A similar introduction of acceptor centers has been obtained with silicon of N-type and 6 ohm-cm resistivity. When this silicon was compressed 2.5 percent at  $725^{\circ}$ C, it remained *N*-type but the resistivity increased to 150 ohm-cm. When the same silicon was compressed 18 percent at 850°C, the resistivity increased to 50 ohm-cm and both N and P regions were found in the sample. These resistivity changes correspond to an introduction of about 1015 acceptor centers/cm3. As in the case of germanium, controls that were heated only were included simultaneously in the furnace. No significant changes in resistivity were obtained in the controls.

Values of mobilities used in calculation were for undeformed material.<sup>5,6</sup> The number of acceptor centers may be different to the extent that mobilities are different in deformed structures.<sup>7</sup>

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## Thermal Conductivity of Copper between 0.25°K and 4.2°K\*

JAMES NICOLT AND T. P. TSENG Department of Physics and Astronomy, Ohio State University, Columbus, Ohio (Received September 18, 1953)

SOME years ago, Heer and Daunt initiated measurements on the thermal conductivity of metals below 1°K, their first observations being on Sn and Ta.1 This work led immediately to the practical realization of superconducting thermal "valves"<sup>2</sup> and to an understanding of the significance of lattice conduction at extremely low temperatures. Subsequently, similar measurements by us have been made on Pb3 and Cu. Whereas many other observations below 1°K on the thermal conductivity of superconducting metals, such as Pb, have since been reported,<sup>4</sup> data below 1°K on normal metals, such as Cu, are unavailable. It is considered that the results, given below, for Cu are of twofold interest, first in relation to the theory of electrons in metals, and second, as a guide in technical problems arising in cryogeny below 1°K.

The experimental arrangements for the observations below 1°K were similar to those used previously,1 consisting of two approximately equal chromium potassium alum cylinders of about 15 cc each, separated from one another by a distance of approximately 30 cm and connected thermally to each end of the specimen of interest by copper mountings of large cross section. The thermal contact between the salts and their copper mountings was made by high-pressure molding. The two salt cylinders were simultaneously cooled to low, but different, temperatures by the magnetic method, and the thermal conductivity of the metallic specimen linking the two was calculated from observations of the rate at which the cylinders equalized temperature. The dimensions of the specimens were so chosen that the time for equalization was long enough (about 1 hour) to enable observations to be made to at least 0.001°K. The stray influx of heat from the surroundings was kept low in order to minimize errors of computation. The temperatures of the salts were obtained from susceptibility measurements, using an ac bridge method.<sup>5</sup> The ac bridge, using a decade mutual inductance constructed by Hayes,<sup>6</sup> has a sensitivity such that, with a primary field of 0.1 gauss rms at 28 c/s, temperature differences of less than 0.1 milli-degrees can be readily observed at, for example, 0.5°K.

For the temperature range 1°K to 4.2°K, customary steady heat flow techniques were used for the conductivity measurements, employing carbon thermometers and direct ohmic heating.

The thermal resistance between the salts was found to be composed of two terms; (a) the resistivity of the Cu sample and (b) the thermal contact resistances between the salts and their copper mountings. This term (b) was found to be proportional to  $T^{-2}$ , as has been discussed previously by Mendoza<sup>7</sup> and by Goodman,<sup>4</sup> and the factor of proportionality was obtained from our observations made at 0.5°K. As will be seen from the table of results given below, this term (b) represented only a small correction to the results down to 0.5°K.

In order to calculate the heat flow between the samples, it was necessary to estimate the heat leak from external sources into each salt individually. On the assumption that these heat leaks were proportional to (a) the difference in temperature between each salt and the surrounding chamber, and (b) the area of each salt, the constant of proportionality could be obtained by calculation from the observed total heat leak at any one instant. It was found that a unique value of this constant allowed computations to be made, regarding the heat leak, which were in good agreement with the experimental data over periods of time exceeding one hour and corresponding intervals of temperature.

The copper sample was a polycrystalline wire of 27.2-cm length and 0.025-cm diameter, and was of commercial grade high-purity magnet wire, supplied by General Electric Company. The observed thermal conductivity, K as a function of temperature is shown in Fig. 1 and Table I. It will be observed that within the

TABLE I. Observed thermal conductivity as a function of temperature.

Obs. mean temp. °K	Obs. temp. diff. °K	Barrier te at salt A °K	mp. drop at salt <i>B</i> °K	Temp. diff. along Cu °K	Corrected mean temp. °K	Thermal cond. of Cu watt units
$\begin{array}{c} 0.810\\ 0.787\\ 0.672\\ 0.657\\ 0.608\\ 0.416\\ 0.400\\ 0.346\\ 0.259\end{array}$	$\begin{array}{c} 0.011\\ 0.059\\ 0.036\\ 0.114\\ 0.108\\ 0.242\\ 0.180\\ 0.046\\ 0.242\\ \end{array}$	$\begin{array}{c} 0.001\\ 0.005\\ 0.004\\ 0.014\\ 0.076\\ 0.047\\ 0.008\\ 0.077\\ \end{array}$	$\begin{array}{c} 0.001\\ 0.004\\ 0.003\\ 0.009\\ 0.001\\ 0.023\\ 0.019\\ 0.008\\ 0.010\\ \end{array}$	$\begin{array}{c} 0.009\\ 0.050\\ 0.029\\ 0.091\\ 0.093\\ 0.143\\ 0.114\\ 0.030\\ 0.155\\ \end{array}$	$\begin{array}{c} 0.810\\ 0.787\\ 0.673\\ 0.660\\ 0.615\\ 0.443\\ 0.414\\ 0.346\\ 0.293\\ \end{array}$	$\begin{array}{c} 1.30\\ 1.17\\ 1.09\\ 0.87\\ 0.92\\ 0.91\\ 0.79\\ 0.55\\ 0.53\end{array}$



limits of experimental error K is a linear function of T down to 0.25°K. If one puts  $K = \alpha T$ , then our observed value of  $\alpha$  is 1.76 watts/cm deg<sup>2</sup>. Previous results in the temperature range 1.2°K to 4°K give  $\alpha = 0.6$ ;<sup>8</sup>  $\alpha = 0.58$ ;<sup>9</sup>  $\alpha = 4.7$ ;<sup>10</sup> and  $\alpha = 2.0$ .<sup>11</sup> The fact that our value of  $\alpha$  is somewhat less than that observed by the two latter groups of workers is due probably to small differences in purity of the samples.

At temperatures below those reported herewith, the thermal resistance between the salts appeared to include more highly temperature dependent terms than those given by terms (a) and (b)above. This additional temperature dependency was not considered to be due to any primary processes occurring in the copper specimen, since similar dependencies were separately observed in experiments on the thermal conductivity of superconducting Pb in the same temperature region. It is possible that these effects were due to diffusional or relaxational processes in the salts themselves.

The observed linear dependence of K on temperature indicates that the thermal conductivity is electronic in character and is limited only by impurity scattering. Moreover, the linear temperature function is a direct reflection of the linear dependence of the electronic specific heat on the absolute temperature. It is of interest to note, therefore, that this linear function appears experimentally to be valid down to as low a temperature as 0.25°K, especially in view of the possible deviations from linearity which have been considered to occur due to exchange and correlation forces.12

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† Now at Amherst College, Amherst, Massachusetts.
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## Paramagnetic Resonance Absorption in Graphite\*

I. G. CASTLE, IR

Department of Physics, University of Buffalo, Buffalo, New York (Received September 22, 1953)

HE two-dimensional freedom of the carriers in graphite is very suitable for the study of graphite's electronic structure by magnetic resonance techniques. Recently the author has observed, with Yale University's spectrometer,1 magnetic resonance absorption in several samples of graphitized materials at 9242 Mc/sec and room temperature. Each sample showed only a single absorption line. The preliminary data are presented now in order to report the first observation of magnetic resonance absorption in systems that are approximately two-dimensional.

The graphite samples were prepared from powdered materials so as to have all of the graphitic planes throughout each sample aligned normal to a selected direction. The samples, in the form of thin films, were mounted on thin dielectric strips. Sample A contained well-purified Ceylon graphite which was powdered, mixed with liquid polystyrene, and oriented with almost all the planes parallel to the supporting film. Visual inspection indicated a high degree of alignment. Samples B, C, and D contained powder made of coke which was milled to a mean particle size of 1-2 microns and graphitized to 3000°C. The graphitic planes in sample B were oriented parallel to the supporting film and in C, perpendicular. For D, the powder was not imbedded in a dielectric medium. Sample E contained machining dust from well-purified aritificial graphite, oriented parallel.

The magnetic field was measured by observing the proton resonance absorption in pure mineral oil. The positional error in the proton frequency was less than three kc/sec. The modulation amplitude of the magnetic field was less than the observed halfwidths.

The g-value for sample A is 1.003 times that of a system of free electron spins, each with the moment  $\mu_0$  (1.00115). The absorption, described in Table I, can be attributed to the spin resonance of the

TABLE I. Spin resonance absorption in graphite at 3 cm.

Sample	Crossover proton frequency Mc/sec	Half-width at half-power gauss
$\begin{array}{c} A - Ceylon \mid \\ B - 1\mu \mid \\ C - 1\mu \perp \end{array}$	$\begin{array}{c} 14.016 \pm 0.005 \\ 14.000 \pm 0.008^{a} \\ 14.00^{a} \end{array}$	$5\pm1+9\pm2$ ~20
$E = \frac{D}{E}$	$14.000 \pm 0.008$ 14.00 <sup>a</sup>	$\sim 10^{9 \pm 2}$

a Slightly asymmetric.

carriers in graphite. The lines are quite sharp and the frequency of collisions with the edges of micron-size crystallites (assuming the small estimated effective mass for motion parallel to the graphitic planes) is of the order of the observing frequency. Therefore, the mechanism of carrier spin absorption requires that the collisions of the carriers with the edges of the planes do not frequently disturb the carriers' spin orientation.

Measurements of the static susceptibility<sup>2</sup> of the same powder as in B, C, and D gave the density of ferromagnetic impurities. On the basis of this density, the amount of ferromagnetic impurity in each of these samples was estimated to be less than fifty millimicrograms. Even in larger amounts, ferromagnetic impurities would not have seriously interfered with the observed line shapes for the modulation used.

With the graphitic planes arranged parallel to the static magnetic field, as for sample A, B, D, and probably E, the cyclotron resonance<sup>3</sup> was undoubtedly quenched. Since the intensity of the line in sample C was approximately the intensity in B, it is unlikely that the cyclotron resonance predominated in sample C. Furthermore, the small effective mass for motion parallel to the graphitic plane, requiring as it does a rather different g-value, dictates against the observed lines being associated with the cyclotron resonance of the carriers.

There is apparently very little artificial broadening of the magnetic resonance lines in graphite as has been observed in metals.<sup>4</sup> The two-dimensional freedom and the sample orientation employed lead one to expect no broadening from the diffusion mechanism and no shift of the g-value due to eddy currents. Several interesting details of the absorption in graphite are under further experimental study.

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Some Consequences of Possible Degeneracy of Energy Bands in Ge†

Edward N. Adams, II Institute for Nuclear Studies and Chicago Midway Laboratories, University of Chicago, Chicago, Illinois

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ALCULATIONS of Herman<sup>1</sup> and Herman and Callaway<sup>2</sup> ✓ indicate that for diamond and germanium a triple degeneracy occurs at the band edge for both the conduction and valence bands. and that the degeneracy in the conduction band is probably six-