

shifting from the natural to the enriched boron was an increase in the intensity of all peaks in about the ratio of the concentration of the B^{10} . The energy of the gamma-rays obtained from the boron bombardment was checked at several different bombardment energies with the $1\frac{1}{2}$ inch thick NaI crystal. The gamma-rays from Co^{60} and $F^{19}(p,\gamma)$ were used for calibration.⁵ The energy was consistently 3.9 ± 0.1 Mev, indicating that the 3.89 Mev level in C^{13} is more strongly excited in this reaction than the 3.09 Mev level. Measurement of the energy of the $Be^9(\alpha,n\gamma)$ gamma-ray was made with the 1-inch thick NaI crystal and found to be 4.2 ± 0.2 Mev. This most likely corresponds to a predominant gamma transition from the well-known 4.47-Mev level in C^{12} .

DISCUSSION OF RESULTS

The beryllium curve has a strong first resonance peak at 1.90 Mev. The previous value was 1.5 Mev.⁶ This would raise the level in C^{13} formerly set at 11.7 Mev to 11.95 Mev. A small but consistent peak appears at

⁵ E. J. Woodbury and W. A. Fowler, Phys. Rev. **85**, 51 (1952).

⁶ I. Halpern, Phys. Rev. **76**, 248 (1949).

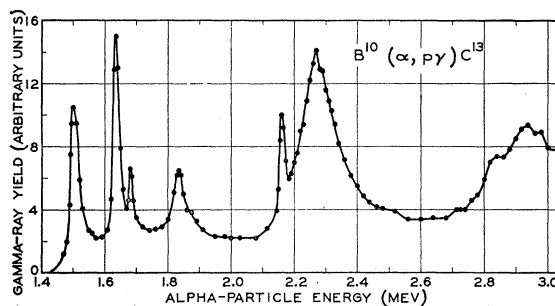


Fig. 2. Relative yield of gamma-rays from $B^{10}(\alpha, p\gamma)C^{13}$ as a function of bombarding energy. Observations taken with thin target at 90° to the beam.

2.65 Mev which would indicate a heretofore unreported level at 12.46 Mev.⁷

The boron yield curve shows fairly sharp maxima at 1.50, 1.63, 1.68, 1.83, and 2.16 Mev and somewhat broader peaks at 2.27 and 2.95 Mev. These values assign energy levels in N^{14} of 12.77, 12.87, 12.90, 13.01, and 13.24 Mev. The two broader peaks probably represent a number of unresolved energy levels lying very close together.

⁷ N. Nereson, Phys. Rev. **87**, 221 (1952), from total neutron cross-section measurements of C^{12} , has reported evidence of a level of 12.3 Mev.

Electrical Conductivity of Single Crystals of Graphite

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The electrical conductivities along the principal directions of graphite crystals have been measured using a large number of well-developed single crystals obtained from Ceylon. The conductivity along a direction perpendicular to the hexagonal axis is about 10^4 times that along the axis. Rectification and other nonlinear effects are totally absent. Thickness plays an important part in the determination of the conductivity normal to the hexagonal axis and attempts have been made to avoid this difficulty. These measurements have been extended to temperatures between $80^\circ K$ and $500^\circ K$. The conductivity perpendicular to the hexagonal axis falls roughly exponentially with rising temperature and that along the axis rises similarly with temperature. A magnetic field has been found to cause a decrease in both the conductivities—the effect on the conductivity normal to the hexagonal axis being more pronounced. This decrement falls roughly exponentially with rising temperature and has a tendency to attain a steady value at higher temperatures.

INTRODUCTION

GRAPHITE is a hexagonal layer-latticed crystal having a perfect basal cleavage and occurs in nature in the form of thin flakes. Investigations of its structure by Bernal¹ revealed that its carbon atoms are arranged in layers parallel to the basal plane, the atoms in each layer forming a regular hexagonal network. The distance of separation between the adjacent layers is 3.40Å , which is much larger than the distance between the adjacent atoms in the same layer, namely, 1.42Å ; this shows that the binding between the adjacent layers

is extremely loose, and is probably of the Van der Waals type. The diamagnetic properties of this crystal have been studied in details by Ganguli² and Krishnan and Ganguli.³ The specific susceptibility (per gram) of the crystal perpendicular to the hexagonal axis χ_{\perp} , is about -0.5×10^{-6} , which is nearly that of diamond. On the other hand, the susceptibility along the hexagonal axis, χ_{\parallel} , is numerically very large, and is equal to -21.5×10^{-6} , i.e., about 40 times χ_{\perp} . The above values refer to room temperature, and measurements have been

² N. Ganguli, Phil. Mag. **21**, 355 (1936).

³ K. S. Krishnan and N. Ganguli, Nature **139**, 155 (1937).

¹ J. D. Bernal, Proc. Roy. Soc. (London) **A106**, 749 (1924).

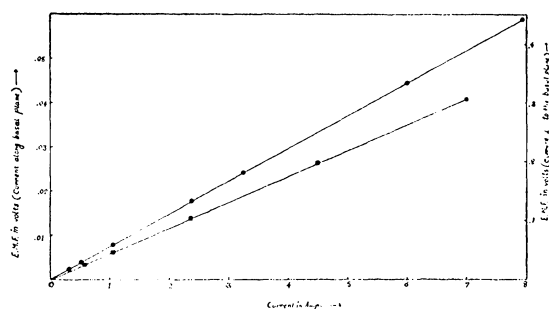


FIG. 1. Current-voltage relation. ●—current along the basal plane; ■—current perpendicular to the basal plane.

extended over a large range of temperatures,⁴ *viz.*, from 80°K to 1270°K. It was found that at high temperatures the anisotropy, *i.e.*, $\chi_{\perp} - \chi_{\parallel}$, tends to obey a simple Curie law, while at low temperatures it has a tendency to be independent of temperature. It has been further shown that within this temperature range χ_{\perp} is practically temperature independent. In a subsequent paper⁵ Krishnan and Ganguli have shown that the abnormal diamagnetism of crystals of graphite is a free electron diamagnetism which is directed almost wholly along the hexagonal axis. Throughout the entire range of temperatures over which investigations were undertaken, this free electron diamagnetism of graphite per carbon atom has been found by them to be equal to the Landau diamagnetism per electron of a free electron gas obeying Fermi-Dirac statistics having a degeneracy temperature of 520°K. From this experimental finding it has been concluded (1) that the number of free electrons in graphite is just one per carbon atom; (2) that the effective mass of these electrons for motion in the basal plane is just their actual mass, which means that the movements in this plane are entirely free and are not influenced by the lattice field; (3) that on the other hand their effective mass for motion along the normal to the basal plane is enormous, about 190^3 times the actual mass, indicating that the free electrons belonging to any basal layer of carbon atoms are tightly confined to that layer, keeping at the same time their complete freedom to migrate over the whole of the layer; (4) that this tight binding accounts for the observed low degeneracy temperature of the electron gas in the crystal. They have further tried to show that this picture of graphite is in accord with the quantal views of the electronic structure of graphite and also with its Brillouin zones. There is such a zone in graphite which can just accommodate three electrons per atom, forming a closed group and leaving one electron which may be treated as free. Thus, in view of the simplicity of the picture of the free electron gas in graphite as well as the low value of

its degeneracy temperature, graphite forms a suitable medium for studying the properties of an electron gas.

It will obviously be even more interesting if the free electron gas in graphite as pictured by Ganguli and Krishnan⁶ is put to a more direct experimental test, namely, a study of its electrical conductivities. Moreover, a number of papers⁶ have appeared during the recent years, in which the authors, presumably unaware of the work of Krishnan *et al.*, concluded theoretically that graphite is a semiconductor and tried to predict its various properties. Experimental verifications of this latter conclusion are not at all satisfactory. On looking into the literature,⁷ one finds that almost all conductivity measurements are either on powders of graphite or for currents along the basal plane only. There is just one preliminary report on the measurement of the electrical conductivities of single crystals of graphite, by Krishnan and Ganguli.⁸ They have shown that for currents along the basal plane the specific resistance of graphite is of the order of 10^{-4} ohm cm, while for currents along the perpendicular direction it is about 2–3 ohm cm. They do not appear to have investigated any temperature variation of the electrical conductivities. It thus appears that an extensive study of the electrical properties of single crystals of graphite will also go a long way toward resolving the above controversy.

The present paper gives a detailed account of experimental studies on the electrical conductivities of single crystals of graphite of high purity obtained from Ceylon, at room temperature and also at higher and lower temperatures, extending from 80°K to 550°K.

EXPERIMENTAL PROCEDURE

For the purpose of measuring the specific resistances of single crystals of graphite, thin flakes parallel to the basal plane were cleaved out of a large piece and were cut suitably in the form of rectangular plates. Lengths and breadths were measured with a very accurate travelling microscope, and the thicknesses with a micrometer, both reading to 0.001 mm. The dimensions of the specimens varied within the following limits: Length (l)—2 cm to 0.2 cm; breadth (b)—1 cm to 0.5 cm; thickness (t)—0.06 cm to 0.01 cm. The crystal

TABLE I.

Crystal thickness in cm	$\sigma_{\perp} \times 10^{-4}$ ohm ⁻¹ cm ⁻¹	σ_{\parallel} ohm ⁻¹ cm ⁻¹
0.0584	0.524	1.1
0.0325	0.8333	1.06
0.0294	0.9901	1.12
0.0253	1.006	1.02
0.0114	1.012	1.01

⁶ C. A. Coulson, *Nature* **159**, 265 (1947); P. Wallace, *Phys. Rev.* **71**, 622 (1947); S. Mrozowski, *Phys. Rev.* **77**, 838 (1950).

⁷ J. Koenigsberger and J. Weiss, *Ann. Physik* **35**, 1 (1911); O. E. Roberts, *Ann. Physik* **40**, 453 (1913); E. Ryschewitsch, *Z. Elektrochem.* **29**, 474 (1923).

⁸ K. S. Krishnan and N. Ganguli, *Nature* **144**, 667 (1939).

⁴ K. S. Krishnan and N. Ganguli, *Z. Krist.* **A100**, 330 (1939).

⁵ N. Ganguli and K. S. Krishnan, *Proc. Roy. Soc. (London)* **A177**, 168 (1941).

flakes thus obtained from different samples of graphite were then tested for purity and also for the possible existence of twinings or strains by taking x-ray Laue photographs. Such examinations indicated no effective impurities, twinings or strains.

Measurement at Room Temperature

(1) For measuring the specific resistance along the basal plane ρ_{\perp} , the two ends of the rectangular crystal specimen are covered electrolytically with a heavy uniform layer of copper for a small distance parallel to the edges and are held at these ends in a special crystal holder. The holder consists of two pairs of small rectangular brass blocks placed over a rectangular sheet of ebonite or of insulating hard fiber, one pair at each end and one above the other in each pair. The pairs of brass blocks can be slid towards or away from each other by means of screw pins attached to the lower faces of the blocks in contact with the insulating sheet, passing through a small rectangular slot cut in the insulating sheet, and can be fixed in any position on the insulating base by tightening nuts attached to the screws. Relative motion of the blocks through the slot has been provided so as to accommodate crystals of different lengths between them. The upper block of each pair is kept in electric contact with the lower by means of two brass screws passing vertically through them. The electroplated ends of the crystal are gripped, one between each pair of blocks. By suitably tightening the screws passing through both the blocks of each pair, good electrical contact with the crystal is obtained. Stout copper wires are soldered to each pair of blocks. A feeble current of the order of a few milliamperes is then passed through the specimen, and the corresponding drop of potential across it is measured by means of a Leeds and Northrup potentiometer reading to 5 microvolts per smallest division. In all these and later experiments, the current through the specimen was reversed and mean values of the potential taken, in order to avoid thermoelectric effects. The resistance of the specimen being thus known, a knowledge of the dimensions of the specimen gives the value of the specific resistance or the specific conductivity.

(2) For measuring the specific resistance at right angles to the basal plane ρ_{\parallel} , the rectangular crystal specimen is placed between two rectangular brass plates, one located above the other. Good electrical contact between one face of the crystal and that of the

TABLE II.

Sample	σ_{\perp} , ohm ⁻¹ cm ⁻¹ . Mean of measurements on 5 different crystals from the sample	σ_{\parallel} , ohm ⁻¹ cm ⁻¹ . Mean of measurements on 5 different crystals from the sample
1	0.98×10^4	1.02
2	1.02×10^4	1.01
3	0.96×10^4	1.03
4	0.99×10^4	1.04
5	1.01×10^4	1.01

TABLE III.

Temp. °K	Without magnetic field			With magnetic field	
	$\sigma_{\perp} \times 10^{-4}$	σ_{\parallel}	$(\sigma_{\perp}/\sigma_{\parallel}) \times 10^{-4}$	$\Delta\sigma_{\perp} \times 10^{-4}$ Change of σ_{\perp} in a field ≈ 3600 gauss	$\Delta\sigma_{\parallel}$ Change of σ_{\parallel} in a field ≈ 3600 gauss
80	1.556	0.865	1.810	0.760	0.057
84	1.530	0.865	1.77	0.740	0.055
90	1.490	0.865	1.727	0.700	0.052
100	1.432	0.866	1.659	0.64	0.047
120	1.332	0.87	1.542	0.54	0.041
140	1.260	0.875	1.444	0.405	0.034
160	1.207	0.885	1.369	0.323	0.027
180	1.170	0.897	1.301	0.257	0.021
200	1.138	0.911	1.245	0.21	0.016
220	1.115	0.927	1.196	0.173	0.013
230	1.102	0.936	1.160	0.158	0.012
240	1.087	0.945	1.148	0.143	0.010
260	1.056	0.964	1.091	0.118	0.008
280	1.027	0.982	1.042	0.100	0.005
300	1.002	0.997	1.023	0.087	0.005
320	0.986	1.007	0.9734	0.075	0.006
340	0.972	1.015	0.9510	0.067	0.006
360	0.958	1.016	0.9294	0.060	0.006
380	0.947	1.022	0.9156	0.052	0.006
400	0.930	1.038	0.8937	0.046	0.006
420	0.912	1.071	0.8569	0.040	0.007
440	0.907	1.118	0.8004	0.034	0.008
460	0.899	1.202	0.7252	0.028	0.008
470	0.895	1.300	0.6876	0.025	...
480	0.887			0.024	
500	0.870			0.020	
520	0.852			0.015	
540	0.830			0.010	
560	0.806			0.007	

brass blocks on the same side is obtained by tightening the nuts upon four screws passing through four holes at the corners of the brass blocks—the screws being insulated from the brass blocks by means of mica washers and glass insulating tubes of suitable size inserted in the holes. Accidental contact between the two blocks is prevented by a mica sheet thinner than the crystals of graphite and with a central rectangular slot to take the crystals. In this case the opposite faces of the crystal are also electroplated. Thick copper wires are soldered to the two blocks. The feeble current that will be passed through the specimen will obviously be along the hexagonal axis (normal to the basal plane). The resistance is then measured as before.

The specific resistances ρ_{\perp} and ρ_{\parallel} and the specific conductivities σ_{\perp} and σ_{\parallel} are calculated using Eqs. (1) and (2):

$$\rho_{\perp} = R_{\perp}bt/l_{\text{eff}} = 1/\sigma_{\perp}, \quad (1)$$

$$\rho_{\parallel} = R_{\parallel}lb/t = 1/\sigma_{\parallel}, \quad (2)$$

in which R_{\perp} , R_{\parallel} denote resistances perpendicular and parallel, respectively, to the hexagonal axis, b is the breadth, t the actual thickness, l the actual length, l_{eff} the effective length, i.e., in the first case the actual length of the nonelectroplated portion of the crystal, and σ_{\perp} ⁹ and σ_{\parallel} are the electrical conductivities per-

⁹ Wallace (see reference 6) on the other hand represents σ_{\perp} as the conductivity perpendicular to the basal plane, i.e., along the hexagonal axis, and σ_{\parallel} as that in the basal plane, i.e., at right angles to the hexagonal axis.

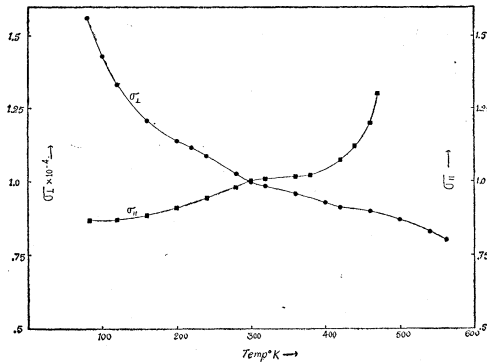


FIG. 2. Change of the principal conductivities (σ_{\perp} and σ_{\parallel}) with temperature. ●—conductivity for current along the basal plane (σ_{\perp}); ■—conductivity for current perpendicular to the basal plane (σ_{\parallel}).

pendicular (along the basal plane) and parallel, respectively, to the hexagonal axis.

Measurements at High Temperatures

For measuring the specific resistances at high temperatures, the crystal specimens are mounted in the respective holders, and each of the holders in turn is inserted into an electrically heated tubular furnace. The furnace is of a special type. It consists of a tube of glazed porcelain, one end open, with a noninductive winding of nichrome wire over its outer surface, embedded in asbestos cement and wrapped over with mica sheet, to insulate the windings from a brass water jacket slipped over the furnace. The mouth of the furnace chamber has a leak-tight cover and can be evacuated. The crystal holder with the crystal is placed within

the heater, and the potential leads are taken out through vacuum-tight joints through holes in the cover. By adjusting the furnace current, the temperature of the furnace can be controlled and raised up to about 600°K. Uniformity of temperature is obtained with a heavy copper tube fitting the inner wall of the furnace chamber and with baffles at the mouth. The temperature near the crystal (which has been found by a blank experiment not to differ appreciably from that at the crystal) is measured with one junction of a previously calibrated copper-constantan thermocouple, the standard junction temperature being melting ice. In practice, the furnace is placed between large rectangular parallel pole-pieces of an electromagnet, so that the effect of a magnetic field on the resistance can also be measured at any desired temperature in the above range.

Measurements at Low Temperatures

In this case the crystal holder with the crystal fixed in it is placed inside the experimental chamber of the gas flow cryostat designed by Bose,¹⁰ for magnetic studies down to 80°K, and measurements are conducted in the usual way, the temperatures being measured by a copper-constantan thermocouple, which has been previously calibrated for low temperatures.

EXPERIMENTAL RESULTS

Validity of Ohm's Law

In order to test the validity of Ohm's law in this crystal, currents ranging from 10×10^{-3} amp to about 7 amp were passed through the crystal along the principal directions and the corresponding drops of potential were recorded potentiometrically. It is found that

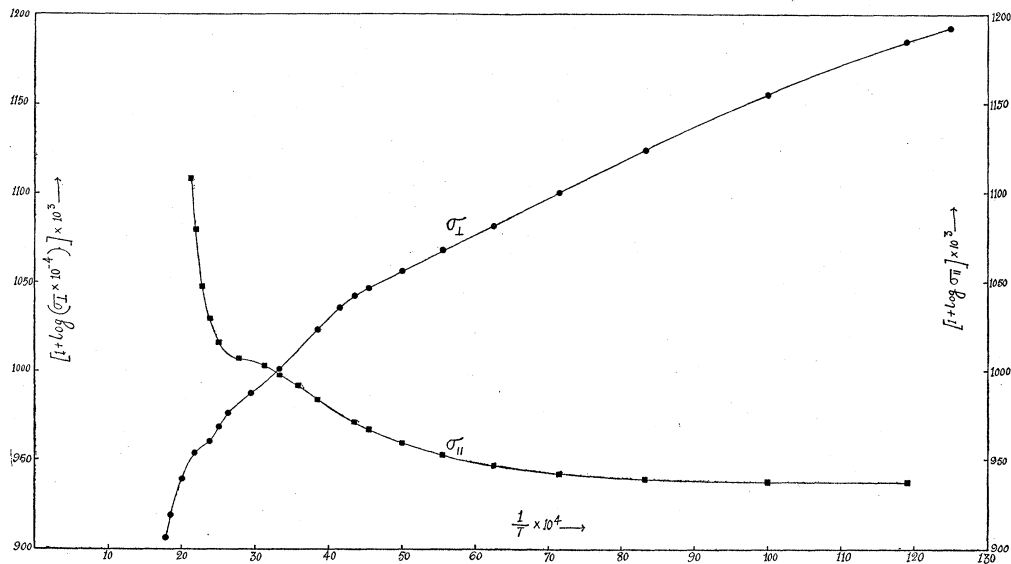


FIG. 3. Variation of the logarithms of the principal conductivities with the reciprocal of the absolute temperature. ●—conductivities along the basal plane (σ_{\perp}); ■—conductivities perpendicular to the basal plane (σ_{\parallel}).

¹⁰ A. Bose, Indian J. Phys. 21, 275 (1947).

the current-voltage relation is a linear one (see Fig. 1) for both directions of the current, i.e., Ohm's law is obeyed perfectly in this crystal and the rectification effect is completely nonexistent. One may refer in this connection to the case of single crystals of molybdenite,¹¹ which when tested under similar conditions give non-linear current-voltage curves, indicating the presence of rectification effects. It has also been observed that there is no appreciable change in σ_{\perp} or σ_{\parallel} by a gradual decrease or increase in the length or breadth of the crystal specimen. Thus, because of this and the previously mentioned x-ray evidence for the homogeneity of the crystals, it was not felt necessary to explore the crystals further with potentiometric probes.

Effect of Crystal Thickness on Conductivities

It has been observed, however, that for currents along the basal plane there is a gradual diminution of conductivity with increasing crystal thickness (see Table I) and that there is no such effect for currents perpendicular to the basal plane. This is due to the fact that in view of the large electrical anisotropy of the crystal, the effective thickness of the crystal (i.e., the

TABLE IV.

Magnetic field strength in gauss	$\sigma_{\perp} \times 10^{-4}$ ohm ⁻¹ cm ⁻¹	$\Delta\sigma_{\perp} \times 10^{-4}$ ohm ⁻¹ cm ⁻¹
0	1	...
1288	0.9901	0.0099
1666	0.9881	0.0119
2032	0.9833	0.0167
2305	0.9756	0.0244
2806	0.9624	0.0376
3000	0.9542	0.0458

equivalent thickness carrying the mean current through the cross section on the assumption of uniform current density) in the measurement of σ_{\perp} with the present arrangement, will be much smaller than the actual thickness of the crystal. Hence the values of σ_{\perp} calculated on the basis that the whole thickness of the crystal is effective in conducting the current, will naturally give values which are too low—the values are smaller the greater the thickness. It thus appears that none of the existing methods are very suitable for electrical measurements with highly anisotropic crystals like graphite. However, it may not be unjustifiable, given a large number of measurements with decreasing thickness of the crystal, to extrapolate to an infinity small thickness, which will give the true conductivity. Though such a procedure was not *strictly* adopted in the present series of measurements because of the difficulty in preparing a large number of very thin crystals of different thicknesses, as would be necessary for proper extrapolation, the results given here are probably not far from the actual ones, since our method of electroplating the ends of the graphite flakes definitely increases the uni-

¹¹ A. K. Dutta, Nature 159, 477 (1947).

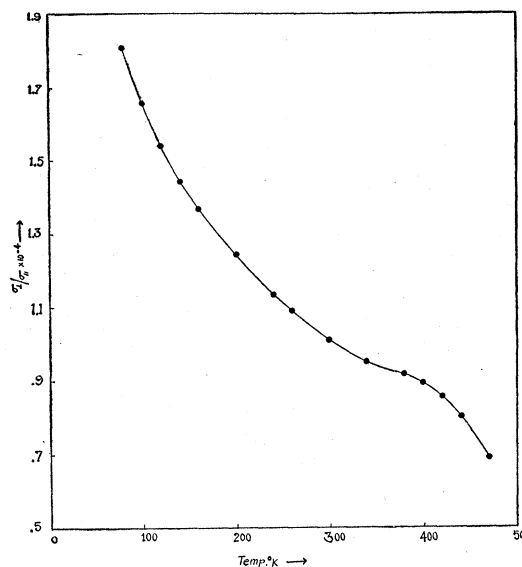


FIG. 4. The conductivity anisotropy ($\sigma_{\perp}/\sigma_{\parallel}$) in single crystals of graphite at different temperatures.

formity of current density at the cross section and also since these results have been checked by a new method developed here in which the difficulties referred to above are overcome. The method is suitable for specimens in the form of thin plates and depends on the observation of the damping produced by eddy currents generated in the specimen oscillating in a uniform magnetic field. The results of this method of observation, the details of which will be published elsewhere, are found to agree well with those obtained by the previous method.

Conductivities at Room Temperature

By sending known currents both along the basal plane, and at right angles to it, the respective conductivities have been determined for a large number of crystals obtained from five different samples. In Table II are shown the values of σ_{\perp} and σ_{\parallel} for different samples of graphite. The values of the conductivities, as is evident from the table, vary slightly from sample to sample, and the mean value may safely be taken to represent the principal conductivities of graphite; i.e., $\sigma_{\perp} = 0.99 \times 10^4$ ohm⁻¹ cm⁻¹ $\sim 1 \times 10^4$ ohm⁻¹ cm⁻¹ and $\sigma_{\parallel} = 1.02$ ohm⁻¹ cm⁻¹ ~ 1 ohm⁻¹ cm⁻¹.

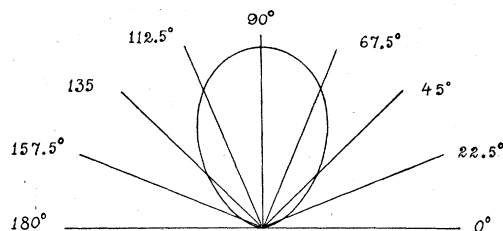


FIG. 5. Variation of the effect of a magnetic field on the conductivity along the basal plane with a change in direction of the field.

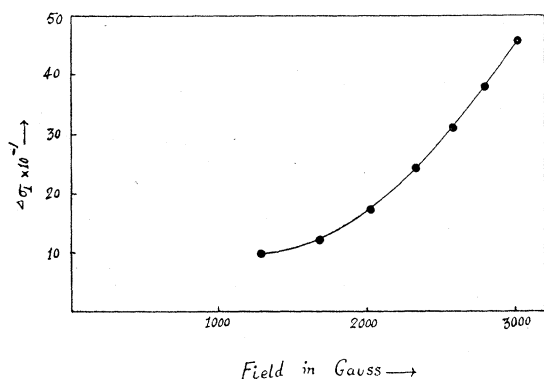


FIG. 6. Effect of a magnetic field on the conductivity along the basal plane, as a function of the applied field.

Temperature Variation of the Conductivities

The effect of a change of temperature on both of the principal conductivities has been observed from 80°K to about 550°K. The conductivity for currents along the basal plane (σ_{\perp}) has been found to decrease more or less exponentially with rising temperature; this consequently represents typical metallic behavior. On the other hand, the conductivity for currents along the normal to the basal plane has been observed to increase with rising temperature, also more or less exponentially, indicating typical semiconducting behavior. The values of the principal conductivities at different temperatures are given in Table III, and the nature of their variations with temperature is shown graphically in Fig. 2. To test whether the curves are represented by a single exponential function over the whole temperature range, the logarithms of the values of the principal conductivities have been plotted against the reciprocals of the corresponding temperatures, and the resulting curves are shown in Fig. 3. It is seen that neither of the curves is a straight line. It is also evident from the graphs that σ_{\parallel} tends to attain a temperature-independent value at low temperatures, and at high temperatures it tends to rise very sharply. The values of σ_{\perp} , on the other hand, fall very sharply with rising temperature and tends to attain a constant value at very low temperatures. It is hoped to extend these measurements soon to liquid hydrogen temperatures with our new hydrogen liquefier, which is nearing completion.

The anisotropy of the conductivity, $\sigma_{\perp}/\sigma_{\parallel}$, on which much importance has been placed by some theoretical workers (Wallace),⁶ is given in Table III for various temperatures and is represented graphically in Fig. 4. The anisotropy rises with falling temperature as has been expected by Wallace, but the order of magnitude

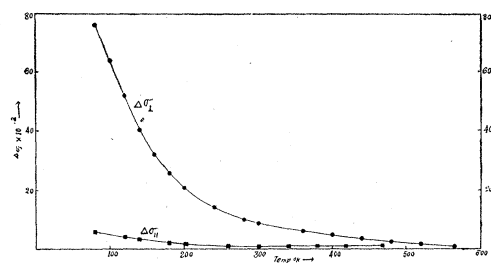


FIG. 7. Effect of a magnetic field of ~ 3600 gauss on the principal conductivities, as a function of temperature. ●—current along the basal plane; ■—current perpendicular to the basal plane.

of the anisotropy is quite different from that computed by him.

Effect of a Magnetic Field at Room Temperature

A magnetic field has been found to have an appreciable effect on the conductivity; *viz.*, the conductivity is decreased by the introduction of a magnetic field. The effect on σ_{\perp} has been found to be more pronounced than that on σ_{\parallel} . The fields at our disposal being rather small, our observations are generally confined to their effect on the conductivity for currents along the basal plane. The effect has been observed to be a maximum when the angle between the field and the basal plane carrying the current along it, is a right angle—the corresponding polar diagram being an elliptical figure (see Fig. 5). The variation of the conductivity (σ_{\perp}) with the magnetic field is shown in Table IV, and the corresponding variation of the decrement of conductivity ($\Delta\sigma_{\perp}$) with the magnetic field is shown in Fig. 6.

Effect of a Magnetic Field at Different Temperatures

The decrements of the two principal conductivities in a magnetic field of ~ 3600 gauss have been measured at different temperatures, ranging from 80°K to about 500°K. The results of these measurements are given in Table III, and the nature of the variation of both of the decrements ($\Delta\sigma_{\perp}$ and $\Delta\sigma_{\parallel}$) with temperature is shown in Fig. 7. It is seen there that while $\Delta\sigma_{\perp}$ has a large exponential variation within this range of temperatures, the changes in $\Delta\sigma_{\parallel}$ are much smaller. $\Delta\sigma_{\perp}$ tends to attain a temperature-independent value at high temperatures and rises exponentially as the temperature is lowered.

The theoretical implications of the results set out here will be discussed in detail in a subsequent paper.

The author wishes to express his best thanks to Professor K. Banerjee for his kind interest in the work and to Dr. A. Bose for constant helpful discussion.