presented here.

Single crystals of high-purity sodium and potassium are grown in vacuum by a modified Bridgeman technique. The single crystal boules of sodium typically have a residual resistance ratio of 8000, whereas the potassium residual resistance ratios varied from approximately 1000 to 5000. The single-crystal boules are oriented optically from the crystallographic etch planes. The accuracy of this method of orientation is about $\pm 1°$. A specimen of the desired orientation is cut from a single-crystal boule using a string saw wet with a mixture of alcohol and water. The specimen surface is carefully lapped smooth on a cloth wet with isopropyl alcohol. The smoothed single crystal is then etched in a mixture of alcohol and xylene to remove any metal that may have been damaged during the lapping. The etched crystal is dipped in mineral oil and covered with a piece of 0.00025-in.-thick Mylar. Most of the excess oil is removed by gentle blotting and the Mylar-covered crystal is lightly clamped to the microwave cavity in preparation for the cyclotron resonance experiment. The surfaces of the single-crystal specimens prepared in this manner were not as flat and smooth as the typical electropolished specimen used in experiments on less reactive metals.

To study the effects of inclining the magnetic field at small angles relative to the surface of the specimen it was necessary to prepare specimens having flat surfaces. Polycrystalline samples having flat surfaces were prepared by simply pressing a lump of the metal between glass plates. Samples prepared in this manner had macroscopically flat surfaces, but crystallographic etch planes developed on the sample surface despite a protective covering of mineral oil and a Mylar film. The development of etch planes indicated that some corrosion of the specimen surface did occur so the surface was not smooth on a microscopic scale. The etch planes made the individual crystallites visible. The crystallites in both sodium and potassium had typical dimensions of 1 to 2 mm.

Azbel' and Kaner[1] have analyzed the behavior of dR/dH versus H and find a variation similar to that shown in Fig. 1. They find that the dR/dH maxima occur very near the resonance fields.[10] This conclusion
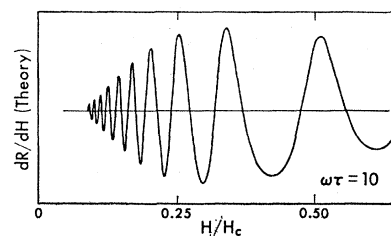

FIG. 1. Absorption derivative curve for a specimen having an isotropic cyclotron effective mass and $\omega_{rf}\tau = 10$, according to the theory of Azbel' and Kaner.

[8] D. Hull and H. M. Rosenberg, Phil. Mag. 4, 303 (1959).

[9] C. C. Grimes, Doctoral dissertation, University of California, 1962 (unpublished).

[10] M. Ya. Azbel' and E. A. Kaner, Zh. Experim. i Teor. Fiz. 39, 80 (1960) [translation, Soviet Phys.—JETP 12, 58 (1961)].

is substantiated by the computer calculations of Kip et al.[6] The computer calculations show that for a finite electron relaxation time a more precise cyclotron mass is obtained from the periodicity of the resonances, $\Delta(1/H)$, than from the resonance fields. For a free electron gas and $\omega\tau=5$, the cyclotron mass values derived from the periodicity of the dR/dH maxima are in error by no more than 0.5% while the use of the fundamental dR/dH maximum position alone may lead to an error as large as 10% (for the case of $\omega\tau\sim5$).

The procedure used to reduce the data is as follows: The data are taken for both increasing and decreasing **H**, and the mean value of the field is determined for each dR/dH maximum. This averaging process tends to eliminate any errors arising from the time constants of the experimental apparatus. A plot is then made of reciprocal resonance fields against the harmonic number, n. A straight line is fitted to the plot, and its slope is determined. The slope of the plot gives the periodicity $\Delta(1/H)$. The cyclotron mass is then calculated from the relation

$$m_c = e/c\omega_{rf}\Delta(1/H).$$

According to theory, a plot of dR/dH maxima against harmonic number is a straight line passing through the origin in the case of an infinite relaxation time. For a finite relaxation time the dR/dH maxima are displaced from the true resonance field by a constant in $1/H$. Consequently the plot of the reciprocal resonance fields against harmonic number does not pass through the origin for a finite relaxation time. The intercept of the straight line plot on the ordinate, when normalized to $\Delta(1/H)$, is called the *phase shift*, $\Delta\Phi$. The inherent phase shift due to a finite relaxation time according to the Azbel'-Kaner theory does not exceed $\Delta\Phi=\pm0.10$ for the specific cases examined by Kip et al.

III. EXPERIMENTAL RESULTS AND INTERPRETATION

A. Potassium

In this section we present the data obtained in the cyclotron resonance experiments on three representative potassium specimens and one sodium specimen and also our interpretation of the data. The potassium specimens include a lightly etched single crystal, a heavily etched single crystal, and a polycrystalline specimen which had a flatter surface than the single-crystal specimens. In the course of these experiments, useful data were obtained from seventeen different potassium specimens including single crystal specimens having (100), (110), (111), and (221) plane surfaces. The data obtained from all specimens are consistent with the data from the three representative specimens discussed below.

An experimental curve for potassium Sample A, which is a lightly etched single crystal, is shown in Fig. 2. This specimen has a (110) plane surface, **H** is

parallel to the sample surface and 20° from the $\langle100\rangle$ axis, and the 66.2-Gc/sec microwave electric field, $\mathbf{E}_{rf}$, is approximately perpendicular to **H**. The dR/dH maxima corresponding to the 4th through 10th sub-harmonics of the fundamental resonance are clearly resolved. The experimental curve closely resembles the Azbel'-Kaner theoretical curve shown in Fig. 1 for a free-electron gas having $\omega_{rf}\tau=10$. Essentially identical experimental curves were obtained for all orientations of the magnetic field parallel to the sample surface. The cyclotron mass of the electrons is obtained from the periodicity of the resonances, $\Delta(1/H)$, as described above. The ratio of the cyclotron mass to the free electron mass, m_c/m, is found to be 1.21 ± 0.02 for all orientations of the magnetic field. The lack of anisotropy in cyclotron mass and the fact that only one resonance series is seen indicate that the Fermi surface is isotropic and that it does not touch the Brillouin zone boundary. The phase shift shows random fluctuations in the range -0.2 to $+0.2$ for different orientations of the magnetic field in the plane of the crystal. The angle between $\mathbf{E}_{rf}$ and **H** is 45° or greater in all of the data taken for this sample. No attempt was made to take data with $\mathbf{E}_{rf}$ parallel to **H** for this sample.

In the course of these experiments it was observed that heavily etched potassium crystals yielded experimental curves with "split peaks." An example of the data from a more heavily etched sample is shown in Fig. 3. The experimental curve in this figure is for Sample B which has a (110) plane surface. Here **H** is along the $\langle100\rangle$ axis, and the $\mathbf{E}_{rf}$ is perpendicular to **H**. This curve deviates considerably from the theoretical curve of Fig. 1 since all peaks above 4 kOe are split. The splitting is the same if both the magnetic field and the microwave polarization are rotated 90° so **H** is along the $\langle110\rangle$ axis. However, if the static magnetic field is rotated while the microwave current remains fixed relative to the sample, then the splitting increases as **H** is rotated from perpendicular to parallel to $\mathbf{E}_{rf}$.
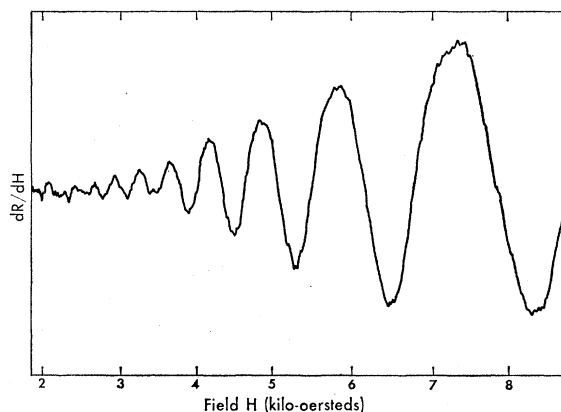

FIG. 2. Experimental absorption derivative trace obtained from a lightly etched single crystal of potassium. Essentially identical traces were obtained for all directions of **H** in the (110) plane. This curve closely resembles the theoretical curve in Fig. 1.
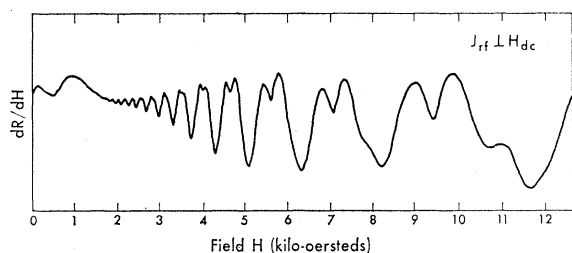
FIG. 3. Experimental absorption derivative trace obtained from a heavily etched single crystal of potassium with the microwave electric field perpendicular to H. This curve yields the same cyclotron effective mass as the curve in Fig. 2 despite the difference in line shape.

The curve shown in Fig. 4 is also from Sample B, but with the magnetic field rotated 90° so H is along the $\langle 100 \rangle$ axis and E_{rf} is parallel to H. We see that the splitting of the peaks is more pronounced for E_{rf} parallel than for E_{rf} perpendicular to H.

When the data for Sample B are reduced by the procedure described above, a straight line plot of reciprocal fields versus integers with $\Delta \Phi = 0$ is obtained if the cyclotron resonances are assumed to occur at the dR/dH minima near 9.4, 7.1, 5.6, $\cdots$ kOe. The cyclotron mass has the same value as for Sample A and is isotropic as before.

The cyclotron resonance experiment on Sample B was repeated with the microwave frequency reduced from 67.5 to 23.5 Gc/sec. Again the resonance peaks were split at fields greater than 4 kOe. The cyclotron mass had the same value and was isotropic as before. The fundamental ($n=1$) resonance, which occurs at too great a field to be observed at 68 Gc/sec, occurs near 10 kOe for the lower frequency. The fundamental resonance peak was split and had the same shape as the peaks with $n = 2, 3, \cdots$ for both E_{rf} perpendicular and E_{rf} parallel to H. No extra peak appeared that could be identified as the conduction electron spin resonance which would have occurred at a field of 8.4 kOe for a spectroscopic splitting factor $g = 2$. This is one of the factors which seems to rule out the possibility, which we have considered, that the split peaks result from combined resonance (transitions involving both changes in Landau level and spin orientation).
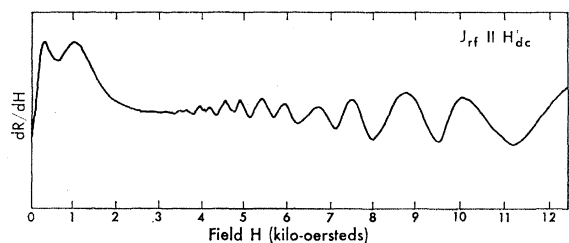

FIG. 4. Experimental absorption derivative trace from the same potassium specimen as Fig. 3, but with the microwave electric field parallel to H.

This possibility is discussed theoretically by Azbel'[11] and by Bloomfield.[12]

It was suspected that the splitting of the resonance peaks for heavily etched specimens was due to the roughness of the surface produced by the etching process. To check this possibility data were taken with H inclined relative to the specimen surface using relatively flat polycrystalline samples of potassium which were prepared as described above. Since the cyclotron mass is isotropic, a polycrystalline specimen is expected to yield the same result as a single crystal specimen. Figure 5 shows examples of the data obtained from Sample C with E_{rf} perpendicular to H at a microwave frequency of 68.5 Gc/sec. The curves in Fig. 5 clearly demonstrate that the splitting of the resonance peaks is a minimum when H is parallel to the surface of the polycrystalline potassium specimen. Inclining H as little as $\frac{1}{2}°$ produces an appreciable splitting of the resonance peaks at the higher magnetic fields. As the angle of inclination, α, increases, the amplitude of the cyclotron resonances decreases, and the splitting of the resonance peaks becomes more pronounced. When α is as large as $5\frac{1}{2}°$, the experimental curve resembles the theoretical curve for a free-electron gas, but the peaks are inverted. Thus in the curve for $\alpha = 5\frac{1}{2}°$, there are minima in dR/dH and the values of H where there are maxima in dR/dH in the curve for $\alpha = 0°$. When the microwave radiation was polarized with E_{rf} parallel to H, the experimental curves closely resembled those in Fig. 5 except the splitting was slightly more pronounced for a given α.

The results of these experiments in an inclined magnetic field confirm our belief that roughness of the sample surfaces caused the splitting of the peaks for severely etched single crystal samples, when H was parallel to the sample surface. Thus, we feel that the splitting of the peaks in Figs. 3 and 4 occurs because portions of the sample surface are inclined with respect to H on a microscopic scale even though H is parallel to the surface on a macroscopic scale. Likewise, in Fig. 5 the splitting of the peaks at 7.0 and 9.3 kOe for $\alpha = 0$ is probably due to a slight roughness of the sample surface.

None of the theories of cyclotron resonance predict the splitting of the resonance peaks in an inclined magnetic field. However, several authors[1,4,5] have stressed that according to theory, the amplitudes of the cyclotron resonances should be diminished in an inclined magnetic field. The amplitudes of the resonances are expected to decrease because the electrons having an appreciable net velocity parallel to H drift into the bulk of the metal and do not contribute effectively to the cyclotron resonances. In an inclined field, only the electrons having essentially no velocity

[11] M. Ya. Azbel' Fiz. Tverd. Tela 4, 568 (1962) [translation: Soviet Phys.—Solid State 4, 415 (1962)].
[12] P. Bloomfield, Bull. Am. Phys. Soc. 8, 206 (1963).

component parallel to H return repeatedly to the skin layer and contribute effectively to the resonances. Azbel' and Kaner[1] find that for

$$\sin\alpha \gg \left(\frac{r}{L}\right)\left(\frac{\delta}{r}\right)^{2/3} \sim 10^{-2},$$

the surface impedance, for a free-electron model with the approximations in their analysis, becomes independent of H and approaches the value for H=0 (here r is the Larmor radius, L is the mean free path, and δ is the microwave skin depth). According to this model, it is expected that all subharmonics will be uniformly attenuated as α is increased. In the experiments on potassium we find that as α increases, the resonance derivative peaks for H between 2 and 3 kOe are rapidly attenuated in agreement with this theory, but for H greater than about 3 kOe, the peaks become split and diminish slower than expected with increase in α. In Fig. 5, resonance signals are shown to persist out to $\alpha=5\frac{1}{2}°$ with relatively minor change in amplitude.

These results for the spherical Fermi surface of potassium are very different from those in tin[13,14] and copper[14] for directions in which peak splitting is produced by tipping. In the latter metals, the low-field harmonics are relatively insensitive to effects of field-tipping and all resonance signals show a marked amplitude decrease at tipping angles beyond one or two degrees. Amplitude decrease is most pronounced for the flattest specimens. We believe the causes of peak splitting in these metals having Fermi surfaces which are far from spherical may be quite different from the causes in potassium. [We exclude from consideration here the special cases of "large angle" resonances (α up to 70°), as seen with the field in certain directions in tin[15] and copper,[14] which are believed to arise from a very different mechanism.]

The split peaks observed for potassium in an inclined field could easily be misinterpreted as two cyclotron masses. Interpreted as two masses, the data for potassium would suggest that the two masses are equal when the field is parallel to the specimen surface, but when the field is inclined one mass increases with tip angle and the other decreases. This interpretation is untenable for potassium because all the data with H parallel to the specimen surface indicate that the cyclotron mass is quite isotropic.

The mechanism responsible for the splitting of the resonance peaks for α>0 is qualitatively understood by analogy with the somewhat simpler case of the spherical limiting point resonances found in the second Brillouin zone in aluminum. In aluminum the special consequence of the spherical caps of the second zone Fermi surface when the magnetic field is along the

[13] M. S. Khaikin, Zh. Eksperim. i Teor. Fiz. **42**, 27 (1962) [translation: Soviet Phys.—JETP **15**, 18 (1962)].

[14] J. F. Koch, R. A. Stradling, and A. F. Kip (unpublished).

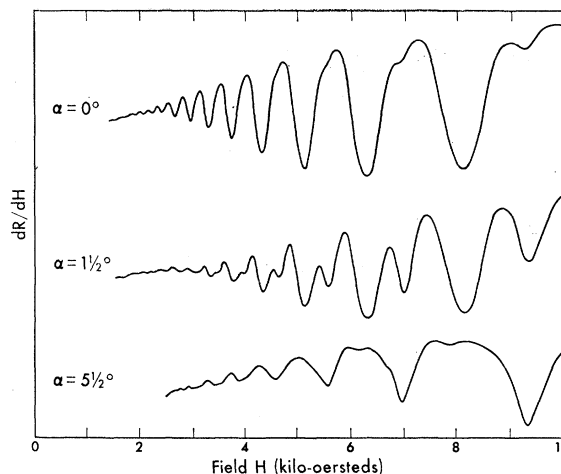[15] J. F. Koch and A. F. Kip, Phys. Rev. Letters **8**, 473 (1962).

FIG. 5. Experimental absorption derivative traces obtained from a relatively flat, polycrystalline specimen of potassium with the microwave electric field perpendicular to H. The angle of inclination of H relative to the specimen surface is denoted by α. When H is parallel to the specimen surface (α=0), the experimental curve closely resembles the theoretical curve in Fig. 1. When H is inclined, the resonance peaks split, and ultimately become inverted when $\alpha \gtrsim 5\frac{1}{2}°$.

⟨100⟩ or ⟨111⟩ direction is a group of electrons, all having the same cyclotron mass but a wide distribution of radii, and a nearly uniform (and high) velocity, v_H, in the field direction. Under the influence of the tipped magnetic field, these electrons are refocussed every cyclotron period, and produce current sheets far below the usual skin depth. Although electrons which are subjected to the rf field at the surface rapidly travel into the metal in helixes directed along the magnetic field, and hence do not reappear in the skin depth, they interact in the current sheets with the upward-coming electrons from the opposite side of the Fermi surface. Upon arriving in the skin depth, these latter electrons modify the surface impedance and thus give rise to the observed resonance curves. The experimental evidence for this model in aluminum, and the analogous case of the complete spherical Fermi surface of potassium will be discussed in a subsequent paper.

A primary argument which seems to rule out the possibility that the peak splitting in potassium is due to combined resonance, as mentioned above, is that the splitting nearly disappears when H is accurately parallel to the surface of our flattest specimens.

B. Sodium

The interpretation of the cyclotron resonance data for sodium is complicated by the existence of a low-temperature martensitic phase transformation[16] in this metal. Even though the phase transformation occurs, useful cyclotron resonance data were obtained from three of the ten samples examined in these experiments. In general, the data obtained from sodium were of
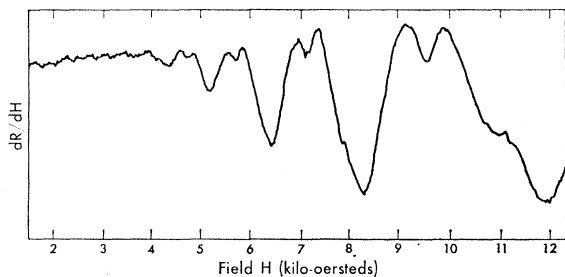
[16] C. S. Barrett, Acta Cryst. **9**, 671 (1956).

Fig. 6. Absorption derivative trace obtained from a specimen of sodium. Essentially identical traces were obtained for all orientations of **H** parallel to the specimen surface.

poorer quality than the data obtained from potassium. The poorer quality of the data for sodium is attributed to the effects of the phase transformation.

A representative experimental curve obtained from the best sodium sample is shown in Fig. 6. This curve is from a single crystal having a (111) plane surface. (Because of the martensitic transformation, all sodium specimens studied, necessarily at temperatures below the transformation temperature, also contained some fraction of hexagonal close-packed crystallites, as explained below.) The microwave frequency is 66.1 Gc/sec, **H** is near a ⟨110⟩ axis, and E_{rf} is perpendicular to **H**. The cyclotron resonance peaks are split, making the curve resemble the potassium curve shown in Fig. 3. The experimental curves for sodium are essentially identical for all orientations of **H** parallel to the sample surface.

The sodium data are reduced in the same manner as the potassium data. The cyclotron resonances in sodium are assumed to occur at the shallow minima in dR/dH near 9.6, 7.2, $\cdots$ kOe. A plot of reciprocal fields versus integers then yields a straight line passing through the origin. The cyclotron mass ratio is $m_c/m = 1.24 \pm 0.02$ and is isotropic within the experimental error.

Another (111) sample of sodium yielded experimental curves resembling cyclotron resonance, but the oscillations in dR/dH were not periodic in $1/H$. No cyclotron mass could be deduced from these data.

A crystal of sodium cooled below 35°K begins to undergo a martensitic or diffusionless phase transformation from a body-centered cubic (bcc) crystal structure to a hexagonal close-packed (hcp) crystal structure with stacking faults.[16] Further cooling produces additional transformation down to 20°K, at which temperature approximately half of the crystal has transformed to the hcp phase.[17,18] Relatively little additional transformation occurs on cooling below 20°K. The martensitic transformation proceeds by a shear mechanism whereby each atom keeps the same nearest neighbor atoms. The transformation progresses until the decrease in free energy of further transformation is just compen-

sated by the increase in stored energy of strain. Some of the strains resulting from the transformation exceed the elastic limits of the material; consequently, the transformation is not reversible and displays considerable hysteresis in a plot of percentage transformed versus temperature.

The shear, characteristic of the martensitic transformation, produces a tilt of the transformed regions relative to the untransformed crystal and permits optical studies of the transformation. Hull and Rosenberg[18] have made such an optical study of the transformation in sodium. They find that the transformed regions of hcp sodium form platelets which occur in four different orientations with respect to the host bcc crystal.

From Hull and Rosenberg's observation that the hcp platelets occur in only four orientations, we can deduce that the platelets lie in planes parallel to the {111} planes of the bcc crystal. If the surface of the host bcc crystal is a (111) plane, then the surface should provide an especially favorable site for the transformation to occur. In this case the host lattice is strained in only two dimensions by the transformation. Thus the platelets of hcp sodium that form on the surface of a (111) host crystal are expected to be larger, less strained, and less faulted than the platelets that form in the bulk of the host crystal.

The above reasoning led us to examine samples of sodium having (111) plane surfaces. Of the three samples that yielded cyclotron resonance signals, two had (111) plane surfaces and the third was polycrystalline. Six of the seven samples that failed to yield useful cyclotron resonance signals had (110) surfaces while the seventh was polycrystalline. It is tempting to conclude that the observed cyclotron resonance signals are from the hcp phase of sodium, and that the (111) crystal surfaces are favorable sites for the transformation to occur. However, in view of the inherent difficulty of the cyclotron resonance experiment, it would be fallacious to draw any conclusions based on the absence of signals from the (110) samples.

If we assume that the bcc and hcp phases of sodium have the same orientation relationship as Barrett[19] has proposed for the two phases of lithium, then the c axis of the hcp structure can be parallel to any one of the six ⟨110⟩ axes of the bcc structure. Furthermore, the hcp structure can assume either of two orientations about the c axis. Consequently, there are 12 possible orientations of the hcp structure relative to the bcc structure for the assumed orientation relationship. Thus a single-crystal specimen of sodium, when cooled to liquid-helium temperature, is expected to contain hcp crystallites having a number of different orientations. From these considerations we see that the

[17] J. S. Dugdale and D. Gugan, Proc. Roy. Soc. (London) A254, 184 (1960).

[18] D. Hull and H. M. Rosenberg, Cryogenics 1, 27 (1960).

[19] C. S. Barrett, *Phase Transformations in Solids*, edited by R. Smoluchowski, J. E. Mayer, and W. A. Weyl (John Wiley & Sons, Inc., New York, 1951), p. 343.

determination of any details of the electronic structure of the hcp phase of sodium may be quite difficult.

The lattice constants of the hcp phase of sodium at 5°K are $a=3.767$ Å, $c=6.154$ Å according to Barrett.[16] The ratio of these constants is $c/a=1.634$ which is very nearly the ideal ratio, 1.633. The appropriate Brillouin zone for hcp sodium is the hexagonal double zone. The use of the double zone requires some explanation.

Cohen and Falicov[20] have shown that spin-orbit coupling removes the degeneracy of electron states over most of the hexagonal face of the first Brillouin zone for the hcp structure. Then the double-zone scheme is no longer applicable. However, the same authors have shown in another paper[21] that in a magnetic field a phenomenon called magnetic breakdown can occur. In magnetic fields strong enough for magnetic breakdown to occur, the orbiting electrons are not Bragg-reflected at those zone boundaries where breakdown has occurred. Consequently, when breakdown has occurred in sodium, the double zone is applicable. Blount[22] has shown that magnetic breakdown is complete when $\hbar\omega_c\gg E_g^2/E_F$. Here E_g is the energy gap across the zone boundary and E_F is the Fermi energy. Following Cohen and Falicov, we can estimate the magnitude of the energy gap produced by spin-orbit coupling to be roughly half the spin-orbit coupling parameter of a $3p$ electron in atomic sodium. We find that E_g is approximately 10^{-3} eV. Now, using the free-electron mass and Fermi energy, we find that magnetic breakdown is complete for $H\gg30$ Oe. At the fields used in the cyclotron resonance experiment magnetic breakdown is complete, and the double zone is appropriate for hcp sodium.

No detailed band calculations have been performed for the hcp phase of sodium. However, we note that in the free electron approximation the Fermi sphere lies entirely within the double zone. In the presence of a weak effective lattice potential the shape of the Fermi surface is derived from a sphere by bulging the surface outward toward the nearest faces of the Brillouin zone. Thus, the Fermi surface is expected to bulge outward toward the centers of the rectangular faces of the double zone. If the Fermi surface does not contact the zone boundary, then the cyclotron resonance experiment should yield a single cyclotron mass for each orientation of $\mathbf{H}$ relative to the hcp structure. If the Fermi surface contacts the zone boundary, then two or more cyclotron masses should appear for some orientations of $\mathbf{H}$ relative to the hcp structure. Our observation of a single series of split resonance peaks for all orientations of $\mathbf{H}$ relative to the sodium specimen suggests that the Fermi surface does not contact the

zone boundary in either phase of sodium. However, the experimental evidence concerning contact with the zone boundary is not conclusive since the cyclotron resonance signals may arise from either or both of the crystal phases, and the signals may contain contributions from crystallites of the hcp phase having several different orientations.

In summary, the experimental results for sodium show cyclotron resonance with split peaks similar to some of the results for potassium. The observed cyclotron mass ratio in sodium is $m_c/m=1.24\pm0.02$ and the mass ratio is isotropic within experimental error. The experimental value of the cyclotron mass is approximately 24% greater than the value obtained from band calculations for the bcc phase.[23] The observed cyclotron resonances may be originating in either or both of low-temperature crystal phases of sodium. If the resonances originate in the bcc phase only, then the isotropy of the data indicates that the Fermi surface does not contact the Brillouin zone boundary. If the resonances originate in the hcp phase only or in both phases together, then the observed resonances may represent a sum of contributions from several Fermi surfaces of different orientations. In this case the isotropy of the data is not conclusive evidence that the Fermi surfaces do not contact the zone boundaries.

IV. SUMMARY AND CONCLUSIONS

We have observed cyclotron resonances in oriented single crystals of sodium and potassium for all directions of the magnetic field parallel to the surface of the specimens. The data for both metals is isotropic within experimental error and yields the cyclotron mass ratios $m_c/m=1.21\pm0.02$ for potassium and 1.24 ± 0.02 for sodium. The interpretation of the cyclotron resonance results for sodium is complicated by a low-temperature phase transformation. Potassium remains in the body-centered cubic-crystal structure at low temperatures so the isotropy of the cyclotron resonance data is evidence that the Fermi surface of potassium is very nearly spherical. The peak splitting observed in both metals is due neither to anisotropy nor combined resonance, and is to be related to the behavior of electrons on spherical regions of the Fermi surface.

Ham[23] has recently calculated the energy band structure of the alkali metals and applied an interpolation procedure to obtain the Fermi energy, the density of states, the dimensions of the Fermi surface, and the thermal, optical, and cyclotron effective masses. His calculated cyclotron masses for potassium are about 14% smaller than our measured value. The discrepancy between the two values may arise from electron correlation and electron-phonon interaction. For a comparison of the cyclotron effective mass with the results of other experiments the reader is referred to Ham's thorough discussion.

[20] M. H. Cohen and L. M. Falicov, Phys. Rev. Letters **5**, 544 (1960).
[21] M. H. Cohen and L. M. Falicov, Phys. Rev. Letters **7**, 231 (1961).
[22] E. I. Blount, Phys. Rev. **126**, 1636 (1962).

[23] F. S. Ham, Phys. Rev. **128**, 82 (1962); **128**, 2524 (1962).

Ham calculates that an anisotropy in $\mathbf{k}_F$ of about 1% would lead to an anisotropy in the cyclotron mass of about 6%. From our experimental data we would place an upper limit of 2% on the anisotropy of the cyclotron mass in potassium. Thus it appears that the anisotropy in $\mathbf{k}_F$ is appreciably less than 1% for potassium. Knowing that the Fermi surface of potassium is essentially spherical, we can use the extremal cross-sectional area obtained from de Haas–van Alphen data[24] to calculate the radius of the Fermi surface, $k_F = 7.44 \pm 0.07 \times 10^7$ cm^{-1}, and then we can use the measured

cyclotron mass to obtain the Fermi velocity $v_F = 7.1 \pm 0.2 \times 10^7$ cm/sec. It may well be that these two numbers provide a more detailed knowledge of the electronic structure of potassium than is known for any other metal!

[24] A. C. Thorsen and T. G. Berlincourt, Phys. Rev. Letters **6**, 617 (1961). After recalibration of the magnet, the revised de Haas–van Alphen period is $5.48 \times 10^{-9} \pm 1\%$ G^{-1} [A. C. Thorsen (private communication)].

Optical Transitions Involving Impurities in Semiconductors*

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The theory of optical transitions between donor levels and the valence band or between acceptor levels and the conduction band has been examined. Expressions for the optical absorption and radiative lifetime due to such transitions are derived. Application of this theory is made to GaAs and it is shown that at relatively high impurity concentrations optical transitions involving impurities can give rise to moderately high absorption constants and short radiative lifetimes. In the intermetallic semiconductors which have a conduction band effective mass much smaller than that of the valence band, the transition probability between acceptor states and the conduction band may be taken to be a constant up to moderate conduction band energies. To test the limits of validity of band to impurity recombination, the minimum spontaneous radiative lifetimes for electrons and holes are calculated. For electrons in GaAs this minimum lifetime is 0.3 nsec.

INTRODUCTION

IN the past several years much attention has been focused on interband transitions in both the optical emission and absorption spectrum of semiconductors. Analysis of such data has yielded information concerning both the band structure and scattering mechanisms in many substances.

More recently, light emitting diodes of GaAs with a high quantum efficiency have been studied by many workers,[1,2] and stimulated emission from such diodes has been observed[3-5] at high current densities. The

light emitted from these diodes is at an energy slightly below the energy band gap, and as a result does not suffer the intense reabsorption which would occur for photons emitted above the direct transition edge. Nathan and Burns[6] have noted the similarity between the emission from GaAs diodes and photoluminescence from Zn-doped GaAs, and it seems that the acceptors are involved in the light emission even though in the more highly doped diodes the acceptor levels would probably not be either localized or discrete in energy.

We have studied transitions between impurities and energy bands in order to discover how important the absorption and recombination given rise to by such transitions might be in a substance such as GaAs. We have found that impurities, particularly acceptors, furnish not only a transition which is below the normal absorption edge, but that transitions to acceptors can provide a strong radiative recombination mechanism able to compete effectively with other recombination mechanisms.

* A brief account of this work was presented at the American Physical Society St. Louis Meeting, March, 1963. [Bull. Am. Phys. Soc. **8**, 201 (1963)].
[1] S. Mayburg, post deadline paper, Am. Phys. Soc. meeting, Baltimore, March 1962.
[2] R. J. Keyes and J. M. Quist, Proc. IRE **50**, 1822 (1962).
[3] M. I. Nathan, W. P. Dumke, G. Burns, F. H. Dill, and G. J. Lasher, Appl. Phys. Letters **1**, 62 (1962).
[4] R. N. Hall, G. E. Fenner, J. D. Kingsley, T. J. Soltys, and R. O. Carlson, Phys. Rev. Letters **9**, 366 (1962).
[5] J. M. Quist, R. H. Rediker, R. J. Keyes, W. E. Krag, B. Lax, A. L. McWhorter, and H. J. Zeiger, Appl. Phys. Letters **1**, 91 (1962).

[6] M. I. Nathan and G. Burns, Appl. Phys. Letters **1**, 89 (1962).