de Haas-van Alphen Effect in Graphite between 3 and 85 Kilogauss

W. J. SPRY AND P. M. SCHERER
Research Laboratory, National Carbon Company, Parma, Ohio
(Received June 22, 1960)

The de Haas-van Alphen effect has been measured in a single crystal of graphite between 3 and 85 kilogauss with the *c* axis of the crystal parallel to the magnetic field. Two periods were observed: 2.05×10^{-5} gauss^{-1} for the electronic component and 1.53×10^{-5} gauss^{-1} for the holes. No new and unexpected oscillations were observed at magnetic fields as large as 100 kilogauss.

INTRODUCTION

THE de Haas-van Alphen effect in graphite was observed first by Shoenberg[1] and subsequently by Berlincourt and Steele.[2] Recently the subject has been studied with great care by Soule[3,4] who observed de Haas-van Alphen type oscillations in the galvanomagnetic properties of graphite single crystals. The band structure of this material also has been studied in detail with several recent publications by McClure.[5,6] Experimental results and theoretical predictions are in very good agreement.[7]

The present experiment was a measurement of the de Haas-van Alphen effect in a single crystal of graphite with a pulsed magnetic field. The intent was to study oscillations in magnetic susceptibility over a wide range of field and to determine whether any unexpected oscillations of short period existed which were not accounted for by the present band theory of this material. These can be observed only at the extreme fields which can be produced by a pulsed magnet.[8,9] The experiment differed from some earlier work on graphite with a pulsed magnetic field[8] in that the present detection system had a very high sensitivity. This made it possible to calibrate the system by measuring the usually observed "low-field" de Haas-van Alphen oscillations with the same equipment on the same sample. This "low-field" measurement also demonstrated the quality of the crystal that was used.

As a consequence of this work, it can be concluded that no short-period oscillations exist, a result which is in agreement with the present band theory. This theory predicts that the relatively small number (10^{-5} per atom) of carriers in graphite, which are responsible for the usually observed de Haas-van Alphen oscillations, are actually the majority carriers for this material. The present work indicates that there are no unsuspected parts of the Fermi surface with more normal, or spherical shape which contain large numbers of carriers.

A second result of this experiment has been an independent determination of the de Haas-van Alphen periods for graphite, with the *c* axis of the crystal parallel to the magnetic field. These were 2.05×10^{-5} gauss^{-1} for the electronic component and 1.53×10^{-5} gauss^{-1} for the holes. The corresponding effective masses, as obtained from the amplitude dependence of the oscillations at 4.2°K, were $0.0426m_0$ and $0.0605m_0$, respectively. The effective masses were obtained by an analysis of the data using an IBM-704 computer.[10]

EXPERIMENTAL TECHNIQUE

The de Haas-van Alphen measurements were carried out in a pulsed magnet. The circuit consists of a 6600-microfarad condenser bank connected in series with the magnet, which is an air-core solenoid with an inductance of 3.82 microhenries. A heavy-duty switch is used to close the circuit and initiate current flow. Between current pulses, the condensers are charged slowly by a separate power supply. It was necessary to design the magnet and the detection equipment for this specific experiment. This was due primarily to the nature of the small signal voltage expected from low-field variations in magnetic susceptibility of the sample. However, there are no unusual design features and the parameters of the magnet and of the condenser bank are based on information presented by Champion.[11] In similar fashion, the method used to detect susceptibility variations is a straightforward adaptation of the technique first used by Shoenberg.[9]

Figure 1 is a block diagram of this detection equipment. The sample coil, with sample inserted, acts as the secondary winding of a transformer of which the magnet is the primary. The induced voltage is proportional to the total coupling between primary and secondary. This is proportional to the magnetic susceptibility of the sample and to geometrical factors such as coil areas and turns ratios. The de Haas-van Alphen oscillations appear as a small signal superimposed on a large induced voltage due to these geometrical effects. The first balance coil is constructed with identical dimensions, but is

[1] D. Shoenberg, Phil. Trans. Roy. Soc. (London) **A245**, 1 (1952).
[2] T. Berlincourt and M. C. Steele, Phys. Rev. **98**, 956 (1955).
[3] D. E. Soule, Phys. Rev. **112**, 698 (1958).
[4] D. E. Soule, Phys. Rev. **112**, 708 (1958).
[5] J. W. McClure, Phys. Rev. **108**, 612 (1957).
[6] J. W. McClure, Phys. Rev. **112**, 715 (1958).
[7] The publications listed above contain extensive references to other work in this field.
[8] D. Shoenberg, in *Progress in Low-Temperature Physics*, edited by J. C. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. 2, p. 226.
[9] D. Shoenberg, Physica **19**, 791 (1953).
[10] J. W. McClure and L. B. Smith, Bull. Am. Phys. Soc. **4**, 168 (1959).
[11] K. S. Champion, Proc. Phys. Soc. (London) **B63**, 795 (1950).

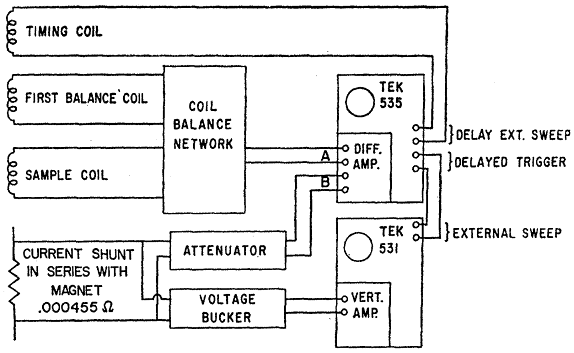

FIG. 1. Block diagram of detection equipment.

wound in the opposite sense. It therefore counteracts the induced voltage due to geometrical coupling when the outputs of the two coils are combined in a coil balancing network. The resultant signal voltage is connected to channel A of a differential amplifier used with the Tektronix 535 oscilloscope shown in Fig. 1.

A small current shunt is placed in series with the magnet coil as shown. This is used both to measure the magnetic field and to provide a further balancing voltage for the signal. This added balancing signal represents the modification made to Shoenberg's original method. Although the magnet and sample coil combination were designed with sufficient sensitivity, adequate electrical balance could not be maintained throughout the entire sweep of the magnetic field pulse. A further balance voltage, proportional to the magnet current, was inserted as shown. This allowed selected field intervals to be balanced with greater accuracy and permitted the use of maximum sensitivity in the oscilloscope amplifiers. Some over-loading of the amplifier circuits occurred as a consequence of the increased gain. This was due primarily to induced voltages when the main magnet switch arced on closing. The resultant "dead time" did not exceed ten microseconds, however, and was not an appreciable source of error. The use of expanded and delayed sweeps made it possible to observe the oscillations over limited ranges of field. Precise measurement of the field was accomplished with a second Tektronix 531 oscilloscope as shown in Fig. 1. The detailed circuits used for this purpose have been described by Gold.[12]

With this circuit-magnet combination, the signal voltage is proportional to $dM/dt=(dM/dH)(dH/dt)$. The letter M represents the magnetization of the sample, H is the magnetic field, and t is the time. The magnitude of dM/dH is inversely proportional to the period of the de Haas-van Alphen oscillation and, consequently, is relatively small for the ordinary oscillations in graphite (10^{-5} gauss^{-1}). For comparison with similar pulsed magnet experiments, a typical observed period in lead is 4×10^{-8} gauss^{-1}.[8] In order to realize a usable signal voltage in the present experiment dH/dt had to be large, and the magnet was designed with a free ringing frequency of 1000 cycles per second.

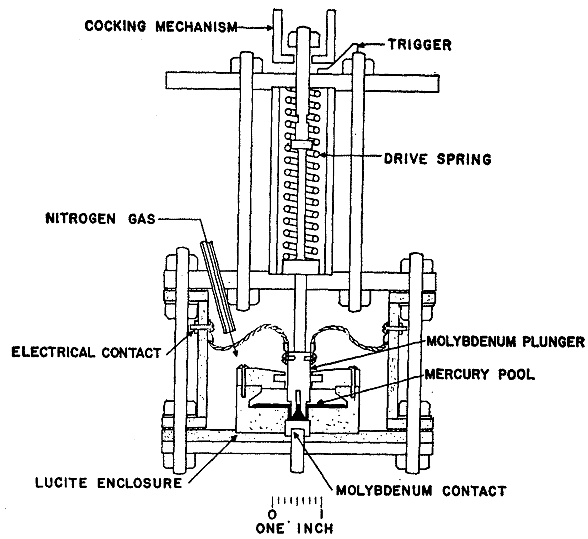

FIG. 2. Control switch for pulsed magnet.

The magnet consists of a solenoid machined from beryllium copper. The inside diameter was chosen so that the tip of a liquid helium Dewar could be inserted. All other dimensions were adjusted so that a field uniformity of one part in 10^4 was maintained over a disk-shaped region, 1 mm high by 2 mm in diameter, which contained the graphite crystal. The uniformity was needed in order to make it possible to detect oscillations with periods as short as 10^{-8} gauss^{-1} at large fields without undue attenuation. Both a large field of approximately 100 kilogauss and excellent field homogeneity are required to detect such oscillations. The remaining degrees of freedom in the magnet design were the capacity and the working voltage of the condenser bank.

With these design parameters, it was apparent that a special low-noise switch was needed to handle a peak current of approximately 20 000 amperes for the required maximum field of 100 000 gauss. Figure 2 is a diagram of the final result. The design of the switch was based on the following considerations: First, that data be recorded during the second quarter cycle of the pulse; thus all arcing on closure had to be completed within the first 250 microseconds of current flow. Given the ionization potential of nitrogen, there is a critical minimum separation between the plunger and mercury pool at which arcing may be initiated.[13] By using a powerful drive spring and light plunger, it was possible to pass through the critical distance within this time interval. Second, the switch should not "bounce" and arc during the recording of data in the time interval between 250 and 500 microseconds after initiation of current flow. This requirement was satisfied by adjusting the depth of the mercury pool and by choosing the dimensions of

[12] A. V. Gold (to be published).

[13] J. Dillon Cobine, *Gaseous Conductors* (Dover Publications, New York, 1958).

the mercury cylinder so that the downward motion of the plunger was hydraulically damped.

The pulsed magnet was calibrated by comparison with a twelve-inch dc magnet. This, in turn, was calibrated by proton resonance. The comparison between this dc field and the pulsed field was accomplished in two steps. First, a test coil was removed mechanically from the dc field and a record of induced voltage versus time was photographed on a calibrated oscilloscope. The same coil then was placed in the position occupied by the sample in the pulsed magnet. The induced voltage versus time again was recorded on the same oscilloscope while simultaneously recording the magnet current versus time on a second calibrated oscilloscope. The dc field was related to the peak current through the pulsed magnet by the usual equation, $E=-\partial\phi/\partial t$. The value of E is in volts, ϕ is the magnetic flux, and t is the time. Each step of the calibration procedure was repeated a sufficient number of times to fit the results to a Gaussian error function. Major sources of error were associated with various test coils, the sensitivity, and the sweep rates of the oscilloscopes. On the basis of this procedure, the calibration has a standard deviation of $\pm 1.6\%$.

DATA AND SAMPLE PREPARATION

Figures 3(a) and 3(b) present examples of the raw data as photographed on the oscilloscope screen. Since the signal increases with increased magnetic field, the low-field data have been emphasized to demonstrate the sensitivity of the equipment. The approximate signal amplitudes and field intervals are indicated on the appropriate axes. The oscilloscopes were calibrated for voltage gain and sweep speed prior to each experimental run. The grid of the oscilloscope screen was photographed as well as the cathode trace and all calibration measurements were recorded with respect to this grid.

The crystal used in this experiment was a selected sample of Essex County Graphite. This was carefully purified and is better than 99.995% carbon. Analysis of the final data indicates that scattering due to all causes in the sample would be equivalent to the increased thermal scattering that would have been expected from a 0.4°K increase in the sample temperature.[14]

EXPERIMENTAL RESULTS

Figure 4 is a graph of reciprocal magnetic field in gauss^{-1} vs the location of maxima and minima in the observed derivative of the magnetic susceptibility. The interference between holes and electrons in the composite de Haas-van Alphen period can be discerned from the uneven progression of the data points. A comparison between the experiment and the theory is shown in Fig. 5. The fit is based upon a two-carrier theory considering only the first and second harmonics in the Landau formula.[15] It is not expected to be valid in the extreme quantum limit, consequently, the fitting was arbitrarily stopped at a maximum field of approximately sixteen kilogauss.

[14] R. B. Dingle, Proc. Roy. Soc. (London) **A211**, 517 (1952).

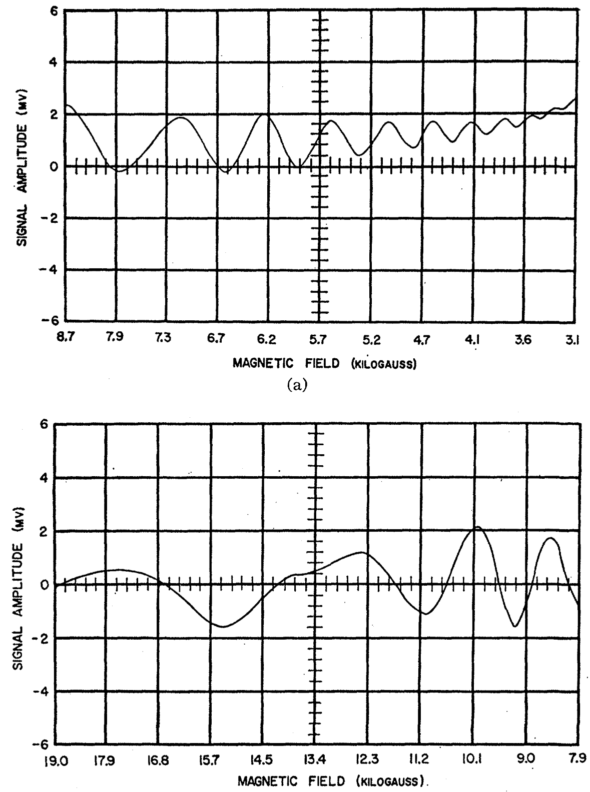

FIG. 3. Photographic traces of the oscilloscope screen showing the variation in magnetic susceptibility with magnetic field. The values assigned to the horizontal and vertical axes are approximate.

An over-all sensitivity can be assigned to the experiment on the basis of observed de Haas-van Alphen oscillations due to conduction electrons at fields as small as three kilogauss. Under the assumptions that $(cA/ehH)\gg 1$ and that $(2\pi^2kT/\beta H)\gg 1$, the signal amplitude is proportional to

$$\frac{dM}{dH}=\frac{4VkT}{h^3}\left(\frac{ehH}{c}\right)^{\frac{3}{2}}\left(\frac{\partial^2 a}{\partial P_{H^2}}\right)_m^{-\frac{1}{2}}\times\exp(-2\pi^2kT/\beta H)\left(\frac{2\pi cA}{ehH^2}\right)^2\times\cos\left(\frac{2\pi cA}{ehH}-2\pi\nu\mp\frac{\pi}{4}\right).$$

The parameters in this formula are expressed in cgs units. The quantity M is the magnetization, H is the magnetic field, V is the atomic volume, k is the Boltz-

[15] L. D. Landau, formula stated as part of appendix to the article by D. Shoenberg, Proc. Roy. Soc. (London) **170**, 341 (1939).

mann constant, and T is the tempearture. The value e is the electronic charge, c is the velocity of light, and $\beta = eh/2\pi mc$. The quantity m is the effective mass of the carrier in terms of the free electron mass, and h is Planck's constant. The quantity $(\partial^2 a/\partial P_{H^2})^{-\frac{1}{2}}$ is dimensionless and can be expressed explicitly for an ellipsoid.[8] The parameter ν is a phase factor, and A is either the maximum or the minimum cross-sectional area of the Fermi surface in the system of planes defined by the direction of the magnetic field. The relation of importance in computing an instrument sensitivity is $S = \exp(-2\pi^2 kT/\beta H)P^{-2}H^{-\frac{5}{2}}$ where $P = eh/cA$. At a field of $H = 3000$ gauss, $T_{\mathrm{eff}} = 4.6$°K (including an assumed 0.4°K rise in temperature to include the effects of collision damping[14]), $m = 0.0426m_0$, and $P = 2.05\times 10^{-5}$ gauss^{-1}; the value of S is 3.5×10^{-4}.

For comparison with short-period oscillations of carriers with a large effective mass, the values $m = m_0$, $P = 10^{-8}$ gauss^{-1}, and $H = 10^5$ gauss (the maximum field used in the present experiment) were considered. These values of period, effective mass, and magnetic field are consistent with the required assumptions that $cA/ehH \gg 1$ and that $2\pi^2 kT/\beta H \gg 1$. On substitution in the relationship for the sensitivity, S now equals 4.6. Consequently, carriers with these characteristics would be expected to produce a signal approximately 10^4 times larger than that which was produced by electrons in graphite at 3000 gauss. Such oscillations were not observed and it is therefore experimentally unlikely that any large number of carriers with large effective masses exist in graphite.

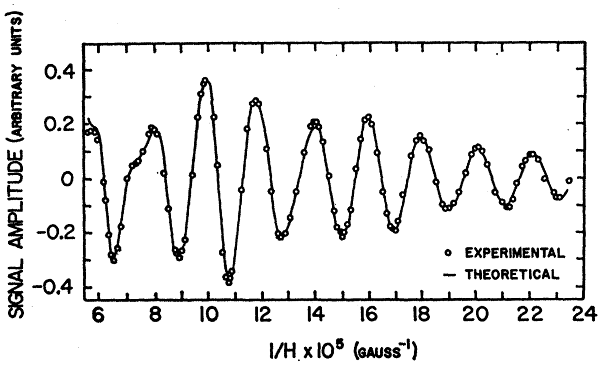

FIG. 5. Comparison between experimental values and the Landau expression for the de Haas-van Alphen effect.

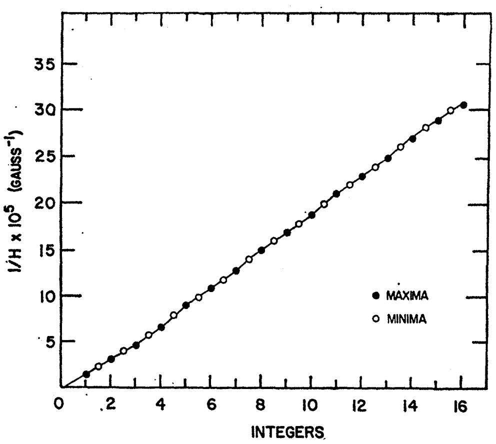

FIG. 4. Integer plot of the de Haas-van Alphen oscillations.

DISCUSSION OF RESULTS

The de Haas-van Alphen effect in graphite and its relation to the band structure have been discussed in considerable detail by a number of investigators.[5,6] This experiment provides additional confirmation of the present theory. It presents an independent measurement of the oscillatory periods evident in graphite and demonstrates experimentally that there are no large and unsuspected regions of the Fermi surface of graphite unaccounted for by the present model of the band structure.

ACKNOWLEDGMENTS

Considerable assistance in this work has been provided by other staff members of the National Carbon Research Laboratories. The crystal used in this experiment was selected and purified by D. E. Soule. J. W. McClure and L. B. Smith were responsible for programming the data for the computer and for the curve-fitting in general. B. Vizi was indispensable in carefully plotting the data and in carrying out much of the work associated with calibrating the pulsed magnet. V. Krajcir was responsible for the accurate machining of the magnet.