Fermi Surface of Potassium as Measured by Helicon Doppler-Shifted Cyclotron Resonance

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Accurate helicon measurements of the surface-impedance anomaly associated with Doppler-shifted cyclotron resonance have been made on single-crystal potassium and sodium. The experiment tests the theory of the surface impedance near cyclotron resonance and also assists in the resolution of the charge-density-wave controversy. The influence of surface scattering and sample purity have been determined and found to be in substantial agreement with the surface-impedance theory. The theoretical and experimental line shapes do not agree precisely. The position of the surface-impedance anomaly can be related to the radius of the Fermi surface. Our measurements show that the experimental position does not agree with the free-electron theory in potassium. The charge-density-wave prediction provides a much better fit. In sodium, the experiment fits the free-electron prediction more closely than the charge-density-wave calculation.

I. INTRODUCTION

We report on accurate cyclotron resonance measurements obtained for potassium and sodium by the helicon method. The helicon is a transverse electromagnetic wave which can propagate in a metal when $\omega_c\tau > 1$, where ω_c is the cyclotron frequency and τ is the momentum relaxation time.[1,2] In a metal cyclotron resonance cannot be observed by merely raising the helicon excitation frequency ω_H to ω_c at a given magnetic field. The helicon ceases to propagate when electrons traveling through helicon wavefronts first experience an electromagnetic field oscillating at ω_c in their moving coordinate system. Doppler-shifted cyclotron resonance (DSCR) will result when

$$\omega_c = \omega_H + \mathbf{k}_H \cdot \mathbf{V}_F, \tag{1}$$

where $\mathbf{k}_H$ is the helicon wave vector and $\mathbf{V}_F$ is the Fermi velocity of an individual electron. In alkali metals, the Doppler-shifted frequency is much larger than ω_H. DSCR will produce a strong damping in the helicon propagation for magnetic fields such that $\omega_c \le k_H V_F$. The edge field is defined as the field for which $\omega_c = k_H V_{\max}$, where $V_{\max}$ is the maximum value of the electron velocity along $\mathbf{k}_H$. This field is a measure of the Fermi momentum k_F and is known as the Kjeldaas edge[3] in sound propagation. Stern[4] noted that the helicon absorption edge could be used to measure k_F point by point for simple Fermi surfaces. In this measurement one obtains a basic quantum number k_F rather than an effective mass as is the case for an ordinary cyclotron resonance experiment.

Taylor[5] verified Stern's prediction and found that DSCR produces a sharp change in the surface impedance at the edge field. Taylor measured the edge position in sodium and potassium, and reported agreement with the free-electron model. Taylor analyzed his data, using an infinite medium dispersion relation. Overhauser and Rodriguez[6] have shown that the boundary conditions inherent in a surface-impedance measurement alter the position of the DSCR anomaly. They concluded that Taylor's results were consistent with a spin-density-wave (SDW) or, equivalently, a charge-density-wave (CDW) ground state in potassium.[7]

It is difficult, however, to compare his experimental results to the proposed model unambiguously. Taylor's main objective was to demonstrate the helicon DSCR, and, therefore, his experimental system was relatively crude. It is the purpose of the present work to repeat Taylor's experiment with the necessary refinements and establish the experimental facts beyond any experimental ambiguity. It is not our intention to interpret our data as being definitive in the question of the CDW (or SDW) or free-electron ground state. It is interesting, however, that the present experimental data do not fit the calculations based on the free-electron model for potassium, while a CDW model gives a reasonable agreement with the data.

II. EXPERIMENTAL TECHNIQUES FOR MEASURING SURFACE IMPEDANCE AT RADIO FREQUENCY

We detected the helicon by measuring the field derivative of the surface impedance $Z = R + iX$, using a magnetic field modulation method. Here R and X are the real and imaginary components of the surface impedance, respectively. Both rf bridge and marginal oscillator techniques were employed. A third method for observing the helicon is the transmission technique,[8] which involves a transmitter and receiver coil at right angles to each other. The transmission measurement is a modification of the bridge technique. With the transmission method the leakage of a main carrier wave is reduced, using geometric decoupling between the coils,

[1] R. Bowers, C. Legendy, and F. E. Rose, Phys. Rev. Letters **7**, 339 (1961).
[2] R. Bowers and M. C. Steele, Proc. IEEE **52**, 1105 (1964).
[3] T. Kjeldaas, Phys. Rev. **113**, 1473 (1959).
[4] E. A. Stern, Phys. Rev. Letters **10**, 91 (1963).
[5] M. T. Taylor, Phys. Rev. **137**, A1145 (1965).
[6] A. W. Overhauser and S. Rodriguez, Phys. Rev. **141**, 431 (1966).
[7] A. W. Overhauser, Phys. Rev. **167**, 691 (1968).
[8] For instance, J. W. Hansen, C. C. Grimes, and A. Libchaber, Rev. Sci. Instr. **38**, 895 (1967).

rather than using electrical bucking, as in the case of the bridge system. All three methods for detecting the helicon have analogs in the techniques of NMR. The bridge and marginal oscillator are well-established techniques in NMR.[9] These methods have been used to observe NMR in metals by measuring the magnetization of finely powdered samples or the surface impedance of bulk samples.[10] The transmission technique is very similar to the nuclear induction technique,[9] where the NMR signal opens the channel between the orthogonal coils.

The relative advantages and disadvantages of the three methods of helicon detection are very similar to those found in NMR experiments. As the application of these techniques is extended to a new field, however, some confusion will be encountered among the researchers in the new field. Since considerable duplication, sometimes incomplete and/or incorrect, about these techniques has been published recently, and since the descriptions of the technique in magnetic resonance literature[9] are not necessarily up to date, it would be worthwhile to present the essential points of the techniques briefly.

The inherent advantages of the bridge method (or its modification, the transmission method) over the marginal-oscillator-detector (MOD) method are: (i) The transmitter rf power can be considerably larger than the rf level the MOD can deliver without losing its marginal condition. Since the signal power is proportional to the driving power, the sensitivity of the bridge system can be much higher than the MOD system. The capability of the high-power operation does not necessarily assure one of the higher sensitivity, in practice, because this system has more components to adjust in order to achieve the optimum sensitivity. (ii) All the rf bridge components are operated in their linear region, except for a homodyne detector part.[8] Most electronic engineers are familiar with these components, including the homodyne detector, and one could expect adequate help from them in order to minimize the noise figure of each component.

The inherent disadvantage of the bridge system is the fact that a complete separation of the R and the X mode is very difficult in its primitive form,[11] and at least cumbersome in its improved form associated with the standard homodyne detection. The mode mixing is not a serious problem if one is mainly interested in detecting the helicon waves and determining the relative positions of their interference fringes.[5] The measurement of detailed line shapes and positions can be seriously complicated by the incomplete separation of R and X. A small but unknown amount of mode mixing produces apparent distortion in the observed line shape. This prohibits precise comparison with the theoretical line shape. It is well known that the simple detecting technique[11] does not assure sufficient mode separation and that the mode adjustment is very unstable.[12] The instability increases with the increase of the rf level more than linearly. The advantage of the bridge system will be lost almost completely.

The instability of mode adjustment can be easily avoided by using a homodyne detection technique, standard in NMR and electron-paramagnetic-resonance (EPR) experiments. The mode selection is performed by an rf phase shifter. As long as the leakage from the bridge is much smaller than the homodyne reference signal, the drift of the bridge balance does not affect the mode selection. The ambiguity of the mode selection can be eliminated by adjusting the phase, using the proton NMR from the sample coil form.

A properly built marginal oscillator, on the other hand, automatically responds only to the R mode. This automatic mode selection and a relatively simpler electronic system is the major advantage of the MOD system. Detailed descriptions of the circuit analysis are found in the classical literature.[13] A Robinson rf spectrometer[14] is a modification of the original MOD system. Since the efficiency of the MOD depends on a subtle nonlinearity of the circuit element, the circuit analysis is more complicated. Usually one cannot expect much help from electronic engineers.[15]

This automatic mode selection can be understood as follows: The change in X of the sample is equivalent to the change in the inductance L of the sample coil. A change of R can be represented as changing an rf resistance r_P in parallel with the coil. A decrease in r_P reduces the maximum height of the resonance curve of a tank circuit. The change in L alters only the resonance frequency. Since the marginal detector oscillates always at the resonance frequency of the tank circuit, the amplitude of the oscillation represents r_P, provided the system sensitivity is independent of the frequency change which is accompanied by the change in X. This condition is very well satisfied for a well-designed marginal detector. If proper care is not taken, however, one might find a relatively strong frequency dependence

[9] E. R. Andrew, *Nuclear Magnetic Resonance* (Cambridge University Press, New York, 1958), p. 56; A. Kumar Saha and T. P. Das, *The Theory and Applications of Nuclear Induction* (Saha Institute of Nuclear Physics, Calcutta, 1957), p. 94.

[10] P. L. Sagalyn and J. A. Hofman, Phys. Rev. **127**, 68 (1962); N. Bloembergen, J. Appl. Phys. **23**, 1383 (1952); A. C. Chapman, P. Rhodes, and E. F. W. Seymour, Proc. Phys. Soc. (London) **B70**, 345 (1957).

[11] H. L. Anderson, Phys. Rev. **76**, 1460 (1949); W. N. Tuttle, Proc. IRE **28**, 23 (1940).

[12] R. L. Collins, Rev. Sci. Instr. **28**, 502 (1958). Collins reported that he had to reject as much as 75% of his NMR curves obtained using this primitive bridge technique because of the drift of the bridge balance.

[13] R. V. Pound and W. D. Knight, Rev. Sci. Instr. **21**, 219 (1950); G. D. Watkins, thesis, Harvard University, 1953 (unpublished). Most detailed analysis of the MOD is found in this thesis. See also Ref. 9.

[14] F. N. H. Robinson, J. Sci. Instr. **36**, 481 (1959).

[15] It is not uncommon for a MOD built by a person who is not familiar with magnetic resonance, even though he may be generally competent in laboratory electronics, to have a poor sensitivity (as low as 1/100 of a well-built MOD) and many spurious responses. This is often the case even when the circuit is an exact copy of a well-publicized MOD.

in the system response, usually due to undamped spurious resonance circuits in the MOD (or in the Robinson spectrometer). For the same reason one should not add a sharply frequency-dependent element in a regenerative feedback circuit in an attempt to increase the frequency stability, as has been suggested in the literature. Any possible distortion from this type of effect can easily be checked by observing a proper NMR signal with well-known shape.

One who is not familiar with this type of instrument might suspect that the exclusive response of the MOD to the coil resistance does not necessarily assure the exclusive response to the surface resistance of the metallic plate in the coil. It is possible to demonstrate the equivalence by circuit analysis,[16] but it may be more convincing to prove it experimentally. The basic physics behind the proof is energy conservation. Energy dissipated as the surface resistance of the metal plate must be supplied by the coil and will appear as coil loss or, equivalently, the real part of the surface impedance. A relevant experimental example is NMR in a bulk metal. In this case, the real part of the surface impedance near the NMR depends on the relative size of the skin depth δ and the sample thickness d. Bloembergen[10] has shown that if $d \ll \delta$, R should be proportional to χ'', which is the absorptive part of the *nuclear* susceptibility. If $d \gg \delta$, the R of a thin plate is predicted to be proportional to $\chi'+\chi''$, where χ' is the dispersive part of the *nuclear* susceptibility. The dispersive part χ' can influence the surface loss of the sample by varying the skin depth. Bloembergen[10] and others[10] have shown that MOD spectrometers yield NMR line shapes which faithfully represented $\chi'+\chi''$ for a thin plate, with $d \gg \delta$, and χ'' alone for $d \ll \delta$. Thus the MOD indeed detects the real part of the surface impedance of the metallic plate.

III. EXPERIMENTAL MEASUREMENT OF DSCR

The principal difficulty in performing the helicon DSCR experiment is that the width of the surface-impedance anomaly is approximately as large as the difference in the predicted positions of the CDW and free-electron lines. Since the linewidth is related to sample purity, samples with the highest possible purity were used to reduce the linewidth. Unfortunately, the linewidths were so large that position could be established with sufficient accuracy only by considering shape. In order to measure the position of the line to a small fraction of its width, it is necessary to compare accurate experimental and theoretical line shapes. The experimental procedures described below were explicitly designed to allow this comparison.

Since the R and the X mode give essentially the same information about the edge position and shape, most of the measurements were performed with the MOD, which is simpler to operate and usually has a better signal-to-noise ratio. As mentioned above, a bridge system can have a better sensitivity than a well-designed MOD, but in practice the more complicated electronics associated with the bridge tends to increase the noise. A bridge method employing homodyne detection was used to confirm the shapes of dR/dB and dX/dB found by Taylor.[5]

A Pound-Knight-Watkins[13] MOD, and balanced MOD's developed by one of the authors,[17] were used in the present measurements. All the spectrometers have long been used in this laboratory for the study of magnetic resonance, and have been proved to be free from the difficulties suggested above. An extensive study of the DSCR line was carried out, using one of the balanced MOD's. This rf spectrometer has the following advantages over conventional ones: (i) a wide frequency range 1–150 MHz; (ii) a very simple, and therefore trouble-free, circuit which has a sensitivity comparable with the best-engineered conventional rf spectrometers; (iii) a wide range of rf level (0.5- to 30-V peak-to-peak tank circuit voltage with a slight modification) without loss of the marginal condition.

Most of the potassium experiment was performed at 33 MHz (crystal-controlled 10-MHz frequency was used for the bridge method; the Pound-Knight-Watkins MOD was used at 10–20 MHz range). The frequency of 33 MHz for K was most adequate to determine the position of the DSCR with a large resolution, and loss in spectrometer sensitivity due to a relatively long rf cable was not a problem. Also 33 MHz allowed the use of $Cu^{63,65}$ and Al^{27} NMR signals as field calibrations very near the edge field in potassium. The Cs^{133} NMR signal in Cs glass was found to be convenient when the spectrometer was operated at about 10 MHz for sodium study. Some of the MOD's used in this experiment had built-in calibrators.[13] The sensitivity of the spectrometer was calibrated frequently. No noticeable change in the sensitivity was observed while the external field was swept over the DSCR line.

The experimental configuration is indicated schematically in Fig. 1. The metallic sample was placed in an rf coil with the static field parallel to the sample normal. The typical sample had a disk shape, approximately 8 mm wide and 1 mm thick. The inside dimension of the rf coil was approximately $2\times9\times9$ mm. The coil was plotted in Epoxy resin, except for the sample space. The sample normal was adjusted to within $\pm3°$ of the magnetic field. This adjustment was not critical, since the edge field varies only as the cube root of the cosine of this angle. The sample was immersed in liquid helium and the static field B_0 was produced by a superconducting magnet. A modulation field was produced by a second small superconducting solenoid. Most of the measurements were carried out using 35-Hz modulation with 60-G peak-to-peak amplitude. Any

[16] Akira Fukumoto and M. W. P. Strandberg, Phys. Rev. **155**, 685 (1967).

[17] G. B. Benedek and T. Kushida, Phys. Rev. **118**, 46 (1960).

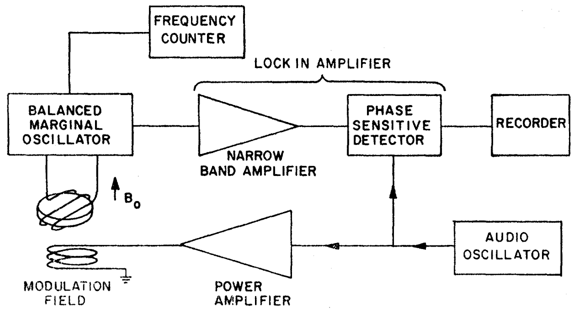

FIG. 1. Electronic configuration used for the measurement of dR/dB by a field modulation technique. The disk-shaped sample was placed in an rf coil with the sample normal parallel to the field B_0 of a superconducting solenoid. The level of a marginal oscillator was phase-detected with respect to a modulation field, while B_0 was swept through the DSCR anomaly in dR/dB.

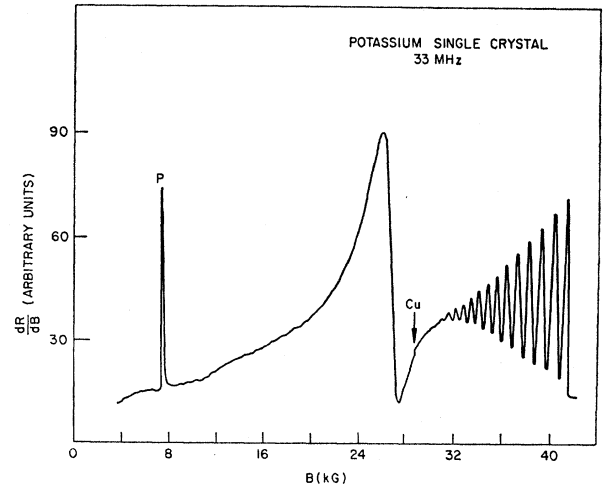

FIG. 2. Typical experimental data for dR/dB. The sample was a single crystal of K with a mirror surface. The surface-impedance anomaly caused by DSCR appears at approximately 27 kG. Propagation of helicons at high magnetic fields is indicated by the fringe pattern. NMR signals of the proton and copper nuclei are at points P and Cu, respectively.

lower modulation frequency tends to increase $1/f$ noise. The modulation frequency was reduced to as low as a fraction of a Hz in order to check any possible effect of modulation skin depth. No change in line shape and position was observed. Various sizes of rf coils and samples were tried without showing any difference in the line shape and its position. This fact excludes any suspicion that the closeness of the coupling between the sample and the coil might affect the function of the MOD's. The coil with a high filling factor was found to be advantageous in getting a good signal-to-noise ratio.

The audio-frequency output of the marginal oscillator was amplified in a narrow band amplifier and then phase-detected. dR/dB was plotted on a chart recorder as a function of the magnetic field at constant frequency. Since the modulation amplitude was much smaller than the observed linewidth, the output of the phase detector was proportional to $\pm dR/dB$. The NMR signal could be used to identify the sign of dR/dB on the recorded curve.

Figure 2 is a plot of typical data from a single crystal of potassium at 33 MHz. At low fields, in the region where the helicon cannot propagate due to cyclotron resonance, dR/dB is relatively constant, except for the proton NMR signal at P. The one-way deflection of the NMR signal, a positive direction in this example, is entirely due to NMR saturation. The electronic components have not saturated. The direction of the deflection would be reversed if the sweep direction were reversed. As the magnetic field is raised to the edge field, there is a large, sharp change in dR/dB, followed by periodic growing changes. The fringes are due to helicon standing waves inside the sample. A Cu^{63} NMR signal of the rf coil is at point Cu. When the detailed shape and the position of the DSCR signal was investigated in the present experiment, the sweep speed of the magnetic field was decreased by approximately a factor of 10, so that the essential part of the curve was displayed in detail with much better signal-to-noise ratio. Another copper isotope in the rf coil, Cu^{65} (whose abundance is about 3/7 of Cu^{63}), was seen clearly at the field about 7% lower than the Cu^{63} field. Since the Knight shift of copper is known, the magnet was calibrated simultaneously with each DSCR measurement at two points around the edge field. The position and shape of dR/dB are in agreement with Taylor's data. The present experimental technique, however, has eliminated all of the possible experimental ambiguities in the previous experiment.

IV. THEORY OF DSCR IN POTASSIUM AND SODIUM

Overhauser, Rodriguez,[18] and Alig[19] have provided us with computer calculations of the surface-impedance anomaly associated with DSCR under a variety of circumstances for potassium and sodium. If the Fermi surfaces of these two metals are assumed to be free-electron spheres, the calculations are straightforward. A sphere could be an excellent approximation to the Fermi surfaces[20,21] of these two metals. These calculations were performed using lattice constants obtained from x-ray studies[22] with assumption of one conduction electron per atom.

The theory of DSCR for a CDW ground state depends on the orientation of the CDW wave vector **Q** with respect to the magnetic field. Evidence that a large magnetic field can orient **Q** parallel to the field has been found in chromium metal.[23] Strain has also

[18] A. W. Overhauser and S. Rodriguez (private communication).
[19] R. C. Alig (private communication); Phys. Rev. **165**, 833 (1968).
[20] F. S. Ham, Phys. Rev. **128**, 82 (1962).
[21] V. Heine and I. Abarenkov, Phil. Mag. **9**, 451 (1964).
[22] C. S. Barrett, Acta Cryst. **9**, 671 (1956).
[23] A. Arrott, S. A. Werner, and H. Kendrick, Phys. Rev. Letters **14**, 1022 (1965); Phys. Rev. **155**, 528 (1967).

been found to orient **Q** in chromium.[24] Since our samples were subjected to a relatively low strain, the calculations for the CDW ground state were all made with the assumption that **Q** and **B** were parallel. This orientation produces the maximum difference in position of the surface-impedance anomaly for the CDW and the free-electron model. If **Q** were not parallel to **B**, smaller deviations would be expected. The magnitude of the CDW energy gaps for K and Na were derived from optical experiments.[25,26] (The difference between the CDW and SDW models does not affect the surface-impedance anomaly.)

Overhauser and Rodriguez[6] objected to Taylor's method of data analysis because he arbitrarily picked a prominent feature of the surface-impedance anomaly and identified it as the edge field. As will be shown below, we have compared the total experimental tracings with the theoretical calculations in order to meet this objection. Several factors can affect the position and shape of the DSCR anomaly: purity,[6] diffuse versus specular reflection,[19] and complicated Fermi surfaces.[27,28] All these factors are considered in the present method of data analysis.

V. SAMPLE PREPARATION

The K stock used in these experiments was purchased from Mine Safety Appliances (MSA), Callery, Pa. Typical resistance ratios at 4.2°K were 2000. Some of the MSA potassium was purified using a high-vacuum distiller with Mo inside lining.[29]

We developed a method for growing single-crystal plates of potassium which had mirror surfaces. A mold was assembled from glass plates with 1-mm microscope slides as spacers. The mold was covered with thoroughly degassed and dried vacuum pump oil, Cenco Hyvac 93050 No. 3 (standard weight). A slab of potassium approximately the size of the final crystal was prepared, and cleaned in a 1% ethyl alcohol-xylene etch. The slab was immersed in the degassed oil and then transferred to the mold. The mold was placed on a hotplate which was held at a temperature a few degrees above the melting point of potassium. As the stock melted, a surface crust would form. The molten metal was gently extruded between the glass spacers. When properly done, clean shiny metal would flow out from the stock leaving the crust behind. The new surface was stable and would remain mirrorlike, even though the metal was still molten. The hotplate temperature was lowered and a brass heat sink placed near the crystal. Within 15 min the metal would solidify into a single crystal with a very shiny surface. The surface would remain shiny for a period of weeks. Sodium single crystals were also produced by this technique.

The crystal was removed from the mold by gently sliding the glass plate off. The pump oil prevented the metal from wetting the glass, and the crystal could be removed with a minimum of strain. The crystal was loaded into the rf coil by one of two methods. The first involved washing the sample with xylene to remove the oil and quickly quenching it in liquid nitrogen. Then it was wedged into the coil with paper at 77°K. The second method was to load the oil-coated crystal into the coil and then freeze the crystal into the coil by quenching in liquid nitrogen.

The single-crystal preparation method was found to retain the purity of the metal stock when the starting material had residual resistance ratios in the neighborhood of 2000. Preliminary tests show that material of a higher purity is degraded by this growing process. X-ray studies of a number of samples revealed a tendency for the sample normal to be parallel to the [110] direction. Over 50% of the crystals grown were within ±5° of the [110] direction.

Polycrystalline samples were produced by slicing the potassium or sodium with thin steel wires. The wires were separated by approximately 1 mm and gently passed through the stock. The surfaces produced were mirrorlike and very stable. The faces were approximately parallel and the bulk of the sample was plastically deformed only slightly. These samples were held in the rf coil with frozen mineral oil. Polycrystalline samples were also produced by pressing stock between plates separated by appropriate spacers.

VI. LINE SHAPE

Figure 3 shows the theoretical line shapes for dR/dB at 10 MHz which result from specular and diffuse reflection.[19] The theory assumes a metal with purity comparable to the experimental values and with a free-electron ground state. The shapes of the curves are very similar for a CDW ground state. Comparison of Figs. 2 and 3 reveals that the experimental line shape is much closer to the specular reflection calculation versus the diffuse reflection case. Figure 2 resulted from a sample with mirror surfaces. If a surface was tarnished, the experimental line shape was much closer to the diffuse reflection prediction. If a mirror surface was allowed to corrode, the definite minimum in dR/dB disappeared. It was also found that tarnished surfaces yield signals whose magnitudes were much smaller than signals from mirror surfaces. This agrees with the predicted magnitude of the two cases, as shown in Fig. 3.

It has been noted that Taylor's data on dX/dB did not show a definite maximum. One might conclude from this that dR/dB resulted from specular reflection while

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[24] T. J. Bastow and R. Street, Phys. Rev. **141**, 510 (1966).
[25] H. Mayer and M. H. El Naby, Z. Physik **174**, 280 (1963).
[26] A. W. Overhauser, Phys. Rev. Letters **13**, 190 (1964).
[27] J. C. McGroddy, J. L. Stanford, and E. A. Stern, Phys. Rev. **141**, 437 (1966).
[28] J. L. Stanford and E. A. Stern, Phys. Rev. **144**, 534 (1966).
[29] Paul H. Schmidt, J. Electrochem. Soc. **113**, 201 (1966). The authors wish to thank Dr. W. M. Walsh and Dr. P. H. Schmidt for providing them with detailed information about the alkali metal distillation.

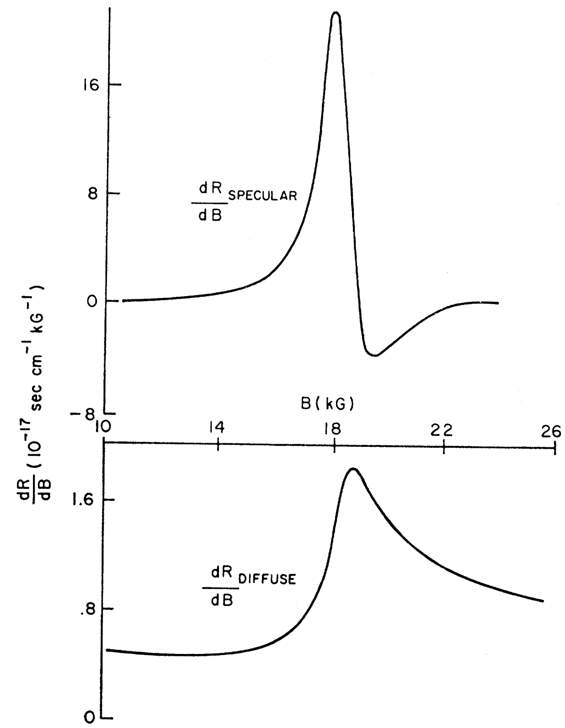

FIG. 3. Calculations of dR/dB for K at 10 MHz assuming a free-electron ground state. The assumption of specular reflection produces a line shape characterized by a definite maximum and minimum. Diffuse reflection yields a much smaller change in dR/dB and only a maximum is predicted. Similar calculations for a CDW ground state are almost identical in shape but slightly shifted in position.

dX/dB was a consequence of diffuse reflection.[19] In our measurements, however, dX/dB was found to have a maximum as well as a minimum, indicating specular reflection for both components.

Since the line shapes and magnitudes agreed well with the specular reflection prediction, we have compared our results with this prediction. Naturally, the experimental observation will be some combination of specular and diffuse reflection. Since the diffuse reflection is an order of magnitude smaller, it will be ignored.[30] We believe that these line-shape arguments prove that specular reflection of electrons has been identified for the first time in alkali metals.

VII. LINE POSITION

An expanded view of the data in Fig. 2 is given in Fig. 4. For comparison, the figure also contains tracings of CDW and free-electron calculations. The theoretical linewidth, defined as the separation in magnetic field between the maximum and the minimum of dR/dB, was adjusted to fit the observed width. It can be seen that the experimental line lies lower in field than the free-electron calculation. By comparison the CDW

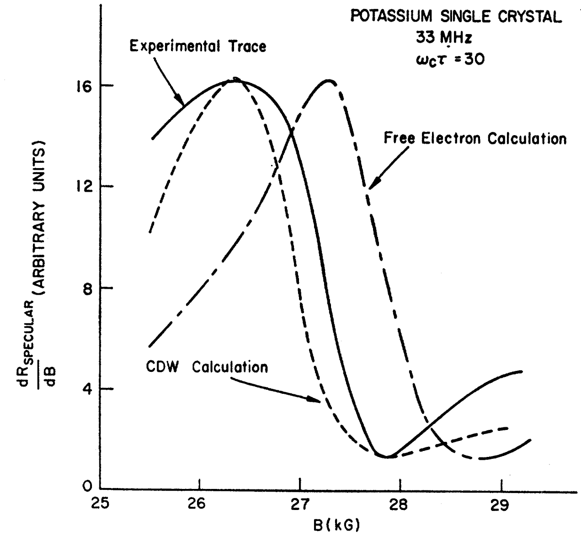

FIG. 4. Comparison of an experimental tracing of dR/dB with theoretical predictions for the CDW and free-electron ground states of K. The measurements were performed at 33 MHz on a single crystal which had a purity specified by $\omega_c(27\ \text{kG})\tau=30$. The theoretical linewidths were adjusted to fit the experimental width. The experimental data lie much lower than the free-electron calculation. There is better agreement between experiment and the CDW theory, especially at the maximum or minimum of dR/dB.

prediction fits the data much better. The maximum or the minimum in dR/dB for the CDW prediction agrees remarkably well with the experimental data. Since the theoretical linewidth was adjusted to fit the data, agreement at the maximum assures agreement at the minimum. The line shape does not exactly fit either the CDW or free-electron prediction, being broader at low fields and narrower at high fields. It must be concluded, however, that the position in the magnetic field of the DSCR edge for single-crystal potassium does not fit the free-electron model.

Measurements on seven single and two polycrystalline potassium samples have been performed. The analysis of these experiments yielded results which were in agreement with the analysis of Fig. 4. In order to present these data concisely, we have arbitrarily chosen one feature of dR/dB to compare the experimental results with the theory. Figure 5 presents a graph of B_{max}, the field where dR/dB was maximum at 33 MHz, as a function of purity $\omega_c(27\ \text{kG})\tau$ for nine samples. As can be seen from Fig. 4, B_{max} and B_{min} (the field at which dR/dB was minimum) are the features of the data which agree best with the CDW theory. The experimental point corresponding to the highest values of $\omega_c\tau$ ($\simeq 56$) was taken, using the vacuum-distilled K. Generally, B_{max} was observed to increase and B_{min} decreased with increasing purity. $\omega_c\tau$ was calculated by comparing experimental and theoretical linewidths. Calculations of B_{max} for the two ground states are also traced in Fig. 5. The claimed uncertainty in B_{max} for the two theories were approximately the same

[30] Except for remarking that it will tend to raise relevant points on the theoretical curve to slightly higher fields than the specular prediction

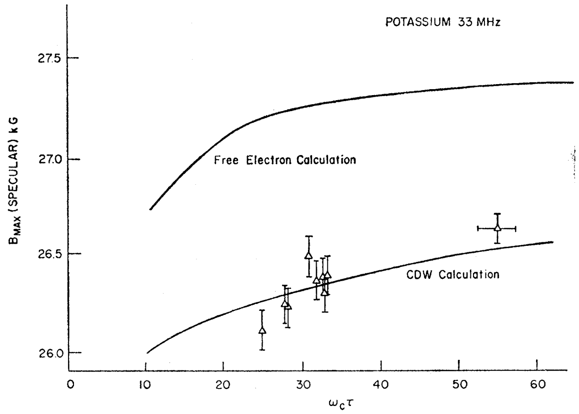

FIG. 5. Comparison for K of the field $B_{\max}$, at which dR/dB is maximum as a function of purity $\omega_c(27\text{ kG})\tau$, with the predictions of a CDW and free-electron ground states. The calculations have an uncertainty similar to the experimental error. Generally, $B_{\max}$ is observed to increase with purity. The experimental position of $B_{\max}$ in nine single and polycrystalline samples agrees, within experimental error, with the CDW calculation. As can be seen in Fig. 4, the maximum (or minimum) in dR/dB is the field for which the experiment best fits the CDW calculation.

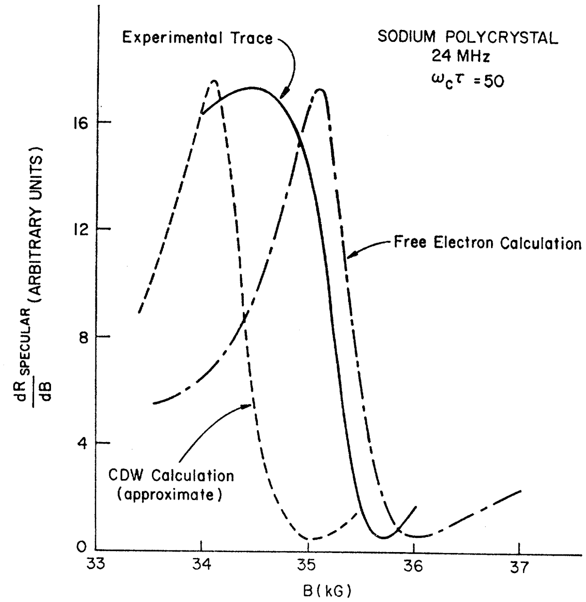

FIG. 6. Comparison of an experimental tracing of dR/dB at 24 MHz, with theoretical predictions for the CDW and free-electron ground states of Na. The measurements were performed on a polycrystalline sample which had undergone a partial martensitic transformation and which had a purity specified by $\omega_c\tau(35\text{ kG})\tau$ $=50$. The theoretical linewidths were adjusted to fit the experimental width. The experimental data lie much closer to the free-electron calculation than the approximate CDW calculation.

size as the experimental error; they were not included in the figure, for the sake of clarity, but should be remembered in comparing theory with experiment. It can be seen that all the samples on which measurements were performed had $B_{\max}$ values close to the CDW theory. No samples were found to have $B_{\max}$ values close to the free-electron prediction, regardless of the degree of the purity and the strain. Both models predict that $B_{\max}$ should increase with increasing purity while $B_{\min}$ should decrease with increasing purity. The agreement between these predictions and the observations expresses the fact that the total experimental shape agrees reasonably well with the prediction. Thus the $\omega_c\tau$ values must be nearly correct. The seven single crystals shown all had different orientations, so the position does not seem to be strongly anisotropic. The excellent agreement of $B_{\max}$ with the CDW theory may be somewhat fortuitous, since the detailed line shapes do not match.

DSCR was observed in Na as a control for the K experiment. The Na experiment was performed using several samples with different degrees of purity and strain. A remnant of the DSCR was observed in relatively impure Na, which originated from a batch which had been used as a dryer of organic liquids in our chemistry department. Some batches of supposedly pure MSA Na, however, did not show a trace of DSCR. Communication with MSA did not clarify the cause. The data for a polycrystalline Na sample measured at 24 MHz are presented in Fig. 6. It is in agreement with Taylor's data. $\omega_c(35\text{ kG})\tau$ equals 50. Traces of CDW and free-electron calculations are shown for comparison. The theoretical linewidths were again adjusted to fit the observed width. The approximate CDW line was calculated using the optical data to determine the energy gap and assuming **Q** parallel to **B**. The experimental tracing does not fit either of the calculations well, but it is closer to the free-electron position. Similar results were found in the other sodium samples tested. These samples had a mixture of bcc and hcp crystal structures due to the partial martensitic phase transformation.[22] The difference in carrier density between the two phases is too small to cause any measurable shift in the edge, if free-electron spheres are assumed to be characteristic of both phases. Overhauser[31] has conjectured that the strain associated with the martensitic transformation will cause domains of **Q**'s which need not be parallel to **B**. Calculation for a heterogeneous sample would be very difficult, but it would be expected to raise the edge in field above the single **Q** position shown in Fig. 6.

The Na data are useful experimentally because they fit the free-electron prediction fairly well. The size of the sample and the coil are the same for the K and Na experiment. The $\omega_c\tau$ of the Na sample was approximately the same as that of the vacuum-distilled K sample. The difference in the rf frequency for the two experiments shown in Figs. 5 and 6 (24 MHz for Na, and 33 MHz for K) does not explain the difference of

[31] A. W. Overhauser (private communication). Severly strained K samples, however, did not shift their DSCR lines toward the free-electron position. These samples were prepared from the stock by squeezing between glass plates at room temperature, and they were immediately frozen into liquid nitrogen. The glass plates were kept clamped with Be-Cu clips.

the DSCR line positions in the two metals. The K experiment was done at 20 MHz as well, leading to the same conclusion. It is concluded that there is no experimental artifact which would cause a systematic deviation from the free-electron edge position. The method that produces agreement with free-electron theory in Na cannot be criticized for yielding a difference from free-electron theory in K. The deviation in K must be intrinsic to the metal and not due to the experimental method.

VIII. LINEWIDTH

The procedure for determining $\omega_c\tau$ in the Figs. 4–6 involved fitting a theoretical trace to the experimental data. The purity assumed in the calculation of the best-fitting curve immediately gave the desired value of $\omega_c\tau$ at 27 kG. A second method for determining $\omega_c\tau$ is to measure the sample resistance. This was done by an eddy-current decay method.[32] The $\omega_c\tau$ derived from the resistance measurement on a given sample was comparable with, but always larger than, the $\omega_c\tau$ derived from the linewidth. The resistance $\omega_c\tau$ tended to be 50% larger than the linewidth $\omega_c\tau$. Part of this difference can be attributed to the linear magnetoresistance known to exist in K.[33] Magnetoresistance $\rho(B)$ was not included explicity in the DSCR theory. It can be included to first approximation since $\rho(B)$ does not change significantly over the width of the DSCR line. The linewidth and line position are determined by the resistance at the edge field $\rho(B)$ rather than the loss at zero field $\rho(0)$. This is because the quality factor for the helicon is the tangent of the Hall angle $R_HB/\rho(B)$, where R_H is the Hall coefficient. Thus the $\omega_c\tau$ value which yields a theoretical fit to an experimental curve will really be a measure of $R_HB/\rho(B)$ rather than $R_HB/\rho(0)$, which is the quantity determined by the resistance $\omega_c\tau$. Most of the discrepancy can be accounted for by a reasonable amount of magnetoresistance, but some may be due to the frequency difference between the two measurements. The $\omega_c\tau$ values used in Fig. 5 were naturally determined from the linewidths.

IX. DISCUSSION

DSCR in K has also been observed using ultrasonic techniques.[34] The slowly moving (compared with the electron velocity V_F) electromagnetic waves associated with ultrasonic sound waves play the same role as the helicon wave in the helicon DSCR experiment.[3,4] The sound result indicates, however, that the edge position agrees with the prediction based on the free-electron model. It is difficult to understand why two very similar experiments dealing with the potassium Fermi surface yield conflicting results. Magnetoacoustic experiments were also reported to be in favor of the free-electron model.[35] In all acoustic experiments, a transducer(s) must be bonded firmly to the sample. Almost inevitably, therefore, a relatively large strain exists in the sample. If the strain thus produced were stronger than we could produce in any of our samples,[31] it would be feasible to explain the discrepancy.

The general reliability of the present data, apart from its interpretation, is judged to be higher than that of the acoustic experiments. The absolute accuracy of the field calibration in each run is just as good as the known nuclear gyromagnetic ratio. The Al^{27} or the Cu^{63} NMR frequency at 4.2°K can be measured as accurately as 10 ppm, because the signal strength is very large (in the magnetic resonance standard).[36] The signal-to-noise ratio and the linearity of the MOD near the DSCR position determine the accuracy of the observed line shape and position. It is noted that the slight bump corresponding to the Cu^{63} NMR line in Fig. 2 has an inherent signal-to-noise ratio of 20 or more. The linearity of the MOD's used in this experiment is better than 1%.

It is also noted that the present DSCR data were taken at magnetic fields as much as three times that of the previously reported data. This leads to increased sensitivity due to higher $\omega_c\tau$ values as well as higher resolution. The higher magnetic fields could also be relevant to the assumption that the CDW wave vector is parallel to the field, although our lower-field measurements did not reveal any indication that the DSCR edge moves towards the free-electron position within the (increased) experimental error.

In the acoustic experiments, on the other hand, the reliability of the data is usually more limited; most of the field calibration of superconducting magnets was not done on line basis. The alignment of the crystal axis of the sample is crucial. The bonding of the transducers is one of the most difficult parts of the experimental technique. Therefore, the chance of the deterioration of the sample while being mounted is higher. None of these difficulties, however, seems to be serious enough to alter the conclusion of these experiments. As was stated previously, a relatively large amount of strain in the sample is inevitable in these experiments.

The present line-shape and line-position calculation was performed using a semi-infinite sample shape as a boundary condition. The helicon wave propagates through the present samples above the edge field. Around the edge, however, the wave propagates only about 0.1∼0.2 mm. Therefore, the semi-infinite boundary condition would be adequate in this region. Calculations for K indicate that under the experimental conditions indicated in Fig. 5, the theoretical free-

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electron edge position should be raised in field by a few tenths of one percent. This correction is well within theoretical and experimental error.[37]

The present calculation did not include the effect of a sound-mode mixing into the helicon mode.[35,38] Since the sound velocity in K is lower than in Na, one might suspect that the modification of the helicon mode due to the sound-mode mixing might be responsible for the observed difference between K and Na. A rough estimate[39] excluded this possibility. The edge field in this experiment is too low to produce any reasonable deviation. Besides, if this effect were playing any appreciable role, the theoretical free-electron edge position would move higher in field, increasing the deviation from the observed edge position. Finally, since the sound velocity is very anisotropic, the observed edge position would strongly depend on the crystalline orientation. This is against the present observation. Thus the possibility of the effect of the sound-mode mixing can be excluded both experimentally and theoretically.

Another experiment which provides us with longitudinal size information of the Fermi surface in a magnetic field is radio-frequency-size effect (RFSE). RFSE measurements of the K Fermi surface have been found to agree with the free-electron model.[40,41] It would be interesting to compare the RFSE results with the present experiment using samples with the same amount of strain.

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Since the experimental facts for the helicon DSCR have been, as we believe, well established, additional theoretical work will be necessary to determine how the helicon measurements can be reconciled with the other related experiments.

X. CONCLUSIONS

We have measured the surface impedance change associated with DSCR in K and Na. In both cases we found that samples with mirror surfaces produced DSCR lines whose shapes fit specular reflection calculations. Diffuse reflection line shapes were observed when the samples had tarnished surfaces. This knowledge of the line shapes permitted fine comparison between the experimental data and the theoretical prediction.

Single and polycrystalline samples of K produced DSCR lines whose positions in field did not agree with the free-electron values. The positions did agree with CDW predictions, especially with regard to the maximum or the minimum in dR/dB. The CDW calculations involved the assumptions that $\mathbf{Q}$ was parallel to $\mathbf{B}$ and an energy gap of 0.6 eV. The widths of the DSCR lines were found to be consistent with the purity of the samples when magnetoresistance was taken into consideration.

The position of the DSCR line in Na was found to be much closer to the free-electron calculation than the CDW prediction. The interpretation of this measurement may be complicated by a martensitic transformation and the associated strain. The Na experiment does demonstrate the absence of systematic errors which would account for the observed line positions in K.

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