

PRESSURE-DEPENDENCE OF CONDUCTION IN NEUTRON
IRRADIATED AND PRISTINE PYROLYTIC GRAPHITE

by

M.L. YEOMAN, B.Sc., M.Sc.

Imperial College of Science and Technology

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CONTENTS

Page

CHAPTER I

INTRODUCTION

1.1	INTRODUCTION	7
1.2	REVIEW OF PRESSURE EXPERIMENTS ON ELECTRICAL PROPERTIES OF GRAPHITE	8
1.3	MATERIALS	13
1.4	PREPARATION OF COMPRESSION ANNEALED PYROLYTIC GRAPHITE	14
1.5	COMPARISON OF COMPRESSION ANNEALED PYROLYTIC AND SINGLE CRYSTAL GRAPHITE WITH THE IDEAL LATTICE	17
1.5.1	The Ideal Lattice	17
1.5.2	Crystal Imperfections	19
1.5.3	Texture of Compression Annealed Pyrolytic Graphite	22

CHAPTER II

MECHANICAL PROPERTIES OF GRAPHITE

2.1	INTRODUCTION	23
2.1.1	Elastic Moduli of the Single Crystal	23
2.1.2	Polycrystalline Material	26
2.2	TEMPERATURE DEPENDENCE OF THE ELASTIC CONSTANTS	30
2.3	VARIATION OF MODULI WITH FAST NEUTRON IRRADIATION	32

CHAPTER III

CONDUCTION PROCESSES IN GRAPHITE

3.1	BLOCH STATES	34
3.2	BAND STRUCTURE OF GRAPHITE	37
3.2.1	The Brillouin Zone	38
3.2.2	Band Model of Slonczewski and Weiss	39
3.2.3	Band Parameters	43
3.2.4	The Fermi Surface	46
3.2.5	Fermi Surface Volume and Area of External Cross-Section	47
3.2.6	Application to Pyrolytic Graphite	51
3.3	THE BOLTZMANN TRANSPORT EQUATION	52
3.4	SOLUTION OF THE TRANSPORT EQUATION	54
3.4.1	Relaxation Time Approximation	54
3.4.2	The Variational Method	57
3.4.3	Mattheisen's Rule	62

CONTENTS
(continued)

	<u>Page</u>
<u>CHAPTER III</u> (continued)	
3.5 SCATTERING PROCESSES	63
3.5.1 The Differential Scattering Cross-Section	64
3.5.2 The Partial Wave Approximation	66
3.5.3 Lattice Vibrations	70
3.5.4 Lattice Controlled Mobility in Graphite	71
3.5.5 Scattering by Crystal Imperfections	73
3.5.6 Imperfection Controlled Mobility in Graphite	74
3.5.7 Particle-Particle Collision Scattering	76
3.5.8 Carrier-Carrier Controlled Mobility in Graphite	84
3.6 CONDUCTION AT HELIUM TEMPERATURES	88

CHAPTER IV

EXPERIMENTAL

4.1 MATERIALS	95
4.2 SAMPLE PREPARATION	95
4.2.1 Basal Plane Samples	96
4.2.2 c-Axis Samples	97
4.3 APPARATUS AND PROCEDURE - NON OSCILLATORY GALVANOMAGNETIC MEASUREMENTS	99
4.3.1 Cryostats and Constant Temperature Baths	99
4.3.2 Electromagnetic	100
4.3.3 Electrical Measurements	101
4.3.4 High Pressure System	101
4.3.5 Procedure	103
4.4 APPARATUS AND PROCEDURE - OSCILLATORY MAGNETORESISTANCE	106
4.4.1 Oxford Instruments Cryostat	106
4.4.2 Isobaric Freezing of Liquid Helium	111
4.4.3 Superconducting Magnet	113
4.4.4 Digital Voltmeter	114
4.4.5 Procedure	115
4.4.6 Calibration of the Superconducting Magnet	117

CHAPTER V

EXPERIMENTAL AND DERIVED RESULTS - OSCILLATORY

5.1 OSCILLATORY DATA	120
5.2 DATA FITTING	121
5.2.1 Integer Plots	124
5.2.2 Iterative Fitting	128
5.3 DERIVED RESULTS	132
5.3.1 Accepted Density	134
5.3.2 Pressure Dependence of Carrier Density	138
5.3.3 Relaxation Times	141

CONTENTS
(continued)

Page

CHAPTER VI

EXPERIMENTAL AND DERIVED RESULTS - NON OSCILLATORY

6.1	PRESSURE EFFECTS IN PYROLYTIC GRAPHITE	143
6.2	PRESSURE COEFFICIENT OF RESISTANCE	146
6.3	PRISTINE MATERIAL - PRESSURE COEFFICIENT OF RESISTANCE	148
6.3.1	<u>c</u> -Axis Conduction	150
6.3.2	Basal Plane Conduction	153
6.4	IRRADIATED MATERIAL - PRESSURE COEFFICIENT OF RESISTANCE	156
6.4.1	<u>c</u> -Axis Conduction	157
6.4.2	Basal Plane - Conduction	160
6.5	DERIVED RESULTS	163

CHAPTER VII

DISCUSSION AND CONCLUSIONS

7.1	INTRODUCTION	166
7.2	TRANSPORT IN PYROLYTIC GRAPHITE	166
7.3	ANISOTROPIC SCATTERING CROSS-SECTIONS	170
7.4	CALCULATED PRESSURE COEFFICIENTS	172
7.4.1	Pristine Pyrolytic Graphite - Basal Plane	172
7.4.2	Pristine Pyrolytic Graphite - <u>c</u> -Axis	174
7.5	ABSOLUTE CARRIER-CARRIER MEAN FREE PATH	177
7.6	IRRADIATED PYROLYTIC GRAPHITE	178
7.6.1	<u>c</u> -axis Transport	179
7.7	COMPARISON OF THEORY WITH EXPERIMENT	180
7.8	CONCLUSIONS	183

APPENDICES

App.A I	LOCATION OF EXTREMAL AREA OF CROSS-SECTION OF MAJORITY HOLE SURFACE INCLUDING γ_4, γ_5	187
App.A II	VOLUME ENCLOSED BY MAJORITY ELECTRON SURFACE INCLUDING γ_4, γ_5	188
App.A III	ANALYSIS OF OSCILLATORY DATA	190
	REFERENCES	194

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ABSTRACT

The pressure dependence of conduction parallel and perpendicular to the basal planes has been studied in pristine and neutron irradiated graphite in the temperature range 4.2-298K. Application of pressure increases the σ -overlap of π -orbitals concentrated between the layer planes resulting in an increase in carrier density. By measuring Shubnikov de Haas oscillations as a function of pressure at 4.2K the pressure dependence of electron and hole densities were determined. In general, the increase in conductivity does not match the increase in density.

A pressure system was built capable of operating over a 300 degree temperature range with a working pressure of 500 bar. The beryllium-copper pressure vessel could be isobarically cooled, enabling pressures of 400 bar to be applied through solid helium 4. A niobium-titanium superconducting magnet, tailored to fit the pressure system, supplied a magnetic field sweeping linearly at predetermined rates to 40 kG.

Quantum oscillations were observed for the first time in material irradiated with fast neutrons. The long period was found to decrease and the short period to increase, resulting in a relocation of hole and electron surfaces at the edge of the Brillouin zone.

A new sample geometry enabled pressure measurements to be made on samples with current along the c -axis. Experiment revealed an anisotropy in the pressure coefficient of resistance measured parallel and perpendicular to the basal planes which decreased with decreasing temperature and with neutron irradiation.

Scattering mechanisms are discussed in detail. A model of conduction which includes carrier-carrier scattering is developed for graphite and is shown to result in anisotropic scattering cross-sections. Failure of the electrical conductivity to follow the carrier density with increasing pressure is shown to be due to the concomitant increase in carrier-carrier scattering. Calculated pressure coefficients of resistance are in good agreement with experimental results.

CHAPTER 1

1.1 INTRODUCTION

In its various textural forms graphite has a wide range of industrial and commercial applications. With the advent of graphite moderated nuclear reactors, in the late 1950's, the basic properties of atomic elemental carbon were required in the form of a material which would withstand the hostile environment of a fast neutron flux. Accordingly research programmes were begun in many parts of the world to investigate graphite, i.e. carbon in a high state of purity and crystalline perfection. An extensive literature has subsequently developed dealing with the properties of carbons and graphite. However care must be taken to ensure that a particular set of observations relate to material which is identical or at least very similar to that in question; the quantitative properties of all but the most perfect graphites are largely dictated by the imperfections of the material. In this work, we shall be concerned with the effect of hydrostatic pressure on the electronic properties and Fermi surface of well oriented, pristine and neutron irradiated, pyrolytic graphite; a material which in certain aspects of its behaviour can simulate even the most perfect single crystals.

The conduction bands of graphite exhibit a very small overlap (~ 0.019 eV) even at the absolute zero of temperature, the material may therefore be classed with Bi, As and Sb as a semimetal. The small carrier concentration of $\sim 10^{-4}$ per atom results in a relatively simple band structure which lends itself to investigation through most of the standard diagnostic techniques for evaluation of Fermi surface location and topology. Detailed galvomagnetic measurements coupled with those on low temperature quantum oscillations have elaborated the Fermi surface topology, while cyclotron resonance and more recently magnetoreflexion experiments

have served to identify the position of the constant energy surface in k-space. The band structure of pristine single crystal graphite is consequently quite well understood. However, only a very limited effort has been applied to the study of change in Fermi surface topology and electrical properties as the Fermi level is altered by application of pressure by neutron irradiation, or by doping with acceptors. In particular, at the beginning of this work, quantum oscillations in neutron irradiated graphite had not been observed, the effect of pressure on the Fermi surface topology was unknown, and an unexplained discrepancy existed between the c-axis and basal plane pressure coefficient of conduction.

1.2 REVIEW OF PRESSURE EXPERIMENTS ON ELECTRICAL PROPERTIES OF GRAPHITE

BRIDGMAN, (1952) pioneered the measurement of graphite electrical properties as a function of pressure. Two specimens cut from a single crystal of Ceylon graphite were subjected to pressures up to a maximum of 100 k bar. Below 20 k bar the basal plane resistance decreased with increasing pressure and gave a pressure coefficient of resistance ($\rho^{-1} d\rho/dP$) of $-4.45 \times 10^{-6} \text{ bar}^{-1}$. between 20 and 40 k bar, some positive curvature occurred while above 40 k bar a pressure coefficient of resistance of $-2.4 \times 10^{-6} \text{ bar}^{-1}$ was recorded. An earlier measurement on Acheson graphite had shown a considerable hysteresis on pressure cycling and a resistance increase of 4.57% at 1200 bar.

No results are available for the c-axis pressure coefficient of resistance in single crystal graphite due to the fragility of the extremely thin specimens, less than 1 mm thick, which makes difficult the attachment of voltage probes. However, pyrolytic graphite can be obtained in pieces thick enough for c-axis measurement, and SAMARA and DRICKAMER (1962) have examined two specimens of material of rather low density with void volumes of $\sim 4\%$, up to pressures of 500 k bar. Both the c-axis and basal plane

resistance initially decreased with increasing pressure up to 60 k bar. At higher pressures, the basal plane resistance increased rapidly with pressure, decreasing again above 230 k bar. c-axis pressure coefficients of resistance for the two samples examined were widely different at - 26 and $-3.3 \times 10^{-6} \text{ bar}^{-1}$, even though the void volume of the samples differed only by 0.8%. Above 200 k bar the coefficient levelled out to $-0.6 \times 10^{-6} \text{ bar}^{-1}$ for both samples. In the basal direction, a low pressure coefficient of $-5 \times 10^{-6} \text{ bar}^{-1}$ agreed with that of Bridgman for single crystal material, while the irregular behaviour above 60 k bar was found to be more pronounced for thicker samples. This was attributed to the pressure generation technique which was less than hydrostatic for thick samples.

Unpublished observations of PAUL and SOULE (1963) showed the basal plane conductivity to be insensitive to pressure. DEUTSCH (1963) measured in pyrolytic graphite a pressure coefficient of resistance of $-14 \times 10^{-6} \text{ bar}^{-1}$ in the c-direction, a value which does not agree with either of the two coefficients recorded by SAMARA and DRICKAMER. Only one other measurement has been reported with current perpendicular to the basal plane, namely the preliminary results of SPAIN (1964) of this laboratory. A pressure coefficient of $-25 \times 10^{-6} \text{ bar}^{-1}$ was measured at room temperature and for hydrostatic pressures up to 2 k bar. With current in the basal plane the pressure coefficient of resistance was too small to be measured.

In addition to the measurements of the effect of pressure on electrical conductivity reported above, the magnetoresistance and Hall coefficient have been studied as a function of pressure by ARKHIPOV, KECHIN, LIKHTEK and POSPELOV (AKLP) (1963) and by LIKHTEK and KECHIN (1964). AKLP developed an approximate theory for the limiting case of high temperature, i.e. $k_B T \gg \gamma_2$ where γ_2 a 2-centre tight binding integral is a measure of the overlap between π bands at the edge of the Brillouin zone

and is approximately 0.02 eV. (The parameters $\gamma_0, \gamma_1 \dots \gamma_5$ and Δ are defined in relation to graphite band structure in section 3.2.) In the AKLP theory, parabolic energy bands were assumed and certain band parameters were neglected. It is shown in Chapter III that quantitative application of this model which omits $\gamma_3, \gamma_4, \gamma_5$ and Δ will result in an error of 10-20%.

Measurements on the temperature dependence of the Hall coefficient and magnetoresistance justified their assumption of a relaxation time expressed as the product of a temperature term and a $\underline{k}$ -vector term, and resulted in an expression for the conductivity which separated the relaxation time from the band parameters γ_0, γ_1 , and γ_2 . The magnetoresistance expressed as

$$T \rho_0 \left(\frac{\Delta \rho_H}{\rho_0 H^2} \right)^{\frac{1}{2}}_{H \rightarrow 0}$$

decreased in single crystal graphite by 9% over an 8 kbar pressure range. This result gave the pressure dependence of the band parameter γ_0 , while a basal plane pressure coefficient of resistance of $-3 \times 10^{-6} \text{ bar}^{-1}$ was interpreted as due entirely to a corresponding increase in the relaxation time. A negative pressure coefficient of basal plane resistance recorded for the single crystal material is in agreement with results of BRIDGMAN and of SAMARA and DRICKAMER. However, for synthetic material, which had a resistivity 50 times that of the best single crystal, they found a positive pressure coefficient of basal plane resistance of $4 \times 10^{-6} \text{ bar}^{-1}$.

When this work was begun the effect of pressure on quantum oscillations in graphite had not been observed. However in 1967 a group at The Institute of Physics of High Pressures, in Moscow, applied to synthetic graphite the method previously used to observe the effect of pressure on the Fermi surfaces of Zn, Cd and Bi. A sample was immersed in a mixture of oil and kerosene within a pressure bomb of beryllium-bronze. The pressure

in the working space was generated at room temperature and fixed mechanically. On cooling to liquid helium temperatures, a range of pressures up to 8 kbar were obtained. The amplitude of Shubnikov-de Haas oscillations were seen to decrease on applying pressure indicating probable sample damage and only the electron period could be identified. From the change in period of $0.045 \times 10^{-5} \text{ G}^{-1}$ per kbar, ITSKEVICH and FISHER (1967) were able to determine the pressure dependence of the quantity $\gamma_1 \gamma_2 / \gamma_0^2$. To separate the band parameters they followed AKLP in assuming that since graphite is elastically very anisotropic with $c_{11}/c_{33} \sim 25$, changes in a_0 are small compared with changes in c_0 , when hydrostatic pressure is applied. Since the tight binding integral γ_0 involves overlap of p_z orbitals parallel to a plane in π -configuration, it may thus be considered as independent of pressure when compared with the pressure dependence of γ_1, γ_2 which involve σ overlap of p_z orbitals between nearest and next nearest planes respectively. The pressure dependence of γ_1/γ_0^2 obtained in the approximate theory of AKLP was used to determine $\gamma_1(P)$ and this result together with the low temperature observations led to estimates of the effect of pressure on γ_1, γ_2 and E_F the Fermi level.

SCHIRDER (1965) has criticized the method of generating high pressure used by ITSKEVICH and FISHER on two counts:

- (1) To change the pressure the bomb must be warmed to room temperature, the pressure adjusted, and cooled again to liquid helium temperatures. Such pressure and temperature cycling can cause the sample to shift bodily through several degrees, e.g. pressure cycling over a range of 40 K was found to cause a shift of 0.47° in a run on zinc whiskers.
- (2) If the solid medium does not flow very easily, the final pressure will depend on the relative thermal expansivities of the bomb, sample and pressure monitor. In particular, for a material with anisotropic compressibilities and thermal expansivities, like graphite, the sample can experience a non-hydrostatic stress distribution.

A great deal of confusion has arisen in the experimental determination of the effect of pressure on the Fermi surface of zinc, because of the use of techniques which do not generate hydrostatic pressure. Results obtained with the frozen medium bomb (GAIDUKOV and ITSKEVICH (1964)) are in quantitative disagreement with those obtained with an isobaric freezing technique. Indeed, early ice bomb work on oscillations in the magnetic susceptibility indicated that the c/a ratio increased with increasing pressure. This result has since been reversed by experiments using low pressure gaseous helium (BALAIN, et al. (1960)) and by isobaric pressure generation techniques (SCHIRBER (1965)).

The pressure dependence of the Fermi surface of synthetic graphite, as measured by the frozen oil - kerosene technique, is therefore open to question. In 1967 ANDERSON, O'SULLIVAN, SCHIRBER and SOULE (AOS S) applied the Schirber technique of isobaric freezing to purified single crystals at pressures up to 4 kbar. Helium gas pressure was applied to the sample at a temperature just above the freezing point of helium at the desired pressure and the temperature of the sample reduced to 4 K. Isobaric freezing was ensured by maintaining the pressure at a constant value as the bomb was slowly cooled from the bottom up, by lowering into a cryostat. The final pressure could then be calculated from the known isochores of solid helium. De Haas - van Alphen Oscillations measured at low and high pressures revealed as expected three independent periods corresponding to the majority hole, majority electron and minority hole Fermi surfaces. All three periods were found to decrease with increasing pressure. In single crystal material the dominant oscillation was produced by holes with a period of $2.09 \times 10^{-5} \text{ G}^{-1}$ and a pressure dependence of $-0.08 \times 10^{-5} \text{ G}^{-1}$ per kbar. The electron period of $1.50 \times 10^{-5} \text{ G}^{-1}$ was found to decrease by $0.052 \times 10^{-6} \text{ G}^{-1}$ per kbar, which is in good agreement with the pressure dependence of the electron period in synthetic graphite at

$0.045 \times 10^{-5} \text{ G}^{-1}$ per kbar. In pyrolytic graphite the dominant oscillations came from the electron with a pressure coefficient the same as that of single crystal material. By making the same assumptions as ITKEVICH and FISHER regarding the pressure dependence of a_0 and γ_0 , AOSS were able to estimate the effect of pressure on the band parameters $\gamma_1, \gamma_2, \Delta$ and E_F .

It may be noted that neither ITSKEVICH and FISHER nor AOSS were able to determine the pressure dependence of the hole period in synthetic material.

In the above review is presented all the published work on the pressure dependence of electronic properties in graphite. The present study provides the first account of detailed measurements on the pressure dependence of conductivity in pristine and neutron-irradiated pyrolytic graphite over the temperature range 1.6 - 300 K. These measurements have led to a theory which accounts for the discrepancy apparent in previous work between the pressure coefficient of resistance in the c and a-axis directions and reveals a much more important role for carrier-carrier scattering in graphite than has hitherto been assumed. Fermi surface topology is examined as a function of pressure through the Shubnikov - de Haas effect. To ensure a truly hydrostatic stress distribution, and thus avoid the problems mentioned above, the pressure was applied through liquid helium; a second method applied at higher pressures employed a modified form of the isobaric freezing technique described earlier.

1.3 MATERIALS

Most of the measurements to be described were made on compression-annealed pyrolytic graphite prepared in this laboratory and discussed in the next section. But, two single crystals were examined at liquid helium temperatures for their Shubnikov - de Haas periods of oscillation and for the Dingle temperatures which provide information on carrier

scattering lifetimes. This material, which was kindly supplied by Dr R. Mayer, had originated in Essex County, New York as flakes of almost perfect graphite imbedded in a matrix of calcite. Concentrated HCl was used to leach the graphite from its host matrix leaving flakes typically 4mm by 4mm but less than 1mm thick. Purification was carried out in flowing argon at 3000°C by M.L. GILLIN of Cambridge. Some crystals were obviously twinned with visible steps on their external surfaces, but from the collection of Dr Mayer, two were chosen as being the most perfect to visible inspection.

1.4 PREPARATION OF COMPRESSION ANNEALED PYROLYTIC GRAPHITE

A full account of the preparation of hot pressed annealed pyrolytic graphite has already been published by MOORE, UBBELOHDE and YOUNG (1964). This section consists of a brief resumé highlighting the main points of the method.

The pyrolysis of methane, acetylene and other hydrocarbons can produce deposits which take the form of highly oriented layers. Precipitation of fine carbon particles may be controlled by dilution with hydrogen, nitrogen or a rare gas and the rate of deposition determined by the temperature and gas pressure used. To obtain deposits of an even thickness, the temperature of the heated former must be maintained to within 10°C along the length of the sample. The most important single factor determining the crystalline perfection of the deposit is the deposition temperature (d.t.) Material deposited at 1600°C is essentially isotropic. An increase in d.t. leads to the development of a preferred orientation of the c-axis perpendicular to the plane of deposition, but the improvement is slow, below 1900°C . Above this temperature the reduction in disorder and increase in density progresses rapidly with increasing d.t. An upper limit on d.t. is set by the graphite volatility. In this laboratory typical gas

pressures were 1.3 mbar resulting in a maximum d.t. of 2200°C and specimens of 2 mm thickness. Higher deposition temperatures have been used in the preparation of commercial graphite resulting in deposits of up to 15 mm thick with, however, an increased density of soot nuclei.

The probability of layer stacking disorder can be determined from X-ray measurements of the c-axis spacing (BACON, (1958)). It was found to range from zero at the highest d.t., corresponding to no disordered layers, to 0.8 at the lowest, indicating that one layer in every 1.25 was disordered. As the stacking order improves with increasing d.t. so the density approaches to within 2% of the ideal limit of 2.266 g cm^{-3} set by the crystal structure. On annealing the as-deposited material at a temperature of 3600°C the distribution of crystallite c-axes perpendicular to the plane of deposition decreases from the 5-10° of unannealed material to $< 2^\circ$, with however an accompanying large drop in density to $\sim 1.9 \text{ g cm}^{-3}$.

At this point it was discovered that if deposits of $> 5 \text{ mm}$ thick are used in the annealing process, then due to the poor thermal conductivity of graphite perpendicular to the layer planes, stress recrystallization of the as-deposited material occurs. The graphite layers next to the heated polycrystalline former can reach temperatures of 3700°C while the outer layers are cooler by $\sim 1500^\circ\text{C}$ and constrain the inner layer expansion. Basal flow occurs, resulting in material with a c-axis distribution function of $< 2^\circ$ and a density almost equal to that of the perfect crystal. Although this 'inner layer' material is almost ideal for basal plane measurements it produces very thin curved samples $< 1 \text{ mm}$ thick which are quite suitable for c-axis measurement.

Samples required for investigating c-axis properties in graphite have been prepared using a uniaxial hot pressing procedure which is a natural development of the stress recrystallisation process outlined above.

Discs of well orientated but often porous pyrolytic graphite are subjected to a uniaxial thrust along the c-axis of ~ 500 bar while being inductively heated to 2850°C in an atmosphere of argon or helium. A polycrystalline susceptor supporting the discs undergoes plastic flow at this temperature and permits the compressed material to expand radially, with a corresponding longitudinal contraction. An increase in diameter of 12-15% is matched by a reduction in length of typically 16-27%. The axial compression combined with resulting shear eliminates almost all the c-axis misorientations; the best samples have a c-axis distribution halfwidth of $< 0.4^{\circ}$. The density of the starting material is improved in some cases by as much as 7% and measured values range from 2.252 to the theoretical limit of 2.266 g cm^{-3} . Further annealing of the samples at 3700°C encourages growth of the well aligned crystallites parallel to the basal plane, while a light axial compression of 10 bar is insufficient to cause further plastic flow but inhibits evaporation loss.

Electron micrograph studies of the graphite before and after hot pressing and annealing, have revealed that soot particles present in the as-deposited material are not always completely removed by the hot pressing and annealing process. Some recrystallisation of the immobile soot particles does occur and those particles which can move leave a series of voids of from $1\text{-}3\mu\text{m}$ in diameter. The starting material for the hot pressing process was consequently carefully selected to be almost free from soot inclusions. Even so one can never be sure that soot nuclei are completely absent from a specimen too thick to be examined by the electron microscope.

1.5 COMPARISON OF COMPRESSION ANNEALED PYROLYTIC AND SINGLE CRYSTAL GRAPHITE WITH THE IDEAL LATTICE

Naturally occurring single crystal graphite approaches the ideal lattice more closely than pyrolytic and other artificial graphites. However, even the best single crystals are still very imperfect. SOULE and NEZBEDA (1968) and BAKER and KELLY (1969) have shown that purified single crystals, obtained from the same source as the single crystals used in this work and subjected to the same purification process, still contain impurity contents of 10-30 ppm, a principal impurity being boron. BENDER and YOUNG (1972b) have recently argued that positively charged iron at concentrations of ~ 1.5 ppm has a controlling influence on carrier collision times at low temperatures. Delamination voids are present with diameters of 0.1-5 μm while basal dislocation-area densities are typically $2 \times 10^6 \text{ cm}^{-2}$. Such material imperfections have a marked effect on the physical properties, which are quantitatively dominated by the deviation of the graphite from the ideal lattice.

1.5.1 The Ideal Lattice

A single layer of the graphite lattice is illustrated in Fig.1.1, together with the primitive translation vectors $\underline{t}_1, \underline{t}_2, \underline{t}_3$, each of length 2.46 Å. Within a plane each atom forms three covalent bonds of the hybrid orbital Sp^2 with an in-plane bond length of 1.415 Å. A fourth electron per atom is employed for interplanar bonding and is described by a $2p_z$ atomic orbital. This electron is responsible for electrical conduction and also contributes to the planar bonding.

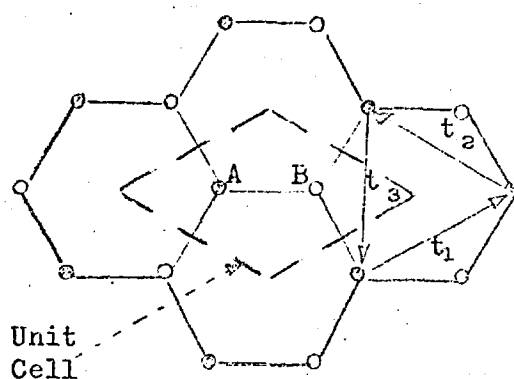


Fig.1.1

A single layer of the graphite lattice showing the unit cell and primitive translation vectors

The atom layers are stacked in an abab... sequence with a spacing of $3.354 \text{ \AA}$. The centres of hexagons in one layer are above the corners

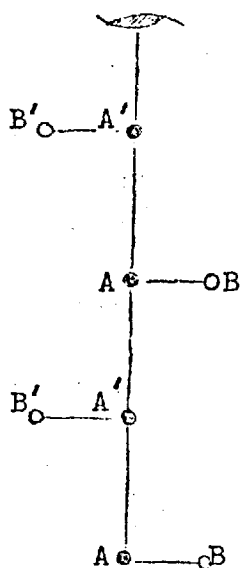


Fig.1.2
The stacking sequence
in graphite

of hexagons in the adjacent layers, thus giving rise to two different atomic sites; those with atoms immediately above and below them in adjacent planes are known as A sites and those with atoms above and below them only in next adjacent planes are called B sites. A atom sites have a triad axis and also a screw diad axis normal to the hexagonal planes, while B atom sites have only a triad axis. Fig.1.2 illustrates the stacking sequence.

The unit cell is required to reproduce the extended crystal by stacking together similar units in similar orientations: thus vectors joining nearest neighbour atomic sites cannot constitute a cell edge, but rather vectors joining next nearest neighbours must be used. The so-called Bernal stacking ensures that the cell edge in the c-direction is twice the interplanar spacing, resulting in a multiply primitive unit cell with a basal plane lattice constant of $2.46 \text{ \AA}$ and a height of $6.71 \text{ \AA}$. There are four atoms in the unit cell, which is shown in Fig.1.3; these are situated at positions $(0,0,0)$, $(0,0,\frac{1}{2})$, $(\frac{2}{3},\frac{1}{3},0)$ and $(\frac{1}{3},\frac{2}{3},\frac{1}{2})$.

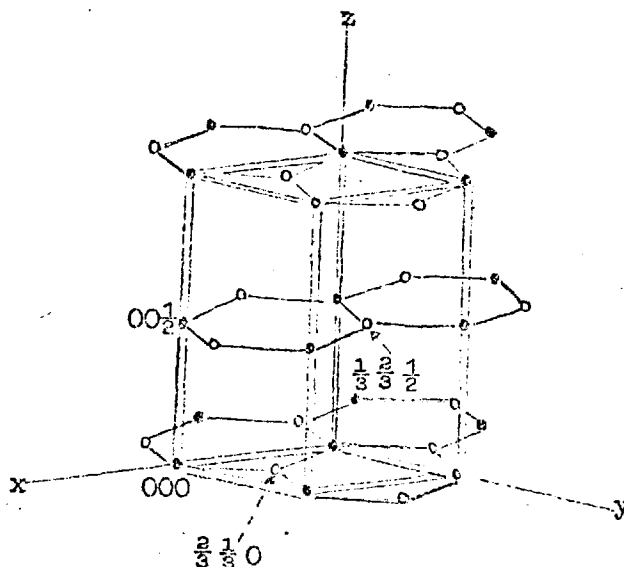


Fig.1.3
The unit cell of graphite with
the crystal axes and the four
different atomic sites

An unstable rhombohedral form with ABCA... stacking can exist in the presence of hexagonal graphite and usually occurs as a region of stacking fault between two Shockley partial dislocations. However, this form has not been isolated and is transformed by heat treatment to the hexagonal form. In their investigation of the pyrolytic graphite used in this work MOORE, UBBELOHDE and YOUNG (1964) found no evidence of rhombohedral graphite, apart from that bounded by partial dislocations.

1.5.2 Crystal Imperfections

It was mentioned earlier that point and line defects are present even in the most perfect graphites. The type and concentration of defect will depend upon the method of manufacture and the treatment which the specimen has received. The only element which has been conclusively shown to enter the lattice substitutionally is boron (LOWELL (1967), KELLY and MAYER (1969)). Substitution increases the basal plane dimensions and decreases the layer separation. X-ray measurements by TURNBULL and STAGG (1966), LOWELL (1967) and MAYER (1969) demonstrate an increase in a spacing by 0.32 times the fractional boron concentration, and a decrease in layer separation by twice this amount. Interstitial boron results in an increase in c-axis dimensions (TURNBULL et al, (1966)), but heat treatment at 1400°C in vacuum removes, by diffusion, interstitial atoms and the layer spacing drops to below the normal value. Hydrogen is the only residual impurity detected in the pyrolytic graphite used in this work, the best samples having concentrations below the analytically detectable limit of 10^{-5} atom/atom. X-ray measurements by MOORE et al (1964) have shown that a and c values for hot pressed and annealed material equal the ideal lattice parameters to within an experimental error of 0.001 Å. Thus impurities affect the lattice dimensions in this graphite by no more than 0.03%.

Vacancy injection in graphite occurs preferentially at cleavage planes, and may be caused in the production stage by the formation of a volatile product with highly active gaseous element, by migration of metal ion impurities, or by neutron irradiation. Electronic properties are greatly affected by the presence of vacancies and the corresponding interstitials, but the overall effect is to lower the Fermi level and to reduce the mean free path at temperatures where impurity scattering is important. Lattice vacancies also play an essential role in the non-conservative motion of edge dislocations normal to their slip plane. The effect of vacancy and interstitial formation is examined in this work through the pressure dependence of the conductivity and Fermi surface, as a function of neutron dose.

The pyrolytic graphite under examination will contain basal plane dislocations of not less than $10^{+4} \text{ cm/cm}^{-2}$. Although the graphite lattice can support three other types of dislocation, the dislocation with line and Burgers vector both in the basal plane, is the one most commonly encountered. These are perfect dislocations and as such have a Burgers vector $\frac{1}{3}(1120)$ of length equal to the primitive translation vector, $2.414 \text{ \AA}$. The Burgers vector can point in any direction within a plane so that screw, edge and mixed dislocations can occur. In unstrained material the dislocation lines are isolated and straight, whereas in grossly strained material triangular and rectangular networks of curved dislocation lines appear. Electron micrograph studies of the present pyrolytic graphite by SPAIN, UBBELOHDE and YOUNG (1967) and of single crystal graphite by BAKER and KELLY (1964) have revealed basal dislocation networks of predominantly straight dislocation lines.

Perfect dislocations can split into two Shockley partial dislocations separated by a ribbon of rhombohedral stacking fault. The stacking fault energy is small with estimates ranging from 0.51 to 0.7 ergs/cm², thus

slight mechanical deformation is sufficient to transform perfect dislocations into Shockley partials with observed ribbon widths in the range 600-1000 Å.

Graphite exhibits an inplanar bond strength which is ~ 30 times that of the interplanar bonds; consequently slip will preferentially occur in the basal plane. However, dislocations can move in a non-basal direction through dislocation climb involving the absorption and emission of vacancies. Since the propagation energy for vacancy movement is ~ 3.2 eV (BAKER and KELLY (1962), climb will only occur at high temperatures and JENKINS et al, (1962) have invoked this process to explain the graphitisation of carbon films and have suggested the presence of arrays of edge dislocations with dislocation line in a non-basal direction. However, the evidence for the existence of such dislocations is slight and is based mainly on electron microscope patterns of crystallites viewed in series (MOIRÉ patterns) which do not lend themselves to unambiguous interpretation. There is no evidence for non-basal edge dislocations occurring in the pyrolytic and single crystal graphite used in this work.

Screw dislocations with Burgers vector and dislocation line in non-basal directions have been observed in single crystal and pyrolytic graphite. The screw density depends upon the annealing temperature, 10^6 screws/cm² were reported for material annealed at a temperature equal to that used on the present pyrolytic graphite (3600°C). Lower annealing temperatures correspond to more screws per square cm. Growth spirals can occur in single crystal material and densities of 10^4 cm⁻² were reported for spirals with a step height of ~ 1000 Å; in pyrolytic graphite the pitch of the screw is generally much smaller and can be as low as a layer spacing. Although such screws are sessile at ordinary temperatures, movement on the slip plane would simply result in atomic displacement in the basal direction. Edge dislocations of this type would cause slip along the c-axis; however, such dislocations have not been observed.

A fourth type of dislocation defect which can occur in graphite consist of loops of dislocations lying in the basal plane. This type of imperfection was produced in the present pyrolytic material by neutron irradiation at 30°C to doses of 10^{18} nvt. Small interstitial clusters $\sim 10 \text{ \AA}$ in diameter are formed together with loops of networks of vacancies occurring individually or in small clusters. At ordinary temperatures, the interstitial and dislocation clusters are sessile but they may be removed by annealing to 3000°C.

1.5.3 Texture of Compression Annealed Pyrolytic Graphite

The single crystal material examined here may be expected to contain imperfections at the concentration levels quoted above for very similar material, pyrolytic graphite is an aggregate of crystallites which are individually subject to these imperfections. Crystallites extend to diameters of 2-5 μm in the basal plane with c-axis dimensions apparently between 1000-2000 $\text{\AA}$. Moiré patterns taken with an electron-microscope suggest that a c-axis boundary is normally marked by a stacking fault formed by rotation of neighbouring crystallites through an angle of 1° about the c-axis. The distribution of crystallite c-axes about a direction normal to the basal plane is extremely small for the hot pressed and annealed material, between 1 and 0.4° , consequently the physical properties of this graphite have anisotropies approaching those of single crystals. Voids are present with volumes ranging from 0.1 to 0.4% and ripples extending from 0.1 to 3 mm can occur in the basal plane. Although materials containing soot nuclei were normally rejected at an early stage in preparation, as mentioned in the previous section, soot is not always removed by hot pressing, and we may expect some soot nuclei to be present. In practice soot nuclei undergo a considerable recrystallization on hot pressing and annealing; even so, material with soot inclusions exhibit irreproducible qualities on thermal cycling, and this provides an extra criteria for material selection.

CHAPTER II

MECHANICAL PROPERTIES OF GRAPHITE

2.1 INTRODUCTION

Either the elastic stiffness constants c_{ijkl} or the compliance constants s_{ijkl} may be used to describe the deformation of the graphite crystals on application of pressure. However, since Young's moduli, Poisson's ratios, and the bulk compressibility may be simply defined in terms of the s_{ijkl} , we shall in this work describe the mechanical properties of graphite in terms of the elastic compliance constants. In the absence of body torques the symmetry of s_{ijkl} in the first two and last two suffices enables us to use the matrix notation in which the stress and strain components are written with a single suffix running from 1 to 6. Hooke's law for a homogeneous stress σ_i and homogeneous strain ϵ_i may then be written:

$$\epsilon_i = s_{ij} \sigma_j \quad (i, j = 1, 2, \dots, 6) .$$

2.1.2 Elastic Moduli of the Single Crystal

LANDAU and LIFSHITZ (1959) show that the elastic properties of an hexagonal crystal are isotropic in a plane perpendicular to the sixth order axis and that only five moduli of elasticity are non-zero and independent. The form of the s_{ij} matrix, dictated by the lattice symmetry, is then as given explicitly by BOAS and MACKENZIE (1950):

$$\begin{pmatrix} s_{11} & s_{12} & s_{13} & 0 & 0 & 0 \\ s_{12} & s_{11} & s_{13} & 0 & 0 & 0 \\ -s_{13} & s_{13} & s_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & s_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & s_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2}(s_{11}-s_{12}) \end{pmatrix}$$

A unit stress acting along the c-axis will result in a fractional change in c_0 , defined as the linear c-axis compressibility, which may be related to the compliance moduli

$$\kappa_{\parallel} = \frac{\Delta c}{c_0} = s_{33} + 2s_{13},$$

while the basal plane linear compressibility is given by

$$\kappa_{\perp} = \frac{\Delta a}{a_0} = s_{11} + s_{12} + s_{13}. \quad \dots (2.1)$$

A complete set of constants has not yet been measured on the same sample of single crystal material. However, RILEY in 1945 was able to give estimates for s_{33} , s_{13} , and $s_{11} + s_{12}$ from X-ray measurements of the thermal expansion of Ceylon natural graphite as a function of temperature, combined with BASSET'S (1941) measurement of the volume compressibility ($\kappa_v = 2s_{11} + s_{33} + 2s_{12} + 4s_{13}$). Perhaps the most striking point to emerge was the large anisotropy between the basal plane and c-axis linear compressibility.

$$\kappa_{\perp} = -25 \times 10^{-14} \quad \kappa_{\parallel} = 500 \times 10^{-14} \text{ cm}^2 \text{ dyne}^{-1}.$$

More recently, SPENCE (1963), has collected the data of BRIDGMAN (1945) on bulk compressibility, RILEY on thermal expansion as a function of temperature, BOWMAN and KRUMHANSL (1958) on low temperature specific heat, and finally KABALKINA and VERESHAGIN (1960) on linear c-axis compressibility, and derived a table of all the elastic constants for natural crystals of Ceylon graphite. The collected data may be compared in Table 2.1 with a set of constants measured by SPENCE and SELDIN (1967) on hot pressed pyrolytic graphite. This material was prepared by a method almost identical to that employed for production of the pyrolytic graphite used in this work, and consisted of subjecting the as-deposited graphite to a pressure of 333 bar at a temperature of 2800°C followed by annealing at 3000°C. BLAKSLEE et al (1965) have shown that the resulting material is composed of crystallites with diameters of 20-50 μm in the basal plane and with their c-axis aligned to within $0.3-1^\circ$ of the normal to the plane of deposition.

Such material compares favourably with the best samples produced by MOORE et al (1964) of this laboratory.

TABLE 2.1
ELASTIC CONSTANTS OF GRAPHITE IN UNITS OF
 10^{-14} cm² dyne⁻¹

	a	b
S_{11}	11.1	9.85
S_{12}	- 0.46	-1.5
S_{13}	-24.9	-6.3
S_{33}	332	275
S_{44}	4350	56,000

(a) Natural single crystals of Ceylon graphite

(b) Hot pressed pyrolytic graphite.

By using the values of the single crystal elastic moduli given in Table 2.1, we may construct a representation surface which shows the variation of Young's moduli with direction. For an arbitrary direction of tension Young's modulus is defined as the ratio of longitudinal stress to the longitudinal strain, let this be denoted by $1/s'_{11}$. Since the compliance constants s_{ij} constitute a fourth rank tensor, they transform on change of axis to s'_{ij} where, e.g.

$$s'_{11} \equiv a_{1m} a_{1n} a_{1p} a_{1q} s_{mnpq} .$$

$a_{1m} a_{1n} \dots$ are direction cosines. On substituting the compliance constants for graphite we have

$$s'_{11} = s_{11} \sin^4 \varphi + s_{33} \cos^4 \varphi + (s_{44} + 2s_{13}) \sin^2 \varphi \cos^2 \varphi ,$$

where φ is the angle between the arbitrary direction of tension and the crystallographic c-axis. If the axis s'_{11} is drawn through the solid and rotated over 4π steradians, then, by using the values from Table 2.1, a surface may be constructed with length or tip of the vector $1/s'_{11}$ in a particular direction, corresponding to Young's modulus in that direction.

For graphite, the surface is one of revolution about the c -axis, a central section is shown in Fig.2.1. The predominance of the shear modulus s_{11} in single crystal and individual crystallites of graphite can clearly be seen from the figure by noting the low minimum in the representation surface when tension is applied at 45° to the c -axis.

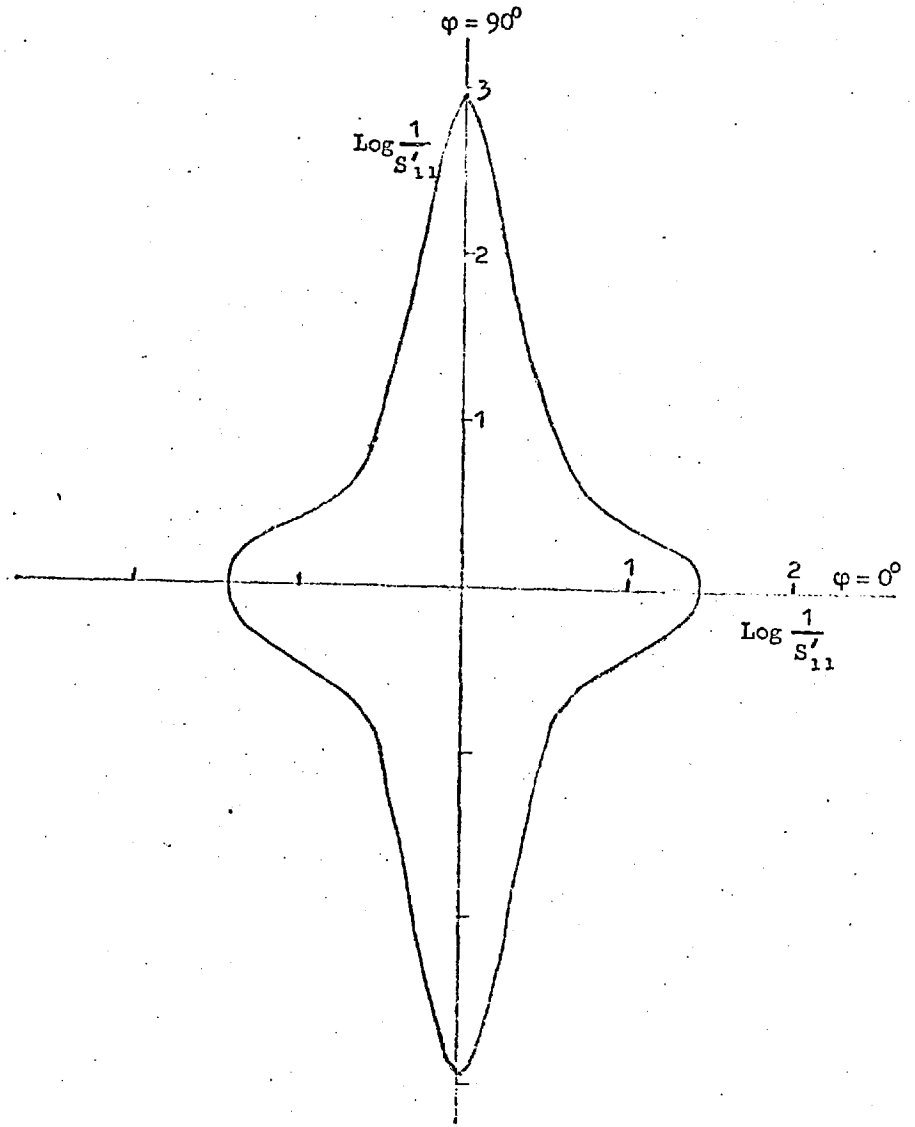


Fig.2.1

Young's modulus as a function of the angle between applied tensile stress and the crystal c axis

2.1.2 Polycrystalline Material

The pyrolytic graph-

ite used in this work is an aggregate of crystallites with their c -axes oriented about a small but finite range of angles to a reference direction often termed the plane normal. Application of a longitudinal stress along, for example, the c -axis will thus involve not only s_{33} but all the elastic moduli including the very large s_{44} . The effective compliance moduli can under these circumstances be quite different from the single crystal elastic moduli shown in Table 2.1. Two approaches have been used to try and express the elastic moduli of the bulk solid in terms of the constants of its constituent crystallites. The first of these (VOIGT (1928)) assumes the strain to be uniform in all the crystallites and space averages the stiffness

constants, while the second takes the other extreme and assumes the stress to be uniform and averages the compliance constants (REUSS (1929)). The two methods give respectively the lower and upper limit of the block moduli; the true constants must lie somewhere between these two values.

PRICE (1965) has measured the Young's moduli of several samples of pyrolytic graphite as a function of the crystallite c-axis alignment. The material examined ranged from almost isotropic graphite to hot pressed pyrolytic graphite with a c-axis distribution function of only a few degrees at half peak height. The measured moduli, $1/S_{11}$ and $1/S_{33}$, were found to increase monotonically as the crystals became better oriented, and for all samples agreed to within a few percent of the values calculated on the uniform stress model. Although the expressions derived by PRICE for the uniform strain model are incorrect, a later analysis by GOGGIN and REYNOLDS (1967) confirmed that in pyrolytic graphite the Young's moduli are more closely represented by values calculated through the uniform stress approach.

If a tensile stress σ applied to the polycrystal is assumed to be the same in all the constituent crystallites, then the average tensile strain is given by the sum of the strains in all the crystallites weighted proportionally to their volume fraction.

$$\epsilon = \sigma \frac{\int_0^{2\pi} \int_0^{\pi/2} \frac{1}{E(\varphi)} I(\varphi, \theta) \sin \varphi d\varphi d\theta}{\int_0^{2\pi} \int_0^{\pi/2} I(\varphi, \theta) \sin \varphi d\varphi d\theta}$$

where $E(\varphi)$ is Young's modulus for a single crystal at an angle φ to the c-axis and $I(\varphi, \theta)$ (known as the Bacon anisotropy function) is the density of crystallite c-axes in the direction φ, θ to the OZ, OX axes. MOORE et al (1964) have shown that the pyrolytic graphite used in this work is isotropic in the plane perpendicular to the c-axis, the strain will thus

have no θ dependence and Young's modulus for the polycrystalline aggregate is therefore

$$\frac{1}{E} = \frac{\int_0^{\pi/2} \frac{1}{E(\varphi)} I(\varphi) \sin \varphi d\varphi}{\int_0^{\pi/2} I(\varphi) \sin \varphi d\varphi} \quad \dots (2.2)$$

The representation surface Fig.2.1 gives directly the variation of Young's modulus with misorientation angle φ while X-ray measurements by MOORE, UBBELOHDE and YOUNG (1964) on the material used in this work have determined the anisotropy function $I(\varphi)$. Equation (2.2) may thus be evaluated graphically and for the hot pressed and annealed graphite produced in this laboratory, we find

$$\begin{aligned} E_{11} &= 88.9 \times 10^{11} \text{ dyne cm}^{-2} \\ E_{33} &= 3.01 \times 10^{11} \text{ dyne cm}^{-2} \end{aligned}$$

By comparison with Table 2.1 column (a) we see that the very small deviation from perfect c-axis alignment has resulted in Young's moduli for this material which are practically identical with that of single crystal graphite.

Using a similar uniform stress analysis, GOGGIN and REYNOLDS (1967) have employed the equations of MARKHAM (1962) to express all the compliance moduli of polycrystalline graphite in terms of the single crystal moduli

$$\begin{aligned} S_{11} &= s_{11} - \frac{1}{2}(2s_{11} - 2s_{13} - s_{44}) I_3/I_1 + \frac{3}{8}(s_{11} - 2s_{13} + s_{33} - s_{44}) I_5/I_1 \\ S_{33} &= s_{33} + (2s_{13} - 2s_{33} + s_{44}) I_3/I_1 + (s_{11} - 2s_{13} + s_{33} - s_{44}) I_5/I_1 \\ S_{13} &= s_{13} + \frac{1}{2}(s_{11} + s_{33} + s_{12} - 3s_{13} - s_{44}) I_3/I_1 - \frac{1}{2}(s_{11} + s_{33} - 2s_{13} - s_{44}) I_5/I_1 \\ S_{12} &= s_{12} + (s_{13} - s_{12}) I_3/I_1 + \frac{1}{8}(s_{11} + s_{33} - 2s_{13} - s_{44}) I_5/I_1 \\ S_{44} &= s_{44} + (3s_{11} + 2s_{33} - s_{12} - 4s_{13} - \frac{5}{2}s_{44}) I_3/I_1 - (2s_{11} + 2s_{33} - 4s_{13} - 2s_{44}) I_5/I_1 \end{aligned}$$

where

$$I_n = \int_0^{\pi/2} I(\varphi) \sin^n \varphi d\varphi, \quad n = 1, 3, 5.$$

The integrals may be evaluated graphically and for the pyrolytic graphite

used in this work we find

$$I_s/I_1 = 6.42 \times 10^{-6} \quad , \quad I_E/I_1 = 8.0 \times 10^{-9} .$$

Thus the effect of the large single crystal shear modulus s_{44} on the polycrystalline moduli will be very small. Estimated values of the aggregate moduli for this material given in Table 2.2 are seen to be almost identical to the single crystal moduli.

However, GOGGIN and REYNOLDS (1967) have shown that for P G A graphite graphite, which is poorly orientated and has a c-axis distribution function of $\sim 30^\circ$ at half peak height, agreement between calculated polycrystalline moduli and observed moduli is only achieved when the material has been subjected to light neutron irradiation. This suggests that the much higher density of planar dislocations in polycrystalline graphite substantially increases s_{44} the shear modulus, and in material with poor c-axis alignment therefore leads to a large increase in all the compliance constants. A large S_{44} value in pyrolytic graphite was confirmed by the static torque measurements of SPENCE and SELDIN (1967) and their estimate is reproduced in column (b) of Table 2.1. It is evident that even in good pyrolytic material, S_{44} can be an order of magnitude greater than that in single crystal graphite. However, due to the very small c-axes misalignment in the material used here, this increase in the shear modulus leads to a maximum increase of less than 10% in the other compliance moduli.

TABLE 2.2
CALCULATED COMPLIANCE MODULI FOR THE
SAMPLES OF PYROLYTIC GRAPHITE

	$10^{-14} \text{ cm}^2 \text{ dyne}^{-1}$
S_{11}	11.24
S_{12}	-0.475
S_{13}	- 25.3
S_{33}	332.5
S_{44}	4349.3

2.2 TEMPERATURE DEPENDENCE OF THE ELASTIC CONSTANTS

Polycrystalline industrial graphites exhibit an unusual temperature dependence in their elastic properties. Young's modulus for the c- and a-axis directions decrease with increasing temperature up to 200°C where a shallow minimum occurs; thereafter the moduli increase to 2000°C and finally decrease above this temperature. MASON and KNIBBS (1960) have attributed this behaviour entirely to material imperfections. Below 200°C, the freeing of dislocations from pinning points through thermal activation results in a steady decrease in the effective value of C_{44} . Since all the moduli for poor grade polycrystalline material are dominated by C_{44} , the Young's moduli will decrease with increasing temperature. However, above room temperature, the thermal expansion coefficients both parallel and perpendicular to the basal plane increase monotonically with temperature. The large and increasing c-axis expansion enables the crystallites to fill in the voids and 'Mrozowski cracks' present in the material thus tightening up the structure and resulting above 200°C in elastic moduli which increase with increasing temperature.

Although this behaviour has been confirmed by many workers for poor grade polycrystalline graphite (ANDREW and SATO (1964); DIGESU and PEARS (1965); KAMOUN and GATEAU (1966)), the temperature dependence of the elastic moduli of single crystal or very good pyrolytic material is unknown. However, we may infer from indirect evidence that the temperature dependence of the intrinsic elastic constants is low. Thus, NELSON and RILEY (1945) developed a theory of the thermal expansion as a function of temperature for single crystal graphite along and perpendicular to the basal plane. Their theory included the compliance moduli s_{11} , s_{12} , s_{13} and s_{33} and assumed these constants to be independent of temperature. Experiments on natural crystals of Ceylon graphite gave results which were within a few per cent of theoretical expectations. More recently KELLET and RICHARDS (1964) have

repeated these measurements on highly oriented pyrolytic graphite. Experimental results were within 10% of those based on the theoretical model employing temperature independent elastic moduli. Finally, KOMATSU (1958) has derived a theory describing the specific heat as a function of temperature which contained as fitting parameters the elastic moduli c_{33} and c_{44} . Excellent agreement with experimentally determined specific heats in single crystal material at 0.4-2K was obtained by using values of the elastic moduli which were within 10% of those measured at room temperature.

Zinc belongs to the same family of metals and semi-metals as graphite, namely those possessing hexagonal symmetry. For this metal the elastic constants have been measured, using the ultrasonic sound techniques, over a range of temperature extending from near its melting point to that of liquid helium. ALERS and NEIGHBOURS (1958) and GARLAND and DALVEN (1958) showed that in single crystals of zinc each of the five independent elastic moduli c_{11} , c_{33} , c_{44} , c_{12} and c_{13} increased with decreasing temperature. The effect began to saturate at ~ 50 K and very little increase occurred below 30K. On reducing the temperature from 300 to 4.2K the compressional stiffness constants c_{11} and c_{13} increased by 9.39 and 8.39 per cent respectively. But, the linear compressibility $\kappa_{\perp}$ decreased by only 2.7% compared with a 9.3% decrease in the c-axis linear compressibility $\kappa_{\parallel}$. The elastic anisotropy of zinc $\kappa_{\parallel}/\kappa_{\perp}$ showed a corresponding decrease from 8.8 at 300K to 8.0 at 4.2K.

Magnesium has an hexagonal structure with an axial ratio c/a of 1.623 which closely approximates to the ratio of 1.633 for ideal close packing. SLUTSKY and GARLAND (1957) have measured the elastic constants over the temperature range 300 to 4.2K. The five elastic constants increased almost linearly as the temperature fell to ~ 100 K. Further reduction in temperature resulted in a temperature dependence which flattened off to zero below ~ 30 K. The percentage variation of the shear modulus c_{44} from 300

to 4.2K was shown to be about 60% greater than the percentage variation in the compressional constants; a behaviour also demonstrated by ALIENS and NEIGHBOURS (1958) for the shear modulus of single crystal zinc.

An elastic anisotropy c_{11}/c_{33} of 2.59 ensures that zinc bears a closer resemblance to graphite than does magnesium, which is almost elastically isotropic, with c_{11}/c_{33} equal to 0.96. We may expect from the results described above and the previous discussion, that reduction of temperature by 300 K will result in an increase in the compressional and shear stiffness constants of graphite by perhaps 10-20%. The ratio of linear compressibilities is likely to be a few percent larger at 300 K than at 4.2 K.

2.3 VARIATION OF MODULI WITH FAST NEUTRON IRRADIATION

A discussion of the dependence on neutron irradiation of the elastic constants can once again be divided into two quite separate categories: that describing the elastic properties of reactor and industrial polycrystalline graphites, and secondly the effect of irradiation on the elastic moduli of single crystal and compression-annealed pyrolytic graphite. As the elastic moduli of poor grade polycrystalline graphites are dominated by C_{44} , the effect of irradiation is to cause an immediate large increase in all the moduli due to pinning of glissile basal plane dislocations. However, in single crystal and highly oriented pyrolytic material the dislocation content affects only the shear modulus.

SUMMERS, WALKER and KELLY (1966) have irradiated very highly oriented pyrolytic graphite to a range of neutron doses up to a maximum of 5×10^{20} nvt. The stiffness modulus C_{33} decreased with irradiation, but the decrease was slow until doses which correspond to charges of c-axis dimensions greater than $\sim 5\%$ was reached. Such a fast neutron dose also marks the onset of a rapid decrease in the c-axis thermal expansion coefficient and amounts to $\sim 1.5 \times 10^{20}$ nvt. The fast neutron doses used in this work range from

11.88×10^{14} to 10^{18} nvt and according to the results of SUMMERS et al. (1966) will cause the stiffness modulus C_{33} to decrease by at most 0.1%. Perpendicular to the c-axis the dimension changes on irradiation were found to be negative and about 30 times less than that in the c direction. Changes in the basal plane compressional stiffness constants are thus likely to be significantly less than those in the c direction, and at doses used in this work may be neglected.

CHAPTER III

CONDUCTION PROCESSES IN GRAPHITE

3.1 BLOCH STATES

Electronic transport in a solid medium is determined by the form of the distribution function, the energy band structure, and by the scattering of free electrons and holes. A fundamental idealization which is often made is to regard conduction particles as free, occupying non-interacting, single electron states in an infinite periodic lattice. We shall subsequently show that this approximation is not sufficient to explain measured transport properties in graphite without including the perturbing effect of carrier-carrier interactions on the steady state distribution function. The concept of perfect periodicity is however retained, and is used to specify a set of translation vectors $\underline{R}_i$ such that the potential energy of an electron is unchanged if the point of observation is displaced by such a vector. $\underline{R}_i$ may be expressed in terms of three independent primitive translation vectors $\underline{a}_i$ which for the hexagonal crystal lattice of graphite may be written :

$$\left. \begin{aligned} \underline{a}_1 &= a_0 \sqrt{3}/2 \cdot \underline{i} + a_0/2 \underline{j} \\ \underline{a}_2 &= -a_0 \sqrt{3}/2 \cdot \underline{i} + a_0/2 \underline{j} \\ \underline{a}_3 &= c_0 \underline{k} \end{aligned} \right\} \dots (3.1)$$

and

$$\underline{R}_i = n_{i1} \underline{a}_1 + n_{i2} \underline{a}_2 + n_{i3} \underline{a}_3 .$$

Bloch's theorem states that for a periodic potential the eigenfunction $\psi_k(r)$ of the wave equation

$$H\psi = E\psi$$

forms a basis for the set of operators which transform $\psi_k(r)$ into $\psi_k(r + R_i)$. That is, $\psi_k(r)$ forms a basis for the group of operators $e^{i\mathbf{k} \cdot \mathbf{R}_i}$ such that

$$\psi_k(r + R_i) = e^{i\mathbf{k} \cdot \mathbf{R}_i} \psi_k(r) .$$

A common approach is to define $\psi_k(r)$ in terms of a function $U_k(r)$ with

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} U_{\mathbf{k}}(\mathbf{r}) . \quad \dots (3.2)$$

Bloch's theorem then demands that $U_{\mathbf{k}}(\mathbf{r})$ have the full periodicity of the lattice.

Each electron has, in the Bloch approach, a separate wave function and obeys a separate Schrodinger equation of the form

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi .$$

The potential V has the full symmetry of the lattice so that the group of the Schrodinger equation is also the space group of the lattice.

The presence of the crystal lattice greatly modifies the propagation properties of electrons and holes. On the one hand it is convenient to use the above wave-like description of an electron state, and on the other, a particle approach is practicable. DAVISSON and GERMER, (1927) and THOMPSON, (1928) have demonstrated that a free electron exhibits wave-like characteristics with the momentum and wavelength related through the De Broglie expression

$$\underline{p} = \frac{h}{\lambda} = \hbar \underline{k} ,$$

where $\underline{k}$ is the electron wave number and propagation vector of equation (3.2). In a dispersive medium the group velocity of the wave packet is given by the gradient of $E(\mathbf{k})$ in wave number space

$$\mathbf{v}_{\mathbf{k}} = \frac{1}{\hbar} \frac{\partial E(\mathbf{k})}{\partial \mathbf{k}} . \quad \dots (3.3)$$

An electron moving through a solid is subject to forces from the crystal lattice as well as to possible external forces. This is reflected in the fact that in a crystal the external force on an electron due, for example, to an electric field $\mathcal{E}$ is expressed not as $m d\mathbf{v}/dt$ as in free space, but rather takes the form

$$e \mathcal{E} = \hbar \frac{\partial \mathbf{k}}{\partial t} ,$$

From equation (3.3)

$$\frac{\partial \mathbf{v}}{\partial t} = \frac{\partial^2 E}{\partial \mathbf{k}^2} \cdot \frac{e \mathcal{E}}{\hbar^2} .$$

By analogy with the classical expression relating force and acceleration,

the quantity $\hbar^2 / \frac{\partial^2 E}{\partial k^2}$ plays the role of an electron mass, and is in fact a second rank tensor with components

$$\left(\frac{m_0}{m^*}\right)_{ij} = \frac{m_0}{\hbar^2} \frac{\partial^2 E}{\partial k_i \partial k_j} . \quad \dots (3.4)$$

In the case of quasi free non interacting electrons

$$E = \frac{\hbar^2 k^2}{2 m^*} ,$$

where m^* is an average electron mass.

If $N(E) dE$ is the number of electron states per unit volume lying between energies E and $E + dE$ for a given spin orientation, then

$$N(E) = \frac{1}{4\pi^3 N_h} \int \frac{ds}{|v_k|} = \frac{1}{4\pi^3 N_h^2} \int \frac{\frac{ds}{\partial E}}{\partial k} .$$

$\frac{1}{4\pi^3}$ is the number of electron states per unit volume of $\underline{k}$ space per unit volume of real space. ds is an elemental area of Fermi surface and N is the number of unit cells in the crystal. Then the density of states is a continuous function of energy and at the Fermi level is given by

$$N(E) = \frac{(2m^*)^{\frac{3}{2}}}{4\pi^3 \hbar^3} E_f^{\frac{1}{2}} . \quad \dots (3.5)$$

Expressions of this form are valid only in the independent particle model in which the motion of an individual electron is assumed to be independent of the motion of all others. In reality the Pauli Exclusion Principle and the mutual Coulomb interaction between electrons lead to position and energy correlations, which reduce the density of states below that given by equation (3.5). Discrepancies between the established theory and observations of the transport properties of graphite, especially as a function of pressure, are resolved in this work by employing a model which uses the quasi-free electron approach, but includes the effect of Coulomb interactions between charge carriers on the overall collision time, τ_c .

In the absence of temperature gradients the current density is the product of the velocity of each carrier and its charge, integrated over all

carriers. In terms of the steady state distribution function f

$$\underline{J} = \frac{e}{4\pi^3} \int \underline{v} \cdot f \, d\underline{k} = -\frac{e^2}{4\pi^3} \int \tau \, \underline{v} (\underline{v} \cdot \underline{E}) \frac{\partial f_0}{\partial E} \, d\underline{k} ,$$

where f_0 is the distribution function in the absence of externally applied fields and thermal gradients.

The conductivity tensor $\underline{\sigma}$ is defined by the relation

$$\underline{J} = \underline{\sigma} \underline{E} . \quad \dots (3.6)$$

Here we are concerned with two components of this tensor, namely σ_{xx} and σ_{zz} with

$$\sigma_{ii} = \frac{e^2}{4\pi^3} \int \tau \, v_{ii}^2 \left(-\frac{\partial f_0}{\partial E} \right) \, d\underline{k} \quad i = x, z . \quad \dots (3.7)$$

Collision processes enter the calculation of σ through the relaxation time τ which is normally dispersive, the band structure enters through the velocity via equation (3.3) and the distribution function defines the occupation of electron states. In graphite the form of the distribution function changes over the temperature range of interest, from a highly degenerate distribution at liquid helium temperatures to a non-degenerate distribution at room temperature. At low temperature the Pauli Exclusion Principle dominates the scattering process. As the temperature is raised the density of states into which electrons are scattered is uncertain, and the relaxation time becomes a complex function of energy and direction.

3.2 BAND STRUCTURE OF GRAPHITE

In this section those aspects of the graphite band structure, which are necessary to the understanding of pressure effects in graphite, are outlined. HAERING and WALLACE (1957) and HAERING and MROZOWSKI (1960) provide early reviews of this topic, the most recent treatment is that of WOORE (1969). Since 1968, the sign of one of the band parameters, namely γ_2 has been reversed and the location of electron and hole surfaces have been interchanged. Differences in the band structure resulting from these

changes, particularly where they affect the interpretation of experimental results, are underlined in section 3.2.3.

3.2.1 The Brillouin Zone

Reciprocal lattice vectors corresponding to the $\underline{a}_1$ of equation (3.1) are of the form:

$$\underline{b}_1 = \left[\frac{2\pi}{\sqrt{3} a_0}, \frac{2\pi}{a_0}, 0 \right]$$

$$\underline{b}_2 = \left[-\frac{2\pi}{\sqrt{3} a_0}, \frac{2\pi}{a_0}, 0 \right]$$

$$\underline{b}_3 = \left[0, 0, \frac{2\pi}{c_0} \right].$$

Bragg reflection of a wave by a periodic lattice usually defines the first Brillouin zone as that surface formed by planes which are normal to the vectors, at their midpoints, which join nearest neighbour reciprocal lattice points. However, in graphite this does not produce a surface which everywhere marks an energy discontinuity. HERRING (1942) has shown that only doubly degenerate states exist on the hexagonal faces of the Brillouin zone where $k_z = \pm \frac{\pi}{c_0}$ and this result implies that no energy gap can exist across the hexagonal zone faces. A composite zone made up of faces which mark a discontinuity in energy employs all of the first zone and part of the second zone, and is shown in Fig.3.1(a). If N_1 is the number of unit cells in real space, the composite zone contains $4N_1$ electron states and, as

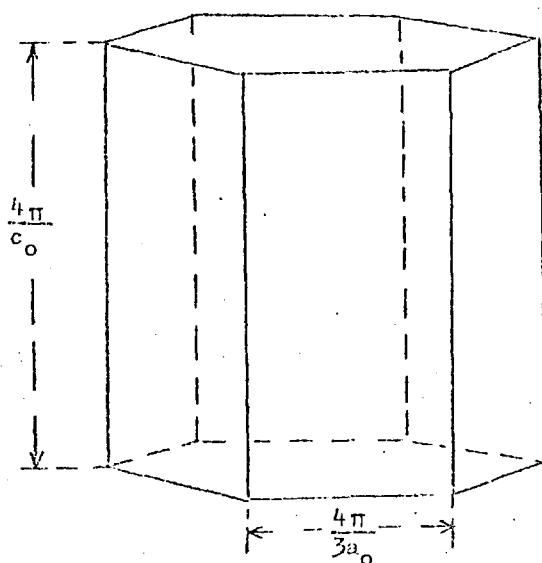


Fig.3.1(a)

The composite first Brillouin zone

the four atoms of the unit cell each provide one conduction electron, then at the absolute zero of temperature the composite zone is full and the

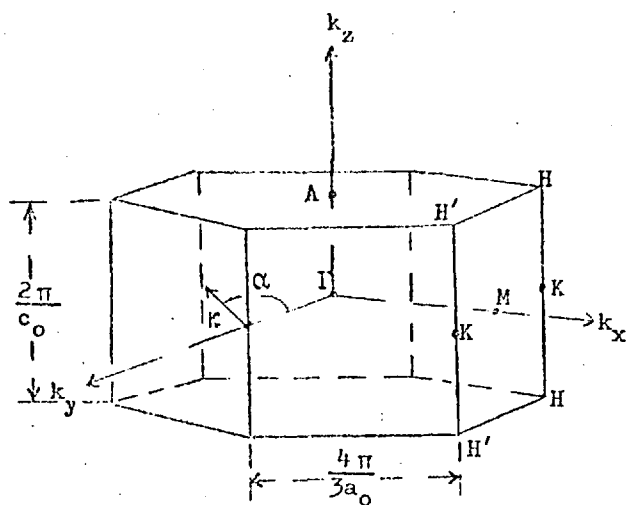


Fig. 3.1(b)

Reduced Brillouin zone with
coordinate system of McClure

second zone empty. The reduced zone is then as shown in Fig.

3.1(b) where the symmetry points have been labelled according to the notation of BOUCKAERT, SMOLUCHOWSKI and WIGNER (1936) and the coordinates of a point near a zone edge according to the notation of McCLURE (1957).

3.2.2 Band Model of Slonczewski and Weiss

Early work on the band structure of graphite applied standard tight binding theory to potential integrals between π -electron wave functions on neighbouring atoms, and led to undetermined parameters in the form of two centre tight binding integrals. A band model based on the two dimensional lattice found no overlap of valence and conduction bands, but from the symmetry properties of the wave function predicted a double degeneracy at the corners of the Brillouin zone. A three dimensional model has four atoms in the unit cell, two associated with each layer. Four bands are formed by the four $2p_z$ orbitals and a small overlap between valence and conduction bands results from a sinusoidal dependence of energy with k_z along the edge of a Brillouin zone.

Matrix elements between σ and π states result in an overlap of the π bands at the zone edge. However, the same result is obtained by considering the next nearest plane π overlap, and excluding σ - π mixing. Since this procedure is mathematically simpler, SLONCZEWSKI and WEISS (1955) and (1958) considered only π orbitals of the four atoms in the unit cell and included overlap of next nearest neighbour planes without attempting to estimate the magnitude of σ - π interaction terms.

Slonczewski and Weiss first made a detailed group theoretical study of the crystal and showed that at a general point on the zone edge, the group of the wave vector has three small representations; two one-dimensional and one two-dimensional. A set of wave functions which transform according to these representations is:

$$\begin{aligned}
 \psi_1 &= \frac{1}{\sqrt{2}} (a + a') = \frac{1}{\sqrt{2}} \left\{ \sum_n \exp(i n k_z c_0) \varphi_2(r - n c_0) \right. \\
 &\quad \left. + \sum_n \exp\left(i\left(n + \frac{1}{2}\right) k_z c_0\right) \varphi_2'(r - n c_0) \right\} , \\
 \psi_2 &= \frac{1}{\sqrt{2}} (a - a') = \frac{1}{\sqrt{2}} \left\{ \sum_n \exp(i n k_z c_0) \varphi_2(r - n c_0) \right. \\
 &\quad \left. - \sum_n \exp\left(i\left(n + \frac{1}{2}\right) k_z c_0\right) \varphi_2'(r - n c_0) \right\} , \quad \dots (3.8) \\
 \psi_{31} &= b' = \sum_n \left(\exp\left(i\left(n + \frac{1}{2}\right) k_z c_0\right) \varphi_1'(r - n c_0) \right) , \\
 \psi_{32} &= b = \sum_n \exp(i n k_z c_0) \varphi_1(r - n c_0) ,
 \end{aligned}$$

where the φ 's possess the full symmetry of the two-dimensional lattice and the prime denotes wave functions based on adjacent planes. The wave functions ψ_{31} , ψ_{32} form the basis of the two-dimensional representation, while ψ_1 and ψ_2 are the basis functions for the two one-dimensional representations except at the points H, H' where these merge to form one two-dimensional representation.

SLONCZEWSKI, (1955) showed that in the tight binding limit where the φ 's are atomic p_z orbitals, 'a' is made up solely from p_z orbitals based on A atoms, while b' is composed of p_z orbitals based on B' atoms only, analogous statements apply to a' , b. Wave functions ψ_{31} , ψ_{32} thus involve layers 1,3,5 ... and 2,4,6 ... respectively, while ψ_1 and ψ_2 involve all layers. The large layer separation ensures that the infinite sums over layers are rapidly convergent and only lowest order terms are retained when the wave functions (3.8) are used to evaluate the energy on the zone edge.

The exponential phase factors $\exp(ik_z c_0)$ of equation (3.8) result in a Fourier series expansion along k_z which is typical of tight binding behaviour. Since the interesting part of the zone entails only 1% of the distance from the edge to the centre, Slonczewski and Weiss employed the K. P. perturbation theory of BOUCKAERT, SMOLUCHOWSKI and WIGNER (1936), and expressed the Hamiltonian to first order in terms of the parameter $(\underline{k} - \underline{k}_0) = \underline{K}$ the shortest vector from the edge of the zone to the point of interest. A change of $\underline{K}$ in the wave vector is equivalent to a perturbation

$$H' = \frac{\underline{K} \cdot \underline{P}}{m} + \frac{1}{2} \frac{\hbar^2 K^2}{m}$$

on the Hamiltonian at $\underline{k}_0$ where the elements of the momentum matrix are defined as:

$$P_{jj'} = \int \psi_j^*(\underline{k}_0, \underline{r}) \left(\frac{\hbar}{i} \nabla \right) \psi_{j'}(\underline{k}_0, \underline{r}) d^3r$$

(Calloway (1964) p.30)

The problem is thus reduced to one of diagonalizing the perturbed Hamiltonian $H_0 + H'$ where H_0 is the Hamiltonian for states on the zone edge.

By using symmetry to determine the angular dependence (α) of the momentum matrix normal to the zone edge, Slonczewski and Weiss wrote the Hamiltonian in the form:

$$H = \begin{bmatrix} E_1 & 0 & H_{13} & H_{13}^* \\ 0 & E_2 & H_{23} & -H_{23}^* \\ H_{13}^* & H_{23}^* & E_{31} & H_{33} \\ H_{13} & -H_{23} & H_{33}^* & E_{32} \end{bmatrix} \quad \dots (3.9)$$

where

$$H_{a+a',b'} = H_{13} = 2^{-\frac{1}{2}} \left[-\gamma_0 + \gamma_4 \Gamma \right] \sigma \exp(i\alpha)$$

$$H_{a-a',b} = H_{23} = 2^{-\frac{1}{2}} \left[\gamma_0 + \gamma_4 \Gamma \right] \sigma \exp(i\alpha)$$

and

$$H_{b,b'} = H_{33} = \gamma_3 \Gamma \sigma \exp(i\alpha)$$

and

$$\sigma = \sqrt{3/2} \cdot a_0 |\kappa|, \quad \alpha = \tan^{-1}(\kappa_x / \kappa_y), \quad \Gamma = 2 \cos(k_z c_0 / 2).$$

κ is the shortest distance from the point in question to the zone edge. The notation and Hamiltonian described is actually that of McCLURE (1957), but WOORE (1969) has shown that a unitary transformation connects this Hamiltonian with that derived by Slonezewski and Weiss. A complete Hamiltonian including spin-orbit coupling, which has been ignored in this treatment, has been worked out by DRESSELHAUSE, G. and DRESSELHAUSE, M.S. (1965). It is found that spin-orbit interaction lifts all band degeneracies and affects the topology of the Fermi surface at the zone boundary $k_z = \pm \pi/c_0$, however Slonezewski and Weiss estimate the splitting to be small, $< 10^{-4}$ eV.

The seven band parameters utilised in the Hamiltonian of equation (3.9) are discussed in section 3.2.3, where the corresponding symbol used by Slonezewski and Weiss (S.W.) is included and the range of values is taken from the recent review of WOOLLAM (1971). It should be stressed at this stage that even today there is no unique completely self-consistent set of parameter values. Generally speaking it is easier to correlate sets of values when results from the optical and secondary electron emission experiments of FEUERBACHER et al. (1971) are excluded. A recent paper by BENDER and YOUNG (1972a) achieved an unusually high level of internal consistency when fitting band parameters to the results of Shubinkov de Haas (SdH) experiments on pyrolytic graphite. PAINTER and ELLIS (1970), recognizing the lack of consistency between experimental determinations of the band parameters, recently attempted an ab-initio variational approach to the problem. Matrix elements of the Hamiltonian were evaluated directly without tight binding approximations and details of the band structure were found to be insensitive to the form of the crystal potential function. The single layer structure was adequate for treating optical transitions in graphite, but for details of the Fermi surface the full three-dimensional model was required. On including the interaction between adjacent planes each energy band obtained for the single layer structure was found to split

slightly, and the average band structure was depressed relative to the bands obtained with the single layer crystal. The energy $E(k)$ calculated as a function of k_z at a zone corner, demonstrated the overlap of the π valence and conduction bands, but the authors predicted hole occupancy at K which in the tight binding approach is equivalent to assigning a positive sign to γ_2 .

Another entirely independent approach was made by van HAERINGEN and JUNGINGER (1969) using the pseudopotential method. A local centrally symmetric pseudopotential of between 150 and 350 plane waves resulted in an overall picture of the energy band structure, which clearly showed that overlap of valence and conduction bands could occur only along the zone corners. The Fermi level was found to lie somewhere between 0 and 0.035 eV, and the Fermi surface obtained located electrons in the neighbourhood of K and holes in the neighbourhood of H, H'. This was in direct contradiction to the generally accepted view of electrons at H, H' and holes at K current at that time but supported the present view. Slight changes in the pseudopotential produced results which were consistent with the new assignment.

3.2.3 Band Parameters

γ_0 (p_0 in the S.W. notation) represents wave function overlap and is, in fact, the two centre tight binding integral between A and B atoms within a plane. This parameter determines the dependence of energy on k and is one of the two undetermined band parameters required to describe the band structure when only nearest neighbour interactions are included. Of the seven band parameters it has received most attention with estimated values ranging from 2.8 to 3.2 eV. The preferred value is 2.88 eV.

Nearest neighbour interactions between layers are described by the band parameter γ_1 , (δ_1 , S.W.). This parameter is responsible for the splitting of the bands E_1 and E_2 caused by the interlayer overlap between

A and A' type atoms with estimated values of 0.027 to 0.40 eV. Two values have recently received much attention, 0.31 eV in SdH studies (Woollam's value) and 0.4 eV in optical studies.

γ_2 (δ_2 , S.W.) represents overlap of B atoms situated on next nearest layers and the effect of σ - π coupling which is neglected in the S.W. model. This parameter determines the amplitude of the sinusoidal variation of the E_3 bands along k_z and is thus responsible for the band overlap. Location of the electron and hole surfaces along the zone edge is determined by the sign of γ_2 . This has been the cause of much controversy. JOHNSTONE (1956) has estimated -0.007 eV from the mixing of σ - π orbitals in adjacent layers, while HORTON and TAUBER (1958) estimated +0.001 eV from second nearest plane overlap between B type atoms. The recent independent theoretical estimates of PAINTER and ELLIS (1970), and of HAERLINGEN and JUNGINGER (1969) are again in disagreement regarding the sign. However, a wealth of experimental work, SCHROEDER, DRESSELHAUS and JAVAN (1968), WOOLLAM (1971) and COOPER, SMITH, WOORE and YOUNG, (1971) makes a very strong case for locating electrons at point K and holes in the neighbourhood of H, H', i.e. for negative γ_2 . The preferred value is -0.0185 eV.

Anisotropy of energy contours in the X-Y plane reach a maximum at point K on the zone edge and is described by the parameter γ_3 (q , S.W.). This parameter which is often neglected in the interpretation of experimental results, is due to nearest layer p_z wave function overlap between B and B' type atoms. Values ranging from 0.14 to 0.29 eV have been estimated, but recent work on the magnetoreflexion spectrum of graphite by SCHROEDER, DRESSELHAUS and JAVAN (1968) gives a most reliable value quoted as 0.29 ± 0.02 eV.

γ_4 (r, S.W.) arises from the interaction between A' and B sites on adjacent planes and has only a quantitative effect on the band structure. Estimated values range from 0.2 to 0.3 eV. In the absence of any difference between A and B atomic sites, this parameter would equate with γ_3 . The latest estimate by Woollam is +0.18 eV.

γ_5 is a term which was included by McClure but not by S.W. It arises from interaction between A sites on second nearest planes and has no effect on the anisotropy of the band structure. Because of the similarity to second nearest plane overlap between B atoms, a value equal to γ_2 , namely -0.0185 eV, is normally assumed.

The four energy bands at the zone corners fall into two groups, namely, E_1 and E_2 having as basis, wave functions based on A type atoms, and the two E_3 band with basis made up of wave functions based on B type atoms. The difference in potential experienced by A and B sites is reflected, together with next nearest layer overlap, in an energy difference Δ at the points H, H' at the Brillouin zone edge where only E_1 and E_2 bands are required by symmetry to be degenerate. Estimated values range from 0.005 to 0.1 eV but the preferred value (WOOLLAM (1971)) is +0.009 eV.

The band structure of graphite is not properly characterised until the relative density of electrons and holes, and therefore the Fermi energy E_f , is determined. Each sample will have a Fermi level determined by the acceptor concentration, donors are rarely observed in graphite. COOPER, SMITH, WOORE and YOUNG (1971) have shown that an acceptor concentration of 3 ppm will depress the Fermi level by ~ 0.001 eV. An intrinsic Fermi energy of 0.019 eV has been estimated by DRESSELHAUSE and MAVROIDES (1964) but it should be emphasized that each sample will have a Fermi level peculiar to that material.

3.2.4 The Fermi Surface

WOORE (1969) has shown how the energy bands may be obtained by evaluating the determinant

$$|H - EI| = 0,$$

where I is the unit matrix. If terms containing H_{33} are neglected the secular equation reduces to a quadratic in E_3 with solution

$$\begin{aligned} E_{1,31} &= \frac{1}{2} (E_1^0 + E_{31}^0) \pm \left\{ \frac{1}{4} (E_1^0 - E_{31}^0)^2 + (\gamma_4 \Gamma - \gamma_0)^2 \sigma^2 \right\}^{\frac{1}{2}} \\ E_{2,32} &= \frac{1}{2} (E_2^0 + E_{32}^0) \pm \left\{ \frac{1}{4} (E_2^0 - E_{32}^0)^2 + (\gamma_4 \Gamma + \gamma_0)^2 \sigma^2 \right\}^{\frac{1}{2}}. \end{aligned} \quad \dots (3.10)$$

The labelling of the energy bands follow that of the matrix elements outlined in section 3.2.3. At the zone edge the four energy bands become

$$\begin{aligned} E_1^0 &= \Delta + \gamma_1 \Gamma + \frac{1}{2} \gamma_5 \Gamma^2 \\ E_2^0 &= \Delta - \gamma_1 \Gamma + \frac{1}{2} \gamma_5 \Gamma^2 \\ E_3^0 &= \frac{1}{2} \gamma_2 \Gamma^2. \end{aligned}$$

The energy is shown as a function

k_z and K in Fig.3.2(a). Of

particular interest is the region of k space where the E_3 bands meet the E_2 band for here an accidental degeneracy occurs between E_2 and E_{32} (HERRING 1937).

When the perturbative interaction between the bands is included as

the matrix element H_{32} , the bands are forced apart, and the only re-

maining degeneracy will be that required by symmetry, namely that the E_1 , E_2 bands be degenerate at $k_z = \pm \pi/c_0$. A hole pocket thus appears due to the E_2 band and is thought to be responsible for the minority carrier oscillations observed by WILLIAMSON, FONER and DRESSELHAUS (1965), and the

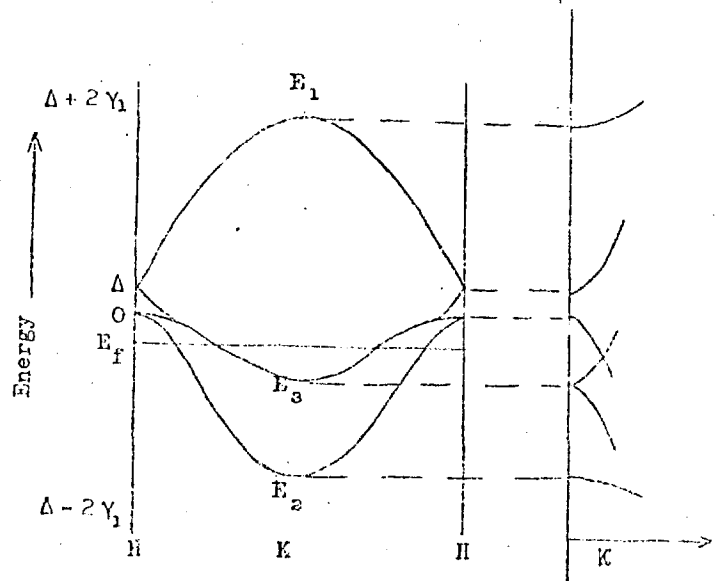


Fig.3.2(a)

Energy of the four bands, at a zone corner, as a function of k_z and K

low temperature field dependence of the Hall effect observed by SOULE (1958) in single crystal graphite, and by WOORE (1969) in pyrolytic graphite. Our

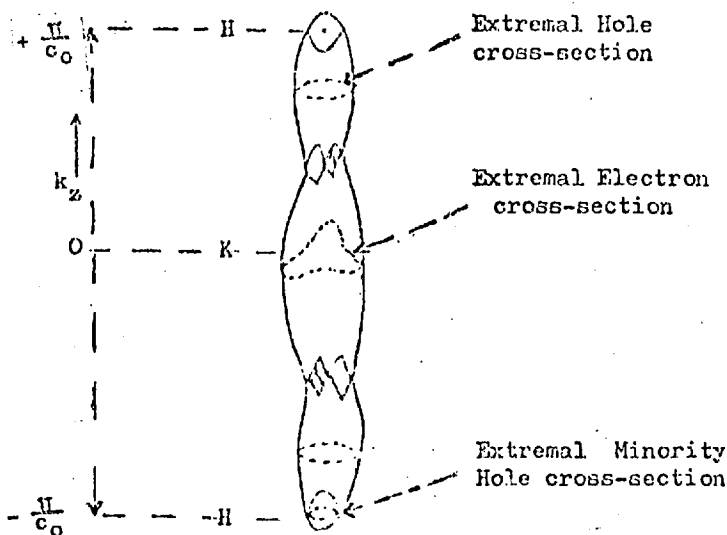


Fig.3.2(b)

Fermi surface of graphite about the zone corner HKH

choice of negative γ_2 places the electrons at the centre of the edge HKH with holes nearer $k_z = \pm \pi/c_0$. Constant energy surfaces are shown in Fig.3.2(b), one electron surface with two majority and two minority hole surfaces are present. Trigonal warping due to the inclusion of γ_3 is

most pronounced at the junction of the electron and majority hole surfaces, where four feet emerge and touch to provide an extra degeneracy discussed by JOHNSTON (1955).

3.2.5 Fermi Surface Volume and Area of External Cross-Section

This work is concerned in part with the change as a function of applied pressure of the external cross-sectional area of the Fermi surface normal to the trigonal axis, and in the pressure dependence of the total volume enclosed. In this section analytic expressions for the volume and cross-sectional area of the majority hole and electron Fermi surfaces are derived.

The appropriate energy bands are :

$$E_{31} = \frac{1}{2} (E_1^0 + E_3^0) - \left\{ \frac{1}{4} (E_1^0 - E_3^0)^2 + (\gamma_0 - \gamma_4 \Gamma)^2 \sigma^2 \right\}^{\frac{1}{2}} \text{ Majority holes} \quad \dots (3.11a)$$

$$E_{32} = \frac{1}{2} (E_2^0 + E_3^0) - \left\{ \frac{1}{4} (E_3^0 - E_2^0)^2 + (\gamma_0 + \gamma_4 \Gamma)^2 \sigma^2 \right\}^{\frac{1}{2}} \text{ Majority electrons} \quad \dots (3.11b)$$

(a) Majority electron surface, Area of cross-section

As σ is a vector lying solely in the k_x, k_y plane, the cross-sectional area normal to the trigonal axis is given by $\frac{4}{3} \frac{\pi}{a_0^2} \cdot \sigma^2$.

Equation (3.11b) may be written

$$\left(E_{32} - E_2^0\right)\left(E_{32} - E_3^0\right) - \left(\gamma_0 + \gamma_4 \Gamma\right)^2 \sigma^2 = 0 .$$

The area of cross-section is therefore:

$$A_e = \frac{4}{3} \frac{\pi}{a_0^2} \frac{\left(E_f - \frac{1}{2} \gamma_2 \Gamma^2\right)\left(E_f - \Delta + \gamma_1 \Gamma - \frac{1}{2} \gamma_5 \Gamma^2\right)}{\left(\gamma_0 + \gamma_4 \Gamma\right)^2} \dots (3.12)$$

An extremum occurs in the electron surface at $k_z = 0$ where $\Gamma = 2$. The corresponding external area of cross-section is obtained by substituting in equation (3.12)

$$A_{e \text{ ext.}} = \frac{4}{3} \frac{\pi}{a_0^2} \frac{\left(E_f^2 - E_f(\Delta - 2 \gamma_1 + 2 \gamma_5 + 2 \gamma_2) + 2 \gamma_2(\Delta - 2 \gamma_1 + 2 \gamma_5)\right)}{\left(\gamma_0 + 2 \gamma_4\right)^2} .$$

If γ_4, γ_5 are neglected, an error of about 16% is incurred in A_e (extremal) and the expression becomes:

$$A_{e \text{ ext.}} = \frac{4}{3} \frac{\pi}{a_0^2 \gamma_0^2} \left(2 \gamma_2 - E_f\right)\left(2 \gamma_1 - E_f + \Delta\right) . \dots (3.13)$$

(b) Majority hole surface, Area of cross-section

The terms of equation (3.11a) may be re-arranged such that:

$$\left(E_{31} - E_1^0\right)\left(E_{31} - E_3^0\right) - \left(\gamma_0 - \gamma_4 \Gamma\right)^2 \sigma^2 = 0 ,$$

with the cross-sectional area given by:

$$A_h = \frac{4}{3} \frac{\pi}{a_0^2} \frac{\left(E_f^2 - E_f\left(\Delta + \gamma_1 \Gamma + \frac{1}{2} \gamma_5 \Gamma^2 + \frac{1}{2} \gamma_2 \Gamma^2\right) + \frac{1}{2} \gamma_2 \Gamma^2\left(\Delta + \gamma_1 \Gamma + \frac{1}{2} \gamma_5 \Gamma^2\right)\right)}{\left(\gamma_0 - \gamma_4 \Gamma\right)^2} (3.14)$$

Γ_m , the value of Γ at which the area has an extremum, is obtained by differentiating equation (3.14) w.r.t. Γ and equating to zero. Band parameters γ_4 and γ_5 have previously been neglected in evaluating A_H .

However, in Appendix A.1 we include γ_4 and γ_5 to obtain:

$$\Gamma_m = \frac{E_f}{\left(\gamma_0 \gamma_2 + \gamma_0 \gamma_5 + \gamma_4 \gamma_1\right) - \gamma_0 \gamma_2 \Delta \pm \left\{\left(E_f\left(\gamma_0 \gamma_2 + \gamma_0 \gamma_5 + \gamma_4 \gamma_1\right) - \gamma_0 \gamma_2 \Delta\right)^2 - 4\left(\frac{3}{2} \gamma_1 \gamma_0 \gamma_2 - \gamma_4 \gamma_2 \gamma_1\right)\left(2 \gamma_4 E_f^2 - \gamma_0 \gamma_1 E_f - 2 \gamma_4 E_f \Delta\right)\right\}^{\frac{1}{2}}}$$

... (3.15)

when $\gamma_4 = \gamma_5 = 0$ equations (3.14) and (3.15) reduce to the expressions of COOPER et al (1971) but with terms in γ_1 having the opposite sign:

$$\Gamma_m = \frac{1}{3} \gamma_1 \left(\Delta - E_f - \left((\Delta - E_f)^2 + 6 \gamma_1^2 E_f (\gamma_2)^{\frac{1}{2}} \right) \right) \dots (3.16)$$

$$A_{h_{ext}} = \frac{4}{3} \frac{\pi}{a_0^2 \gamma_0^2} \left[\frac{\left(E_f - \gamma_2 \Gamma_m^2 \right) \left(E_f + \gamma_1 \Gamma_m - \Delta \right)}{2} \right] \dots (3.17)$$

If band parameters γ_4 and γ_5 are neglected, an error of about 20% is incurred in $A_{h_{ext}}$.

(c) Volume enclosed by the electron surface

Equation (3.12) describes the area of cross-section for a general value of k_z and may be integrated to give the volume enclosed by the electron Fermi surface

$$V_e = 2 \cdot \frac{4}{3} \frac{\pi}{a_0^2} \int_{\Gamma=2}^{\Gamma_F} \frac{\frac{1}{4} \gamma_2 \gamma_5 \Gamma^2 - \frac{1}{2} \gamma_1 \gamma_2 \Gamma^3 + \Gamma^2 \left(\frac{1}{2} \gamma_2 \Delta - \frac{1}{2} E_f \gamma_2 - \frac{1}{2} E_f \gamma_5 \right) + \Gamma E_f \gamma_1 + E_f (E_f - \Delta)}{(\gamma_0 + \gamma_4 \Gamma)^2} d\Gamma$$

where the factor 2 is included since the surface is symmetric about $\Gamma = 2$. Γ_F the vertical limit of the Fermi surface occurs when $E_f = E_3^0 = \frac{1}{2} \gamma_2 \Gamma^2$

$$\Gamma_F = \sqrt{\frac{2 E_f}{\gamma_2}}.$$

The above integral is evaluated in Appendix A2, including γ_5 and to first order in γ_4 . If γ_4 and γ_5 are put equal to zero, the volume expression reduces to that of COOPER et al (1971) with terms in γ_1 having the opposite sign.

$$V_e = \frac{16 \pi}{3 a_0^2 \gamma_0^2 c_0} \left[\sqrt{\frac{2 \gamma_2 - E_f}{2 \gamma_2}} \left(-\frac{4}{3} \gamma_1 (2 \gamma_2 - E_f) - \gamma_2 (E_f - \Delta) \left(\frac{E_f}{2 \gamma_2} \right)^{\frac{1}{2}} + (E_f - \Delta) (E_f - \gamma_2) \cos^{-1} \left(\frac{E_f}{2 \gamma_2} \right)^{\frac{1}{2}} \right) \right] \dots (3.18)$$

An approximate formula for the volume obtained by assuming parabolic bands with ellipsoidal Fermi surfaces takes the form:

$$V_e = \frac{4}{3} A_c \frac{2}{c_0} \cos^{-1} \left(\frac{E_f}{2 \gamma_2} \right)^{\frac{1}{2}} \dots (3.19)$$

COOPER et al (1971) have shown that computation of the volume enclosed by

the electron surface using the approximate formula differs from that using the more precise formula of equation (3.18) by less than 8%.

(d) Volume enclosed by the majority hole surface

Contiguous with the electron surface are two majority hole surfaces. The volume enclosed is obtained by integrating equation (3.14) between the value of k_z at which the electron and hole surface meet, namely

$$k_{z1} = \frac{2}{c_0} \cos^{-1} \left(\frac{E_f}{2\gamma^2} \right)^{\frac{1}{2}}$$

and

$$k_{z2} = \frac{2}{c_0} \cos^{-1} \left(\frac{\Gamma E}{2} \right),$$

the value of k_z at which the area of the outer body is a maximum.

$$V_h = \frac{4}{3} \frac{\pi}{a_0^2} 2 \int_{k_{z1}}^{k_{z2}} \frac{\left(E_f - \frac{1}{2} \gamma_2 \Gamma^2 \right) \left(E_f - \Delta - \gamma_1 \Gamma - \frac{1}{2} \gamma_5 \Gamma^2 \right)}{\left(\gamma_0 - \gamma_4 \Gamma \right)^2} dk_z.$$

The integral differs from that describing V_e only in the signs of γ_1 and γ_4 and in the limits employed; the analysis of Appendix A2 can be used to evaluate the integral by changing the signs of terms containing γ_4 and γ_1 . In the approximation $\gamma_4 = \gamma_5 = 0$ the expression reduces to

$$V_h = \frac{16\pi}{3a_0^2\gamma_0^2c_0} \left[+4\gamma_1^2 - (E_f - \Delta)^2 \right]^{\frac{1}{2}} \left(E_f - \frac{4}{3}\gamma_2 + \frac{\gamma_2}{12\gamma_1^2} (E_f - \Delta)^2 \right) + \left(\frac{2\gamma_3 - E_f}{2\gamma_2} \right)^{\frac{1}{2}} \left\{ -\frac{4}{3}\gamma_1 (2\gamma_2 - E_f) + \gamma_2 (E_f - \Delta) \left(\frac{E_f}{2\gamma_2} \right)^{\frac{1}{2}} + (E_f - \Delta) (E_f - \gamma_2) \left\{ \cos^{-1} \left(+\frac{E_f - \Delta}{2\gamma_1} \right) - \cos^{-1} \left(\frac{E_f}{2\gamma_2} \right)^{\frac{1}{2}} \right\} \right\} \dots (3.20)$$

The ellipsoidal model is here a good approximation, and volumes calculated using the approximate formula

$$V_h = \frac{8}{3} A_h \times \frac{2}{c_0} \left\{ \cos^{-1} \frac{\Gamma E}{2} - \cos^{-1} \left(\frac{E_f}{2\gamma_2} \right)^{\frac{1}{2}} \right\} \dots (3.21)$$

differ from those calculated using equation (3.20) by less than 0.2%.

3.2.6 Application to Pyrolytic Graphite

Band theory and Fermi surface models are usually based on the nearly free electron approximation with its implicit assumption of a well ordered host lattice. However, in graphite the form of the band structure has been successfully evaluated from the symmetry properties of the crystal structure. The symmetry of good pyrolytic graphite is to a very good approximation, identical to that of the single crystal, we may therefore expect the band structure, outlined in the previous section, to apply in most respects to the compression annealed pyrolytic graphite used in this work. Experimentally this is found to be the case; WILLIAMSON et al (1965) studied the D.HvA effect in single crystal graphite and compression annealed pyrolytic graphite. By rotating the magnetic field with respect to the c -axis they were able to map the Fermi surface topology and to show that the Fermi surface of both materials is well represented by the S.W. model.

More recently COOPER et al (1971) have measured the extremal area of Fermi surface cross-section normal to the c -axis, and found the pyrolytic cross-section to be slightly larger than that in single crystal graphite. However the major difference between the two types of graphite occurs at the zone corners H and H' . Here the minority carrier oscillations for pyrolytic graphite have an anisotropy ratio, some five times greater than that for the single crystal, while the absolute value of the period is greater by 66%. The difference is explained within the framework of the S.W. model, due to a value for Δ which is an order of magnitude less in pyrolytic graphite than in single crystal material. Since Δ represents the difference in potential between A and B type atoms, and can be expressed in terms of next nearest overlaps, a low value for this parameter indicates little difference in the two types of lattice site. In this respect pyrolytic graphite behaves more like a two-dimensional solid than the single crystal, a view which is supported by the Alven wave propagation studies of SURMA

et al (1964). Conversely SdH oscillations with magnetic field directions other than normal to the basal plane are readily observed.

It is clear that pyrolytic graphite may be considered to be an assembly of crystallites each with a band structure well represented by the S.W. model.* However, the limitation on crystallite size and the common occurrence of stacking faults will affect observation of the band properties; quantum oscillations are reduced in amplitude due to scattering at crystallite boundaries resulting in an increase in effective Dingle temperature, and rotation of carriers about the Fermi surface in a non-basal plane is inhibited by stacking fault imperfection and by the c -axis misorientation function. These questions have recently been discussed in two papers by BENDER and YOUNG (1972a, 1973).

3.3 THE BOLTZMANN TRANSPORT EQUATION

A function $f_{\mathbf{k}}(\mathbf{r})$ may be defined to describe the distribution of electrons and holes in graphite such that the number of carriers in the volume element $d\tau$ with wave vector $\mathbf{k}$ in the element $d\mathbf{k}$ is on the average

$$\frac{1}{4\pi^3} f(\mathbf{k}, \mathbf{r}) d\mathbf{k} d\tau .$$

The analysis of SdH oscillations reported in Chapter V, shows that graphite has a low carrier density which at 300 K is only $\sim 1.5 \times 10^{19} \text{ cm}^{-3}$. Because of this the condition of extreme degeneracy which normally applies to metals at ambient temperatures, does not apply to graphite. However, at liquid helium temperatures all the low lying energy levels are occupied, the system is highly degenerate and $f(\mathbf{k}, \mathbf{r})$ is the Fermi Dirac distribution function

$$f(\mathbf{k}, \mathbf{r}) = f(E) = \frac{1}{1 + e^{(E-E_f)/kT}} .$$

E_f the Fermi level is determined by the number of electrons per unit volume and at absolute zero is the quantum state for which the probability of occupancy is half. A Fermi energy in graphite of 0.019 eV corresponds to a

degeneracy temperature of 220 K, as the temperature is raised towards ambient the thermal energy exceeds the Fermi energy. But the system does not approach the classical limit where $\exp(-E_f/k_B T) \gg 1$ and Maxwell-Boltzmann statistics apply.

We may reasonably assume that with the sample geometry and mounting techniques described in Chapter IV, temperature gradients are absent in the samples used for electrical measurements. Two factors then contribute to changes of the distribution function with time; first, acceleration of charge carriers by electric and magnetic fields, and secondly, collisions of charge carriers with other carriers, with thermal vibrations and with imperfections in the host lattice. The rate equation describing the change of distribution function with time is for the steady state situation:

$$\left(\frac{\partial f_k}{\partial t}\right)_{\text{diff.}} + \left(\frac{\partial f_k}{\partial t}\right)_{\text{fields}} + \left(\frac{\partial f_k}{\partial t}\right)_{\text{coll.}} = 0, \quad \dots (3.22)$$

where the first two terms describe the drift of carriers and the last term collisions.

In the presence of electric and magnetic fields the distribution function changes, because of the fields, at the rate

$$-\frac{e}{\hbar} \left(\mathcal{E} + \frac{1}{c} \mathbf{v}_k \times \mathbf{H} \right) \frac{\partial f_k}{\partial t}.$$

Similarly by assuming Liouville's theorem on the invariance of volume occupied in phase space, the rate of change of f_k due to diffusion can be shown to equal:

$$-\mathbf{v}_k \cdot \nabla_r f(k, r).$$

Substituting for spatial and potential gradients in equation (3.22), results in the Boltzmann transport equation:

$$e \left[\mathcal{E} + \frac{1}{c} \mathbf{v} \times \mathbf{H} \right] \cdot \frac{1}{\hbar} \nabla_k f(k, r) + \mathbf{v} \cdot \nabla_r f(k, r) = \left(\frac{\partial f}{\partial t}\right)_{\text{coll.}} \dots (3.23)$$

ADAMS and ARGYRES (1956) have pointed out that this equation is correct only to first order in the applied force, so that deviations from Ohm's law are not included.

3.4 SOLUTION OF THE TRANSPORT EQUATION

In Chapter VII the experimental results obtained in this work are analysed with a multi-band model based on the assumption that the energy band structure of graphite may be approximated by two bands of different curvature which overlap at the Fermi level. Evidence is presented for marked anisotropy in the carrier energy; the bands are clearly not of standard form. However, BARRIE (1956) has shown that formulae based on the assumption of standard bands can be used, provided the effective mass is replaced by expression of the form given by equation (3.4) evaluated at the appropriate energy. This consideration is of particular importance to graphite where there exist well established electron and hole effective mass spectra.

3.4.1 Relaxation Time Approximation

The collision term of equation (3.22) can be described quite generally in terms of scattering processes which take an electron from state k into a state k' . The probability of this process depends on f_k the number of carriers in the state k and on $(1 - f'_k)$ the number of vacancies in the available state. Similarly the reverse process from k' to k is weighted with $f'_k(1 - f_k)$. If we denote by $S(k, k')$ the probability per unit time that an electron in state k makes a transition to state k' , due to collisions, the nature of which is as yet undefined, the rate of change in the distribution function is:

$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll}} = \int \left\{ S(k', k) f(k') [1 - f(k)] - S(k, k') f(k) (1 - f(k')) \right\} dk'.$$

According to the principle of Microscopic Reversibility $S(k, k') = S(k', k)$, then:

$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll}} = \int \{f(k') - f(k)\} S(k, k') dk' . \quad \dots (3.24)$$

Solution of the Boltzmann equation is greatly simplified by the introduction of a collision or relaxation time τ such that

$$\frac{\partial f}{\partial t} = - \left(\frac{f - f_0}{\tau} \right) ,$$

then

$$(f - f_0)_t = (f - f_0)_{t=0} e^{-t/\tau} .$$

After a disturbance at time zero the out of balance distribution function decays to the equilibrium value with an exponential time constant τ .

PIPPARD (1965) has shown that when determining the current in the relaxation time approximation, it is sufficient to imagine the Fermi surface as a sharp division between occupied and unoccupied states, and thus to consider one electron at each point on the Fermi surface. This is due to the fact that the conductivity is independent of temperature except through changes in τ ; formulae which describe the conductivity at finite temperature also hold at $T = 0$ K when the edge of the Fermi surface is perfectly sharp. The conductivity may be evaluated from the displacement of such a hard Fermi surface. Application of an electric field $\mathcal{E}$ shifts the surface in $\underline{k}$ space by an amount $(e\tau/\hbar \cdot \mathcal{E})$ and the distribution function changes from the equilibrium value $f^0(E_k)$ to

$$f_k = f^0(E_k + e\tau v_k \cdot \mathcal{E}) .$$

Charge carriers acquire extra energy from the applied field which is equivalent to a drift velocity

$$\delta v = \frac{e\tau}{m} \underline{\mathcal{E}} .$$

If there are n particles per unit volume, the conductivity is given by equation (3.6) such that

$$\sigma = \frac{n e^2 \tau}{m^*} . \quad \dots (3.25)$$

A mean free path λ may be defined as the average distance moved by an electron in an average collision time τ_{av} . More than one process may

contribute to the scattering of charge carriers resulting in a composite mean free path and a total conductivity

$$\sigma = \sum_i \frac{n_i e^2 \lambda_i}{m_i^* v_i} \quad \dots (3.26)$$

(summation over all carriers)

with

$$\frac{1}{\lambda_i} = \sum_j \frac{1}{\lambda_j} \quad \dots (3.27)$$

(summation over all scattering processes)

The relaxation time approximation assumes the existence of either a unique or an average collision time which is independent of direction, i.e. $\underline{k}$, and of carrier energy E_k . These conditions are rarely satisfied in real conductors but the approximation can readily be generalised to take in anisotropic relaxation times, providing the scattering probability is properly weighted with respect to the scattering angle between $\underline{k}$ and $\underline{k}'$. A more serious limitation is that imposed by the fact that the relaxation time $\tau(k)$ is assumed to connect states on the same energy surface, such that the scattering process has the effect of randomising the distribution function over each surface of constant energy independently. Interactions between different energy surfaces are not accounted for, and the equilibrium distribution function for inelastic scattering processes is unknown.

At low temperatures lattice vibrations are only weakly excited and conduction is limited by imperfections in the lattice. Crystal imperfections are largely interstitials, vacancies, grain boundaries, dislocation and stacking faults, and are locked to the lattice so that a colliding electron is elastically scattered with no transfer of momentum to the imperfection. Similarly at high temperatures the phonon energy of the order $k_B \Theta$, where Θ is the Debye temperature, is small compared with the electron energy of order $k_B T$. The scattering of electrons by the phonon distribution is then once again elastic resulting only in a change of direction.

In these circumstances the relaxation time approximation is a good description of the return of the perturbed distribution function to its equilibrium value.

Processes which involve a change in energy of the current carriers occur in the cases of; electron-phonon scattering at intermediate temperatures, and carrier-carrier scattering at all temperatures. When conduction is limited by such inelastic scattering mechanisms, a better approach to the evaluation of the conductivity tensor is through the Variational Method of KOHLER (1948, 1949) and SONDHEIMER (1950).

3.4.2 The Variational Method

Solution of the integro differential Boltzmann expression of equation (3.23) has been transformed by Kohler into a variational problem by expanding the distribution function in terms of the variable which is most convenient for treating the dominant scattering mechanism, and using an appropriate variational principle to determine the coefficients. We consider the case of an electric field $\mathcal{E}$ parallel to the x-axis and in accordance with the experimental procedure outlined in Chapter IV, assume that temperature gradients in the specimen are absent. The steady state distribution function may then be written in terms of a function which measures the deviations from equilibrium in the electron distribution and takes into account the energy dependence of the equilibrium distribution

$$f = f_0 - \Phi(v) \frac{\partial f_0}{\partial E},$$

In graphite Fermi statistics apply and

$$\frac{\partial f_0}{\partial E} = f^0 \frac{(1 - f^0)}{k_B T}.$$

At the Fermi surface, the probability of an electron occupying a quantum state changes rapidly with energy and $\partial f_0 / \partial E$ reaches its maximum value.

In the absence of temperature gradients the Boltzmann equation for transport in the x direction takes the form:

$$v_x e \frac{\partial f_k^0}{\partial E_k} \cdot \mathcal{E} = \int \left\{ \left(f_k - f_k^0 \right) - \left(f_k' - f_{k0}' \right) S(k, k') \right\} dk' \quad \dots (3.28)$$

Writing

$$f_k = f_k^0 + \frac{\Phi}{k_B T} f_k^0 (1 - f_k^0)$$

and substituting in the RHS of equation (3.28) leads to a rate equation in terms of the variable φ

$$v_x e \frac{\partial f_k^0}{\partial E_k} \cdot \mathcal{E} = \frac{1}{k_B T} \int \left(\varphi_k - \varphi_k' \right) P_k^{k'} dk' \quad \dots (3.29)$$

where $P_k^{k'}$ is the transition rate between states k and k' when the system is in thermodynamic equilibrium.

If we define the scattering operator $L(\varphi)$ as equal to the RHS of equation (3.29) then L is that operator which transforms $\varphi(k)$ into another function of k through integration over $\underline{k}$ space. A convenient property of the scattering operators so defined is the fact that different scattering mechanisms represented by scattering operators are additive.

If electron-phonon, electron-ionized impurity, and electron-electron scattering are represented by L_{e-p} , L_{e-i} and L_{e-e} respectively, then

$$v_x e \frac{\partial f_k^0}{\partial E_k} \cdot \mathcal{E} = L_{e-p}(\varphi) + L_{e-i}(\varphi) + L_{e-e}(\varphi) \quad \dots (3.30)$$

When the LHS of this equation is written symbolically as $\mathcal{F}$ then

$$\mathcal{F} = \sum_i L_i(\varphi) ,$$

where the summation is over all scattering mechanisms.

Equation (3.29) can readily be generalised to account for scattering events which involve more than one current carrier. Thus the collision term of the Boltzmann equation becomes for electron-electron scattering

$$\left(\frac{\partial f_k}{\partial t} \right)_{e-e} = L_{e-e}(\varphi) = \frac{1}{k_B T} \iiint \left(\varphi_k + \varphi_{k'} - \varphi_{k''} - \varphi_{k'''} \right) P_{kk'}^{k''k'''} dk' dk'' dk'''$$

where the integration is over all electron states except that represented by the wave number $\underline{k}$.

Since $\mathfrak{F} = L\varphi$ then

$$\langle \varphi, L\varphi \rangle = \langle \varphi, \mathfrak{F} \rangle \quad \dots (3.31)$$

where $\langle \varphi, L\varphi \rangle$ is defined to equal $\int \varphi(k) L\varphi(k) dk$.

The variational principle states that of all trial functions φ_i which satisfy equation (3.31) the solution of equation (3.30) makes the integral equation $\langle \varphi, L\varphi \rangle$ a maximum. This is equivalent to saying that the solution of equation (3.30) is one which gives to the variations function

$$\frac{\langle \varphi, L\varphi \rangle}{\{\langle \varphi, \mathfrak{F} \rangle\}^2} \quad \dots (3.32)$$

its minimum value.

In physical terms the variational integral $\langle \varphi, L_\ell \varphi \rangle$ multiplied by $1/T$ is the rate of entropy production due to a scattering process of type ℓ . (APPEL (1961))

$$\dot{Q}_{\text{entropy}} = - \frac{1}{T} \int \varphi_k L_\ell \varphi_k dk.$$

A circuit such as that described in section 4.3.3 consisting of an applied electric field $\mathcal{E}$ causing a current J to flow through a resistivity ρ has a rate of entropy production equal to $\rho \frac{J^2}{T}$.

Since

$$J = \int e v_k f_k dk \quad \text{and} \quad f_k = f_k^0 - \varphi \cdot \frac{\partial f_0}{\partial \mathcal{E}}$$

then

$$J = \int e v_k \varphi \frac{\partial f_0}{\partial \mathcal{E}} dk$$

and the electrical resistivity in the steady state takes the form

$$\rho = \frac{1}{2k_B T} \iint \frac{(\varphi_k - \varphi_{k'})^2 P_k^{k'}}{\left| \int e v_k \varphi \frac{\partial f_0}{\partial \mathcal{E}} dk \right|^2} dk dk' \quad \dots (3.33)$$

Thus the electrical resistivity can be expressed in terms of the function φ without invoking the concept of a relaxation time. On comparing equation (3.33) with (3.32) it is clear that the resistivity is just the variational function in unit magnetic field.

The problem when evaluating the resistivity through the variational approach, is to obtain the function φ which makes the variational function

a minimum. In practice it is usual to define a trial function made up of known functions but with variable coefficients, the coefficients are then varied until the variational function is at its minimum value. SONDEHEIMER (1950) and APPEL (1961) have written c^n for the φ_i of the previous section, such that the variational principle requires the correct solution c^n to make the integral

$$\langle c^n, L c^n \rangle = \int_{-\infty}^{\infty} c^n L(c^n) \frac{\partial f_0}{\partial \eta} d\eta ,$$

a maximum subject to the subsidiary condition

$$\int_{-\infty}^{\infty} c^n L(c^n) \frac{\partial f_0}{\partial \eta} d\eta = \int E^n c^n \frac{\partial f_0}{\partial \eta} d\eta ,$$

i.e. $\langle c^n, L c^n \rangle = \langle c^n, \mathcal{F} \rangle$, where $\eta = (E - E_f)/k_B T$ and where the LHS of the Boltzmann equation has been replaced by E^n with corresponding solution c^n . At this stage the function to be determined namely c^n is expanded in a power series in η

$$c^n(\eta) = \sum_{\mu=0}^{\infty} c_{\mu}^n \eta^{\mu}$$

and the variational integral becomes

$$\langle c^n, L c^n \rangle = \sum_{\mu=0}^{\infty} \sum_{\nu=0}^{\infty} a_{\mu\nu} c_{\mu}^n c_{\nu}^n \quad \dots (3.34)$$

where

$$a_{\mu\nu} = \langle \eta^{\mu}, L \eta^{\nu} \rangle = \int_{-\infty}^{\infty} \eta^{\mu} L(\eta^{\nu}) \frac{\partial f_0}{\partial \eta} d\eta$$

with the subsidiary condition

$$\sum_{\mu=0}^{\infty} \sum_{\nu=0}^{\infty} a_{\mu\nu} c_{\mu}^n c_{\nu}^n = \sum_{\mu=0}^{\infty} \alpha_{\mu}^{(n)} c_{\mu}^n \quad \dots (3.35)$$

and $\alpha_{\mu}^{(n)}$ the matrix element of the operator $\mathcal{F}$ representing the LHS of the Boltzmann equation, such that

$$\alpha_{\mu}^n = \int_{-\infty}^{\infty} E^n \eta^{\mu} \frac{\partial f_0}{\partial \eta} d\eta .$$

The functions c^n which satisfy the variational principle, make the variational integral of equation (3.34) a maximum. Differentiating wrt c_{μ}^n the maximum value of the variation integral is obtained subject to the

subsidiary condition of equation (3.35) by those coefficients which satisfy the infinite set of equations

$$\sum \alpha_{\mu} \nu c_{\nu}^n = \alpha_{\mu}^n \quad \mu = 0, 1, 2 \dots$$

The evaluation of the conductivity tensor may be approached through the current density J expressed as an integral over the variable η (WILSON (1953))

$$J = \frac{16 \pi^2}{3 h^4} (2m)^{\frac{3}{2}} e \int_{-\infty}^{\infty} E^{\frac{3}{2}} c(\eta) \frac{\partial f_0}{\partial \eta} d\eta.$$

APPEL (1961) has determined $c(\eta)$ in velocity space through the expression

$$\varphi(v) = v_x \frac{m^*}{h} c(\epsilon) = v_x e \mathcal{E} c^{\frac{3}{2}}$$

where $\epsilon = E/k_B T$ is equal to η for a non-degenerate electron gas. Then

$$L\varphi(v) = \frac{v_x m^* L c(\epsilon)}{h} = v_x e \mathcal{E} L(c^{\frac{3}{2}}). \quad \dots (3.36)$$

If

$$L(c^n) = \left(\frac{\epsilon k_B T}{k_B T} \right)^{n-\frac{3}{2}} \cdot \frac{\partial f_0}{\partial \epsilon} \quad \dots (3.37)$$

Substituting for $L(c^{\frac{3}{2}})$ in equation (3.36) leads to equation (3.30).

Thus equation (3.37) is a restriction placed on the c^n by the need to satisfy the Boltzman equation. Substituting for $c(\eta)$

$$J = \frac{16 \pi^2}{3 h^4} (2m)^{\frac{3}{2}} \int_{-\infty}^{\infty} E^m c^n(\eta) \frac{\partial f_0}{\partial \eta} d\eta \left[\frac{h}{m^*} e \mathcal{E} \right].$$

Then

$$J = k_{\frac{3}{2}, \frac{3}{2}} e^2 \mathcal{E} \quad \text{and} \quad \sigma = e^2 k_{\frac{3}{2}, \frac{3}{2}}$$

where

$$k_{\frac{3}{2}, \frac{3}{2}} = \frac{16 \pi^2}{3 h^4} (2m)^{\frac{3}{2}} \int E^m c^n \frac{\partial f_0}{\partial \eta} d\eta.$$

But

$$\alpha_{\mu}^m = \int_{-\infty}^{\infty} E^m \eta^{\mu} \frac{\partial f_0}{\partial \eta} d\eta$$

and

$$c^n = \sum c_{\mu}^n \eta^{\mu}$$

therefore

$$k_{\frac{3}{2}, \frac{3}{2}} = \frac{16 \pi^2}{3 h^4} (2m)^{\frac{3}{2}} \sum_{\mu=0}^{\infty} \alpha_{\mu}^m c_{\mu}^n$$

and the infinite set of equations

$$\sum_{\nu=0}^{\infty} \alpha_{\nu}^m c_{\nu}^n - \alpha_{\mu}^n = 0 \quad \mu = 0, 1, 2 \dots$$

must be solved for the coefficients c_{μ}^n ,

Sondheimer has shown that for a non singular matrix $d_{\mu\nu}$

$$\sum \alpha_{\mu}^m c_{\mu}^n = \frac{\begin{vmatrix} \vdots & \alpha_0^m & \alpha_1^m & \alpha_2^m & \dots \\ \alpha_0^n & d_{00} & d_{01} & d_{02} & \dots \\ \alpha_1^n & d_{10} & d_{11} & d_{12} & \dots \\ \vdots & \vdots & \vdots & \vdots & \\ \vdots & \vdots & \vdots & \vdots & \end{vmatrix}}{\begin{vmatrix} d_{00} & d_{01} & d_{02} & \dots \\ d_{10} & d_{11} & d_{12} & \dots \\ d_{20} & d_{21} & d_{22} & \dots \\ \vdots & \vdots & \vdots & \end{vmatrix}} = \frac{D_{mn}}{|d_{\mu\nu}|} \quad \dots (3.38)$$

Thus finally, the conductivity is determined from the expression

$$\sigma = e^2 k_{\frac{3}{2}} \frac{e^2 16 \pi^2 (2m)^{\frac{3}{2}}}{3 h^4} \frac{D_{mn}}{|d_{\mu\nu}|}$$

by approximating the infinite determinants D_{mn} and $|d_{\mu\nu}|$ to a finite number of rows and columns.

3.4.3 Mattheisen's Rule

In Chapter VII the analysis and interpretation of experimental results is tacitly based on the application of Matthiesen's rule to the ideal and residual resistivities of pyrolytic graphite. However, Matthiesen's rule does not automatically apply, and it is only under certain circumstances that the resultant resistivity is equal to the sum of resistivities due to each type of scattering process. In the presence of, for example, carrier-carrier and carrier-ionized impurity scattering there are two equilibrium transition probabilities each defining a scattering operator. Since transition probabilities are additive then the resultant scattering operator is $L = L_{e-e} + L_{e-i}$. Substituting in equation (3.33) for the electrical resistivity

$$\rho = \frac{\langle \varphi, L_{e-e} \varphi \rangle + \langle \varphi, L_{e-i} \varphi \rangle}{\{ \langle \varphi, \mathcal{F} (\mathcal{E} = 1) \rangle \}^2}$$

φ is here the solution of the Boltzmann equation for the resultant scattering operator L and will therefore not necessarily be a solution of the

Boltzmann equation for L_{e-e} or L_{e-i} acting alone. By the variational principle such a function will make the variational function a minimum so that

$$\frac{\langle \varphi, L_{e-e} \varphi \rangle}{\{\langle \varphi, \mathcal{F}(\mathcal{C}=1) \rangle\}^2} \geq \rho_{e-e} .$$

According to this argument the resultant resistance ρ will either equal or be greater than the sum of the resistances due to each scattering mechanism acting alone.

$$\rho \geq \rho_{e-e} + \rho_{e-i} .$$

SONDHEIMER (1950) has shown that deviations increase with impurity content and are largest in that temperature region where the ideal resistance is comparable with the residual resistance. Strict application of Matthiesen's rule is only valid at high temperatures and at very low temperatures. However the rule is always a good approximation and for values of T/Θ ranging from 0.01 to 1.25 Sondheimer has shown that deviations amount to less than 1% of the total resistance.

A single relaxation time is defined in Chapter VII for each class of scattering process operating in graphite. Matthiesen's law is assumed to hold by writing the total relaxation time τ as

$$\frac{1}{\tau} = \frac{1}{\tau_{e-e}} + \frac{1}{\tau_{e\text{-phonon}}} + \frac{1}{\tau_{e\text{-ion imp.}}} + \dots .$$

The working temperature range of 300K represents values of T/Θ of between 0.009 and 1.6. Matthiesen's rule will thus apply to graphite to an accuracy of better than $\sim 1\%$.

3.5 SCATTERING PROCESSES

More than one characteristic time can be used to describe the relaxation of a perturbed distribution function due to scattering processes, but the relaxation time appropriate to electrical conductivity is the time required to randomize the velocities and restore the distribution function to the symmetrical form existing prior to the application of an electric field.

Elastic scattering will take an electron from a state moving in the direction of $\underline{C}$ to another state on the Fermi surface, making some angle θ with the applied field. The flow of current will be affected most by large angle scattering. If we define a single relaxation time it should therefore be an average of all collision times but weighted towards large angle scattering events, such that:

$$\frac{1}{\tau_c} = \left\langle \frac{1}{\tau(\theta)} [1 - \cos \theta] \right\rangle_{\text{average}}$$

where τ_c is the collision time appropriate to electrical conductivity.

Even in the presence of carrier-carrier collisions a Bloch wave of equation (3.2) would, in a single partly filled band in a perfect lattice, give rise to infinite conductivity. The finite relaxation time observed experimentally is in fact due to imperfections which destroy the perfect periodicity of the lattice.

3.5.1 The Differential Scattering Cross-Section

The probability that an electron is scattered by an imperfection in the ideal lattice can be expressed in terms of the differential scattering cross-section $Q(\theta, \varphi)$; the ratio of the number of particles scattered per unit time into an element of solid angle $d\Omega = \sin \theta d\theta d\varphi$ to the flux density of electrons. For example a spherical Fermi surface and a density N_i of impurities will give rise to an average distance λ_i between electron-impurity collisions such that

$$\frac{1}{\lambda_i} = N_i \int_0^\pi (1 - \cos \theta) Q(\theta) \sin \theta d\theta,$$

where as before the fact that we are dealing with the conductivity mean free path introduces the weighting factor favouring large angle collisions.

McCLURE and SMITH (1961) have formulated a theory for the electron transport properties of single crystal graphite when all the scattering is due to phonons. This type of scattering process is not elastic in the

temperature range considered, but McClure and Smith considered a particular group of final states 'm' having nearly the same energy as the initial unscattered electron states 'k', and assumed that the scattering potential and final density of states were almost independent of $\underline{k}$. The Golden Rule for transition probabilities (SCHIFF (1955) p.199) then gave the relaxation time in terms of the scattering potential and density of states:

$$\frac{1}{\tau} = \frac{2\pi}{\hbar} |\langle k|H|m\rangle|^2 N(E) . \quad \dots (3.39)$$

The reciprocal relaxation time $1/\tau$ is equivalent to the transition probability per unit time from one group of states to another connected by the matrix element $\langle k|H|m\rangle$.

Expressions of the form given by equation (3.39) are valid when the first Born approximation applies, i.e. when the wave function for the scattered electron is very nearly equal to that describing the electron state before the scattering event. For small relative energies this reduces to the requirement that the kinetic energy of the colliding particles be much greater than the potential energy of interaction.

In this work scattering by a screened Coulomb potential of the form

$$V(r) = z_1 z_2 \frac{e^2}{r} \exp - \left(\frac{r}{r_0} \right) \quad \dots (3.40)$$

is important because of the predominance of ionized impurity scattering in graphite at low temperatures and the contribution of carrier-carrier scattering at temperatures above about 70 K. APPEL (1960) has shown that application of the Born approximation to such scattering events requires the electron wavelength to be very much less than the Debye screening length

λ_D , i.e.

$$1 \ll \frac{\lambda_D m_{red}^* (v_1 - v_2)}{\hbar} \quad \dots (3.41)$$

where $(v_1 - v_2)$ and m_{red}^* are the relative velocity and reduced mass of the colliding particles. However, SCHIFF (1955) has pointed out that the conditions for applicability of the Born approximation outlined above,

although sufficient may be more stringent than is actually required.

Collisions resulting in small changes of momentum such as low angle scattering events, may be correctly described by formulae based on the Born approximation, while large angle scattering which corresponds to a large perturbation of the wave function, may not. Thus in Chapter VII the calculation of electron-hole scattering cross-sections, using formulae based on the Born approximation, lead to mean free paths which are in close agreement with those measured experimentally, even though equation (3.41) is not satisfied.

The differential scattering cross-section can be evaluated in the first Born approximation for the screened Coulomb field of equation (3.40).

If the initial and final states of the plane waves are described by

$$\varphi_a = e^{ik_a \cdot r} \quad \text{and} \quad \varphi_b = e^{ik_b \cdot r}$$

respectively, then the matrix element for the transition is given by

$$\langle \varphi_a | V(r) | \varphi_b \rangle = \frac{4\pi z_1 z_2 e^2}{|k_b - k_a|^2 + \frac{1}{r_0^2}}$$

and the differential scattering cross-section by

$$dQ = \left[\frac{2\mu z_1 z_2 e^2}{4\mu^2 v_R^2 \sin^2 \frac{\theta}{2} + \frac{\hbar^2}{r_0^2}} \right] d\Omega \quad \dots (3.42)$$

μ is the reduced mass of the system and v_R the relative approach velocity.

As $r_0 \rightarrow \infty$ and the screening vanishes, equation (3.42) becomes the Rutherford scattering formula, with

$$dQ_R = \left(\frac{z_1 z_2 e^2}{2 \sin^2 \frac{\theta}{2}} \right)^2 \cdot \left(\frac{1}{\mu v^2} \right)^2 \quad \dots (3.43)$$

3.5.2 The Partial Wave Approximation

In situations where the Born approximation does not apply and where the scattering potential is spherically symmetric, the partial wave approximation provides alternative expressions for the differential scattering cross-section.

The problem of the scattering of an electron wave from a field of force is identical analytically with the problem of the scattering of light from a region of varying refractive index, and the method to be outlined here is that which was first used by Mie and Debye for describing the scattering of light by molecules (BORN and WOLF (1959) p.96).

The general solution of Schrodinger's equation for a spherically symmetric potential separates the radial and angular components through the equation

$$\varphi_a(r) = \sum_{\ell=0}^{\infty} (2\ell+1) i^{\ell} j_{\ell}(kr) P_{\ell}(\cos\theta), \quad \dots (3.44)$$

where $j_{\ell}(kr)$ are spherical Bessel functions and the P_{ℓ} are Legendre polynomials of order ℓ . Thus a wave packet incident upon a spherically symmetric potential field has components corresponding to electron states each having a quantum number ℓ specifying the angular momentum. The incoming and outgoing waves can be represented as a superposition of partial waves, each corresponding to a different value of the angular momentum. If it is assumed that the scattering potential $V(r)$ can be neglected for r greater than some distance r_0 , then at large distances from the centre the Bessel functions simplify, and the solutions of wave number k and angular momentum ℓ take the form

$$\varphi(k, \ell) = \frac{A_{\ell}}{kr} \sin\left(kr - \frac{\ell\pi}{2} + \delta_{\ell}\right) P_{\ell} \cos\theta, \quad \dots (3.45)$$

where the scattering phases or phase shifts δ_{ℓ} are zero for zero scattering potential.

The differential scattering cross-section is determined by matching the solution for a plane wave representing the initial state e^{ikz} to the solution $U(r, \theta, \varphi)$ representing the scattered wave

$$U(r, \theta, \varphi) \xrightarrow[r \rightarrow \infty]{} \left[e^{ikz} + r^{-1} A(\theta, \varphi) e^{ikr} \right]; \quad \dots (3.46)$$

$A(\theta, \varphi)$ is here the scattering amplitude for the spherically symmetric

scattering potential and the differential scattering cross-section is given by

$$Q(\theta, \varphi) = |A(\theta, \varphi)|^2 .$$

Substituting the asymptotic form of equation (3.44) into (3.46) and comparing with the sum of equation (3.45) over all quantum numbers ℓ leads to an expression for $A(\theta, \varphi)$ and a total scattering cross-section Q_T of the form:

$$Q_T = \frac{4\pi^2}{k^2} \sum (2\ell + 1) \sin^{-2} \delta \ell .$$

The total scattering cross-section can thus be written as the sum of partial cross-sections Q_ℓ referring to particular values of the angular momentum quantum number

$$Q = \sum_{\ell=0}^{\infty} Q_\ell ,$$

where

$$Q_\ell = \frac{4\pi}{k^2} (2\ell + 1) \sin^{-2} \delta \ell .$$

Thus

$$k^2 = \frac{(\mu v_R^2)}{\hbar^2}$$

and the phase shifts $\delta \ell$ completely determine the scattering and the cross-section in zero when $\delta \ell$ is $\pm n\pi$.

The partial wave method is often used when the scattering potential has a short range of influence, or for scattering problems where the incident particles are of low energy. In fact the method is most commonly employed when $kr_0 \ll 1$ when only s-waves with $\ell = 0$ participate. If several values of ℓ are involved, the cross-section is determined by the interference of waves with different values of ℓ .

BENDER and YOUNG (1972b) have shown that point defects introduced into pyrolytic graphite by neutron irradiation, reduce the amplitude of majority and minority SDH oscillations primarily through s-wave scattering; this paper brings attention to an important difference between scattering cross-sections, calculated via the partial wave approximation, and those calculated

through the Born approximation. A repulsive potential results, in the partial wave approximation, in a negative value for the phase shift δ_l so that the radial wave function is retarded in phase, whereas a positive potential results in a positive value for the phase shift and a radial wave function which has phase advanced over $j_l(kr)$. Differences in the scattering cross-section for attractive and repulsive potentials are therefore to be expected. BLATT (1957) and SCLAR (1956) have estimated the scattering of carriers by charged impurities using the partial wave approach. Blatt used the screened Coulomb potential of equation (3.40) as discussed by DINGLE (1955), while Sclar used a square well for an attractive potential, and a square barrier to represent a repulsive potential. Sclar was able to obtain analytical solutions for s-wave scattering. Blatt on the other hand numerically integrated the radial wave equation for angular momentum up to $l = 5$. The results of the two approaches were in good qualitative agreement and showed that in the Born approximation attractive and repulsive potentials lead to identical cross-sections. However, at low temperatures the Born approximation fails and considerably over-estimates the cross-section. In the partial wave approach an attractive potential scatters more effectively than a repulsive potential, the ratio Q_{attr}/Q_{rep} is typically 2-3 at intermediate temperatures, increasing with decreasing temperature. Sclar has suggested that attractive potentials scatter low energy particles more strongly than repulsive potentials because at low temperatures there is a chance that a particle may be bound by an attractive potential. At high temperatures there is little probability that a particle will swing into orbit about the scattering centre, and repulsive and attractive potentials should present equal scattering cross-sections, diverging as the temperature is reduced.

3.5.3 Lattice Vibrations

Thermal motion of the ions in a crystal lattice result in lattice vibrations which are able to scatter current carriers and thereby to contribute to the electrical resistivity. Since the spectrum of lattice vibrations can be reduced to a set of simple harmonic oscillators, the vibrations are quantized such that the average total energy of the system is given by

$$E_{\text{Lattice}} = \sum_{\underline{q}, s} \frac{\hbar \nu_{\underline{q}, s}}{\left(e^{\hbar \nu_{\underline{q}, s} / k_B T} - 1 \right)}$$

where the summation is over all wave vectors $\underline{q}$ and polarisations s .

The vibrational quanta each carry an energy $\hbar \nu(\underline{q}, s)$ and momentum $\hbar \underline{q}$. A collision in which an electron of wave number $\underline{k}$ is scattered into a state $\underline{k}'$ by a phonon of wave number $\underline{q}$ must conserve momentum:

$$\underline{k} - \underline{k}' - \underline{q} = 0.$$

Since momentum can be transferred to the lattice as a whole Umklapp processes can occur in which

$$\underline{k} - \underline{k}' - \underline{q} = \underline{K}$$

where $\underline{K}$ is a principal vector of the reciprocal lattice.

Phonon scattering is inelastic but at low temperatures when the electron kinetic energy is much greater than the phonon energy, lattice scattering is assumed to be almost elastic with electrons scattered from one point on a constant energy surface to another. The transition probability has been calculated through the Born approximation resulting in an expression for $S(\underline{k}, \underline{k}')$ of the form

$$S(\underline{k}, \underline{k}') = \frac{2\pi}{\hbar} |\langle \underline{k}' | U | \underline{k} \rangle|^2 \delta(E(\underline{k}) - E(\underline{k}')) \dots (3.47)$$

van WIERINGEN (1954) has investigated the validity of this approach and carried the perturbation theory to fourth order in the perturbing potential. Corrections were found to be of order $\hbar / \tau_0 E_f$, where τ_0 is the relaxation time calculated in lowest order, and should generally be negligible providing $k_B T < E_f$. For graphite with a degeneracy temperature of

220 K the condition is satisfied only at low temperatures. However the correction terms are of order 10^{-3} and the Born approximation applies over the whole 300 degree temperature range examined in this work.

3.5.4 Lattice Controlled Mobility in Graphite

McCLURE and SMITH (1961) employed the deformation potential theory of BARDEEN and SHOCKLEY (1950) to evaluate the scattering potential U of equation (3.47) and the Golden Rule of equation (3.39) to calculate transition probabilities, without explicitly including the frequency spectrum of lattice vibrations. Separate deformation potentials for electrons and holes were varied in a numerical integration of equations of the form (3.7). It was found that the characteristic knee in the resistance versus temperature curve of Fig.7.1, was not reproduced unless electron-hole surface interband scattering was included. A reasonably good fit to the resistivity curve was obtained with this model, but the calculated magnetoresistance at 77 K was only half the experimental value and the calculated Hall coefficient for pure graphite was of the wrong sign. Clearly a model of the ideal resistivity in graphite seeking to explain effects in which the two types of carrier oppose, cannot afford to neglect the phonon spectrum.

In the temperature range from absolute zero to 60 K lattice vibrations in graphite are well described by the semi continuum model of KOMATSU (1951,1955). In this work elastic constants within a layer plane were calculated from a modified form of the force constants of the benzene molecule and the compressional coupling constant determined from the measured compressibility. By neglecting the shearing coupling between planes, the secular equation could be solved for two roots, resulting in a complete separation of the lattice vibrations into two independent parts, namely vibrations with displacements normal to the planes and those with displacements parallel to the planes. Debye's three-dimensional theory was employed to estimate formulae for the specific heat resulting in a characteristic

temperature Θ_z of 180.5 K for lattice waves propagating along the c-axis and 2480 K for vibrations parallel to the layers. Above 60 K calculated values were consistently lower than measured specific heats. The continuum treatment describes correctly long wavelength, low frequency vibrations but fails at higher temperatures where short wavelength phonons sample the atomic nature of the graphite lattice.

An atomistic Born-von Karman treatment of the graphite lattice by YOSHIMORI and KITANO (1955) considered the actual restoring forces between atoms displaced by lattice vibrations, with the potential energy expressed as quadratic terms of the displacement. Again the secular determinant could be separated into two parts representing in-plane vibrations and phonons with polarization vectors perpendicular to the layer planes. Debye temperatures of 1400 K and 180 K were estimated for longitudinal acoustic vibrational modes in and perpendicular to the planes respectively. Optical modes of vibration were shown to be effective only at temperatures exceeding about 1800 K and the specific heat arising from vibrations in the plane obeyed a simple T^2 law. However, vibrations perpendicular to the layer were not simply two-dimensional, off axis components reflected the strong forces due to bonding in the layer planes, and resulted in a complex temperature dependence for the specific heat due to vibrations propagating along the c-axis.

Theoretical calculations of the electrical conductivity of graphite parallel to the layer planes by SUGIHARA et al (1963, 1966, 1968) assumed that lattice scattering is dominant in the temperature range 77 to 25 K. This is possibly the case for good single crystal specimens, but in pyrolytic graphite scattering by ionized impurities causes the mobility to deviate from the usual $T^{-1.2}$ dependence at temperatures as high as 100 K. It is shown in Chapter VII that a third scattering mechanism, namely first order carrier-carrier collisions, plays an important role in determining electrical

conduction at temperatures above that of liquid nitrogen. Sugihara calculated the electron-phonon interaction in the rigid ion approximation and according to the work outlined above, grouped the lattice vibrations into two modes with polarization in and perpendicular to the basal plane. In the long wavelength limit the dispersion curve in the q_x, q_y plane is linear

$$w_{\parallel} = v_{\parallel} q_{\rho} \quad v_{\parallel} = 2 \times 10^6 \text{ cm/sec}$$

$$q_{\rho}^2 = q_x^2 + q_y^2$$

Perpendicular to the basal plane the dispersion relation becomes:

$$w_{\perp} = v_{\perp} |q_z| \quad v_{\perp} = 3 \times 10^5 \text{ cm/sec}$$

The maximum value of $hw_{\parallel}$ which could scatter electrons in the basal plane was shown to be of order 10^{-3} eV. Scattering of charge carriers at the Fermi surface of graphite is thus to a good approximation elastic and the Born approximation applies.

The very large increase of charge carrier concentration on application of pressure, described in Chapter VI, supports the view proposed by YOUNG (1968) that the coupling between charge carriers and the longitudinal c-axis vibrational mode of YOSHIMORI and KITANO (1956) is very strong. So strong in fact, that a composite phonon composed of longitudinal q_z and q_{xy} components have parent modes consisting solely of q_z and slight off axis vibrations. As the temperature of the specimen is raised from 0°K off axis phonons and those with wave vector q_z will scatter charge carriers contributing to c-axis conduction, through large angles above ~60 K. At higher temperatures basal plane conduction will be similarly affected.

3.5.5 Scattering by Crystal Imperfections

Crystal imperfections of the type discussed in section 1.5.2 function essentially as static obstacles. Specifically neutral impurity atoms and interstitial ions are at least 10^3 times heavier than current

carrying electrons and holes. Scattering by static crystal imperfections is thus, to a good approximation, an elastic process. In this case the equilibrium Boltzmann distribution for scattered carriers can be equated to the distribution appropriate before the scattering event $f_0(k') = f_0(k)$.

The collision term of equation (3.23) becomes

$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll}} = - f_1(k) \int \left[1 - \frac{f_1(k')}{f_1(k)}\right] S(k, k') dk',$$

where the integral is over the constant energy surface defined by $E(k) = E(k')$.

In the case of elastic scattering, a relaxation time may therefore be formally defined as:

$$\frac{1}{\tau_{\text{elas}}} = \int \left(1 - \frac{f_1(k')}{f_1(k)}\right) S(k, k') dk'. \quad \dots (3.48)$$

The perturbing potential due to crystal imperfections is, with the exception of line and planar defects, normally considered to be spherically symmetric. Thus a material with parabolic energy bands has a transition probability $S(k, k')$ which is determined only by the magnitude of $|\underline{k} - \underline{k}'|$ and the scattering angle, i.e. the transition probability is independent of the direction of scattering, relative to the crystal axes. However in graphite, with its elongated cigar shaped Fermi surfaces, the relaxation time described by equation (3.48) is highly anisotropic and reflects the anisotropy in the scattering cross-section.

3.5.6 Imperfection Controlled Mobility in Graphite

At low temperatures collisions of current carriers with ionized impurities and stacking faults are by far the most important scattering events. FRIEDEL (1954) has shown that the Born approximation cannot normally be applied when calculating the scattering cross-section of ionized impurities in metals. However the formula of CONWELL and WELSKOFF (1950) is commonly used to describe the relaxation time and the corresponding 'imperfection mobility'.

The total scattering cross-section of a Coulomb potential, as expressed by the Rutherford formula of equation (3.43) diverges because of the large contribution from small angle scattering. Conwell and Weiskopf by-passed this difficulty by assuming that if $2\bar{d}$ is the average distance between impurity ions, an electron is scattered only when it approaches to within a distance $\bar{d}$ of that ion. Such a restriction on the impact parameter sets a lower limit on the integral of differential scattering cross-section over the scattering angle and leads to a mean free path given by:

$$\lambda_{c-imp} = \frac{\xi^2 m^2 v^4}{\pi N e^4 \ln \left(1 + \frac{\xi^2 m^2 v^4 \bar{d}^2}{e^4} \right)}$$

where ξ is the dielectric constant, v the carrier velocity and N the concentration of ionized impurities. This formula is used in section 7.6 to calculate limitations on carrier mean free path imposed by neutron damage in pyrolytic graphite.

Vacancies, which are already present in pristine graphite, can be produced together with vacancy pairs by irradiation with fast neutrons. This type of imperfection acts as an acceptor, trapping electrons from the conduction band and lowering the Fermi level. The negatively charged point defects so formed dominate the relaxation time in basal plane conduction over the whole of the temperature range 0 - 300 K. But, in pyrolytic graphite at least, the c -axis mean free path at room temperature is already limited to approximately the interlayer spacing, and irradiation has only a slight effect on the carrier mobility.

There has been some discussion as to whether stacking faults can scatter conduction electrons at all strongly. BLATT, HAM and KOEHLER (1956) concluded that they are not effective in scattering electrons in Cu and Ag but make a significant contribution in Au. In graphite stacking faults are common and although their distribution and spacing are largely unknown, there appears to be no doubt that scattering at stacking faults enhance

Dingle temperatures as the carrier orbit is tilted to sample more c-axis motion. This finding supports the conclusion of SEEGER (1956) that stacking faults are strong scatterers of conduction electrons. An upper limit of $\sim 1370 \text{ \AA}$ for the stacking fault spacing was estimated by BENDER and YOUNG (1973), although it is more common to quote values in the range 20-30 $\text{\AA}$ for stress annealed pyrolytic graphite.

Dislocations are known to act as electron acceptors in Ge and Si (SHOCKLEY (1953)). If this were the case in graphite, the high concentration of basal plane dislocations would result in a dislocation becoming a negative line charge exerting a strong perturbing potential and acting as a very effective scatterer of conduction carriers. However, there is evidence (SPAIN, UBBELOHDE and YOUNG (1967)) to show that at low temperatures basal plane relaxation times are determined by scattering at boundaries of grains typically 1-3 μm in extent. The dislocation concentration appeared to be effective only in causing some selective loss of amplitude in the electron term of SdH oscillations, due presumably to the greater trigonal fluting of the electron surface.

3.5.7 Particle-Particle Collision Scattering

The charged particle concentration in a metal constitutes a very dense plasma; three or four orders of magnitude more dense than plasmas known to be collision dominated. Particle-particle collisions occur which reduce the current carrying capabilities of the plasma and thus contribute to the resistance.

Charged particles interact through the Coulomb potential of equation (3.40) but the scattering cross-section diverges for the Coulomb field, in the Born approximation, for collisions which result in an increasingly diminished change of momentum. At the same time the phase shifts δl calculated with the partial wave method, increase logarithmically with

increasing r and an exact solution of the problem again yields the Rutherford scattering formula which diverges for small angle scattering. It therefore appears that the transition probability becomes very large for small changes of momentum and electrons are constantly undergoing small angle scattering events. However, the fact that the interaction between distant electrons does not fall off fast enough as the distance tends to infinity, which is the source of the divergence, also means that the movement of any one electron causes all other electrons to move in sympathy. Any local movement in the charge cloud induces the whole cloud to move and try to neutralize the region of density deficit. The movement overshoots forming an excess of charge which the cloud attempts to remove by expanding; long wavelength oscillations are set up in the plasma with a frequency given by BOHM and PINES (1952) as $\omega_p = (4\pi ne^2/m)^{\frac{1}{2}}$. However, particles moving with velocity almost equal to the phase velocity of the wave can be trapped in a stable position by the wave and carried along with it. If there are more particles moving slower than the phase velocity than there are moving faster, energy will be transferred from the wave into thermal energy and the wave will suffer the familiar 'Landau damping'. The criteria for the oscillation to be undamped defines a minimum wavelength λ_D equal to $2\pi/(\omega_p/v)$. In a metal, v is the velocity at the Fermi surface, although in a non-degenerate distribution it is the particle thermal velocity. COHEN, SPITZER and RUTLY (1950) have shown that in an ionized gas the cut-off distance, beyond which a charged particle is completely screened from its neighbours, is the minimum wavelength for collective plasma oscillations, namely the Debye length $\lambda_D = (k_B T / 4\pi ne^2)^{\frac{1}{2}}$.

For degenerate distributions FRIEDEL (1954) has assumed the Fermi energy to be constant throughout the material, and on introducing a test charge, has shown that the range of influence of the perturbing charge is reduced to a screening length $\{6\pi e^2 N(E_F)\}^{-\frac{1}{2}}$. The density of states

function $N(E_f)$ is only rarely given by the nearly free electron formula of equation (3.5), and provides a major difficulty in evaluating screening distances in degenerate distributions.

By limiting the range of influence of the Coulomb field, the perturbation due to a point charge falls off rapidly at distances greater than the screening length, and transition probabilities no longer diverge for collisions which result in small changes of momentum. However, large range collisions corresponding to small angle deflections are still possible within the Debye sphere and CHANDRESEKHAR (1943) has shown that such interactions will dominate the scattering process. Both large and short range collisions lead to a scattering cross-section which is a strong function of energy.

Thus if b_0 of Fig.3.3 is the impact parameter and the incoming particle is scattered through 90° corresponding to a short range collision then the distance of closest approach is $2b_0$. The electron which is being scattered will continue to approach the scattering electron until the relative

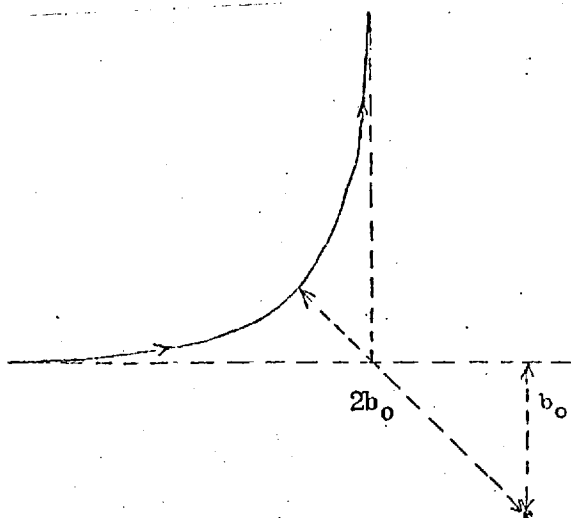


Fig.3.3
Short range Coulomb interaction
resulting in 90° deflection

kinetic energy of the two particles equals the mutual potential energy, i.e.

$$W_{k.e.} = \frac{e^2}{2b_0} .$$

Those particles which approach with an impact parameter b_0 or less, will be scattered through 90° or more. The area of cross-section is defined as the area of a circle with radius b_0

$$Q_{s.r.} = \frac{\pi e^2}{4 W^2}$$

$Q_{s.r.}$ the short range scattering cross-section is thus given by

$$\frac{\pi e^2}{2\mu v_R^2}$$

where μ is the reduced mass of the system and v_R the relative approach velocity.

The scattering cross-section for long range collisions $Q_{l.r.}$ is obtained by calculating the mean square change of momentum on collision and contains the Debye length λ_D as a parameter

$$Q_{l.r.} = \frac{2\pi e^2}{W^2} \ln \frac{\lambda_D}{b_0}.$$

The $\ln$ term is a slowly varying function of temperature and the cross-section is again dominated by the square of the relative kinetic energy of the colliding particles. It is this energy dependence which causes the resistivity due to carrier-carrier and ionized impurity scattering to decrease with increasing temperature according to $T^{-\frac{3}{2}}$.

In a solid, carrier-carrier scattering is very rarely the only scattering mechanism of importance, and the variational approach of section 3.4.2, in which scattering mechanisms are additive, is commonly employed to describe the collision term of equation (3.23). Electrical resistivity is described by the variational function of equation (3.33), for carrier-carrier scattering. the variational integral takes the form:

$$\langle \varphi, L_{c-c} \varphi \rangle = \frac{1}{8k_b T} \iiint \left\{ \varphi_{k_1} + \varphi_{k_2} - \varphi_{k'_1} - \varphi_{k'_2} \right\} P_{k_1 k_2}^{k'_1 k'_2} dk_1 dk_2 dk'_1 dk'_2$$

for collisions in which carriers of wave vectors k_1 and k_2 are mutually scattered into states k'_1 and k'_2 . If the conductor consists of a single energy band and the scattering probability depends only on the angle between k and k' , and not on their orientation in the crystal, ZIMAN (1960) has shown that an exact solution of the Boltzmann equation is $\varphi_k = \alpha \underline{k} \cdot \underline{u}$, where $\underline{u}$ is a unit vector parallel to the electric field. Then:

$$\left\{ \varphi_{k_1} + \varphi_{k_2} - \varphi_{k'_1} - \varphi_{k'_2} \right\} = \left\{ \underline{k}_1 + \underline{k}_2 - \underline{k}'_1 - \underline{k}'_2 \right\} \cdot \underline{u}.$$

The Law of Conservation of Momentum requires the bracketed term on the RHS of this equation to equal zero. Carrier-carrier scattering has therefore no effect on the resistivity expressed as the minimum value of the variational function in unit electric field. In fact it is generally stated that carrier-carrier scattering has no influence on carrier mobility since the total momentum remains unaltered in such collisions. However, this is not always the case since electric current is proportional, not to the total momentum, but to the charge times the particle velocity. If the resistivity is to be unaffected, then it is the total velocity in the direction of the applied field which must be conserved. The current corresponding to an electron in a state k_1 is $e\hbar k_1/m_1$ and the change produced is the current by a collision between states k_1 and k_2 is:

$$e\hbar \left(\frac{k_1 - k'_1}{m_1} + \frac{k_2 - k'_2}{m_2} \right) = e\hbar \left(\frac{1}{m_1} + \frac{1}{m_2} \right) (k_1 - k'_1) .$$

Thus when there are two or more effective masses present the change in current due to carrier-carrier collisions is proportional to the change in momentum $\hbar(k_1 - k'_1)$ of one of the carriers, and this is not necessarily conserved. Carrier-carrier collisions can in this situation make zero order contributions to the total resistance.

Conservation of momentum is described by an equation of the form

$$\underline{k}_1 + \underline{k}_2 = \underline{k}'_1 + \underline{k}'_2 \quad \dots (3.49)$$

where k_1, k_2 are the original carrier states, and k'_1, k'_2 the final states. Umklapp processes can occur, in which momentum is conserved, through the addition of the reciprocal lattice unit vector to equation (3.49). ZIMAN (1960) has shown that the resistivity due to electron-electron Umklapp scattering is determined by an interference term, which introduces the lattice explicitly by expressing the wave function in Bloch form, and by the term $(k_D T/E_f)^2$.

Interband scattering as discussed by BABER (1937) and APPEL (1961) makes a zero order contribution to the resistivity which is determined by the ratio of the effective masses m_1/m_2 of the scattering carriers, and by the factor $(k_B T/E_f)^2$. Large values of the effective mass ratio occur for s-d scattering in transition metals, and MENDELSSOHN (1956) and WHITE and WOODS (1959) have shown that Fe, Co, Ni, Pt, Pd, In, Mo and Rh exhibit, at low temperatures, a T^2 temperature dependence consistent with carrier-carrier scattering.

Both N and U processes have a temperature dependence determined by $(k_B T/E_f)^2$. This term, which applies only to degenerate distributions, arises from a double application of the Pauli exclusion principle to the scattering carrier. The carrier which is scattered suffers a loss of energy which must be less than $k_B T$ since it must jump to an unoccupied state. Thus the scattering electron cannot gain energy more than $k_B T$. As this electron must also jump to an unoccupied state, then before the collision it must already be within $k_B T$ of the Fermi level. The scattering carrier must therefore be within $k_B T$ of the Fermi level before and after the scattering event. Thus, if E_f is the Fermi energy for the scattering carrier, then of all possible collisions only a fraction $(k_B T/E_f)^2$ is allowed by the exclusion principle. The analysis of Chapter VII employs this term to account for the diminished importance of carrier-carrier scattering in graphite with decreasing temperature.

A second consequence of the Coulomb interaction between particles is the fact that even if certain types of carrier-carrier collisions do not affect the current density directly, they do tend to randomize the way in which the total momentum is distributed among the different velocity groups. When an electric field is applied to a distribution in equilibrium, a steady state is reached by collisions between accelerated electrons and

the lattice. The distribution, previously represented by f_0 acquires a perturbation f_1 and becomes $f_1 = f_0 + f_1$. In the presence of carrier-carrier collisions it is the perturbation f_1 which induces a further small perturbation f_2 and the total perturbation $f_1 + f_2$ is responsible for determining the current. However the size of the perturbation f_2 depends on f_1 creating a non-uniform velocity distribution, i.e. it depends on the scattering mechanism favouring one part of the velocity distribution. Carrier-carrier collisions will then be instrumental in transferring momentum from carriers which dissipate momentum less efficiently through collision with the lattice to those which dissipate it more efficiently, resulting in a more rapid transfer of carrier momentum and a lower mobility.

When several scattering mechanisms are operative, McCLEAN and PAIGE (1960) have pointed out that the reduction in mobility caused indirectly by carrier-carrier scattering, is determined by the energy dependence of the net relaxation time τ_R due to all the scattering mechanisms, where

$$\frac{1}{\tau_R} = \sum_i \frac{1}{\tau_i}.$$

The reduction of ionized impurity controlled mobility was found to be by a factor of 0.58 for equal concentrations of carrier and ionized impurities, while the mobility due to phonon scattering was reduced by $\sim 12\%$. In the limit of carrier-carrier collisions being completely effective in randomizing the drift velocities, the electron distribution in an electric field would be f_0 centred on a velocity equal to the drift velocity due to the applied field. HERRING (1950) has shown that in this situation the maximum effect of collisions would be to reduce the mobility due to ionized impurity scattering by a factor 0.3 and that due to phonon scattering by a factor 0.88.

APPEL (1960) has applied the generalised variational principle to show that the elements of the determinant D_{mn} of equation (3.38) which

describe a binary scattering process, are of the form:

$$d_{rs}^{e-e} = \frac{4}{k_B T} \left(\frac{m^*}{h} \right)^6 \int_v \int_{v_1} \int_{\chi} \int_{\gamma} \exp (\mathcal{E} + \mathcal{E}_1 - 2\rho / k_B T) f_0 f_{01} f'_0 f'_{01} \\ \times \left(\frac{v_x}{v} \right)^2 \eta^r \left[v \cdot v \eta^s + v \cdot v_1 \eta_1^s - v \cdot v' (\eta')^s - v \cdot v'_1 (\eta'_1)^s \right] \alpha(\chi, g) \sin \chi \, d\chi \, d\gamma \, dv_1 \, dv .$$

Where $\sin \chi \, d\chi \, d\gamma$ is the scattering solid angle $d\Omega$ and $2/g \cdot \alpha(\chi, g) d\Omega$ represents the effective scattering cross-section for electrons.

When the law of conservation of momentum also implies conservation of velocity $dr_s^{(e-e)} = 0$ for r or s equal to zero. Thus electron-electron scattering will not affect the first term in the expansion of c^R . But this term largely determines the resistivity; carrier-carrier scattering in this situation will not affect the electrical conductivity to zero order in the energy parameter η . The convergence of the conductivity $\sigma^{(n)}$ is determined by the energy dependence of the perturbation $c(\epsilon)$ and in practical cases this converges rapidly after first order correction. The indirect effect of carrier-carrier collisions on the electric current is thus chiefly a correction to first order in the energy parameter η . When equation (3.49) does not imply conservation of velocity, particle-particle scattering is effective to zero order. Since the cross-section for Coulomb scattering described either by the Born approximation or the partial wave method is inversely proportional to the square of the total approach velocity, the scattering process has a strong energy dependence. First order carrier-carrier scattering will then be effective in randomizing the momentum among the different velocity groups. Thus if carrier-carrier scattering is effective to zero order, first order contributions will increase the effectiveness of this scattering process by up to a maximum of 70%.

3.5.8 Carrier-Carrier Controlled Mobility in Graphite

Transport processes in graphite have previously been discussed almost entirely in terms of a model based on the assumption that carrier-carrier scattering may be neglected. However, SUGIHARA (1966) when attempting to explain the positive sign of the zero field Hall coefficient in terms of the scattering by majority holes of minority electrons showed that in the Born approximation the relaxation time of the majority carriers is reduced due to the zero order influence of carrier-carrier scattering by a factor of 1.3 at 77 K. This effect which has been overlooked by workers in this field is of crucial importance in the understanding of hitherto unexplained changes in the electrical conductivity resulting from the applications of hydrostatic pressure.

The parameters which determine the effectiveness of carrier-carrier scattering are the carrier density and the ratio of the effective mass of the majority carriers. In graphite these parameters are very similar to those found in semiconductors known to be dominated by carrier-carrier scattering. Thus, electrical conductivity in the intrinsic range of Ge is dominated at 1000 K by zero order electron-hole scattering, which decreases the sum of electron and hole mobilities by a factor of 0.6; (MORIN and MAITA (1954), APPEL and BRAY (1962)). Carrier density at this temperature is 10^{19} cm^{-3} and the effective mass of the electron is almost twice that of the hole. Such values are almost identical to those applying to single crystal and pyrolytic graphite at room temperature. InSb has a carrier mobility which although very large should be larger, and zero order electron-hole scattering is invoked, to bring theory into agreement with experiment (EHRENREICH (1957), 1958)). Carrier-carrier scattering first becomes important in this material at 500 K where the total carrier concentration is only 10^{18} cm^{-3} . At 1000 K the concentration has risen by a factor of 10 and electron-hole scattering is the dominant scattering process.

Further evidence for the importance of Coulomb interactions in graphite becomes apparent when the energy of a plasma quanta ($\hbar \omega_p$) is compared with the measured Fermi energy. At room temperatures a typical value for electron and hole densities is $7.2 \times 10^{18} \text{ cm}^{-3}$. But the basal plane effective mass m_{11}^* at $\sim 0.05 m_0$ is some 200 times smaller than the corresponding c -axis effective mass m_{33}^* . Assuming a high frequency dielectric constant ϵ equal to 4 (McCLURE (1964)) the energy quanta of plasma oscillations, given by $\hbar(4\pi e^2 n / m \epsilon)^{\frac{1}{2}}$ for the above parameters is $\sim 0.22 \text{ eV}$ parallel to the basal plane and $\sim 0.015 \text{ eV}$ for motion along the c -axis. Plasma quanta therefore propagate along the c -axis with energy approximately equal to the graphite Fermi energy and Coulomb interactions will not play a dominant role. But the basal plane quanta are an order of magnitude larger than the Fermi energy. PINES (1963) has shown that when $(\hbar \omega_p / E_f) > 4$ the Coulomb interaction is so strong that the ground state corresponds to an electron solid. Coulomb interactions between charged carriers are therefore expected to greatly influence transport properties in which carriers propagate along the basal planes and will influence c -axis properties to a lesser extent. This result is consistent with the conclusions of Chapter VII, namely that carrier-carrier scattering is much more effective in reducing the mobility of basal plane current carriers than those propagating along the c -axis.

DRESSELHAUSE and MAVROIDES (1964) have shown that the effective mass of the graphite majority hole carrier m_{11}^* (hole) increases from near zero at point H in the Brillouin zone to a maximum singularity at $k_z \frac{c_0}{2} \approx 0.24$. The electron effective mass is however only weakly dependent on $\frac{k_z}{2}$ and takes an average value of $0.057 m_0$ which is almost constant over the length of the Fermi surface. Hole-hole scattering, effective to zero order, will thus contribute to the resistivity with heavy, less mobile, carriers acting as scattering centres for mobile current carriers of low effective mass. Electron-electron scattering on the other hand will not influence the conductivity to zero order. Umklapp scattering can occur in graphite only for those carriers situated near the nose of the cigar shaped Fermi surface

SUGIHARA and SATO (1963) and can be neglected in both carrier-carrier and phonon-phonon scattering events.

Interband electron-hole scattering will reduce the conductivity to zero order in two ways:

- (a) When the density of electrons and holes are not equal, or the mass of one type of carrier is greater than the other, then drag occurs in which one type of carrier experiences a retarding force in the opposite direction to the current.
- (b) Even with equal electron hole masses and equal densities, electron-hole scattering will still influence the conductivity to zero order because of the relative motion of the two types of carrier. This effect is analogous to ionized impurity scattering and has the same temperature dependance namely $T^{+\frac{3}{2}}$ in the mobility term.

APPEL (1963) has evaluated a zero order approximation to the total electrical conductivity limited solely by interband electron-hole scattering:

$$\sigma^{(0)} = \frac{\sigma_e + \sigma_h + \sigma_e \sigma_h \left(\gamma + \frac{1}{\gamma} - 2 \right) C \left(\frac{k_B T}{E_f} \right)^2}{1 + \left(\gamma \sigma_h + \left(\frac{1}{\gamma} \right) \sigma_e \right) C \left(\frac{k_B T}{E_f} \right)^2}$$

where

$$\gamma = \frac{n_e}{n_h} \left(\frac{m_h}{m_e} \right)^{\frac{1}{2}} \quad \text{and} \quad C = \frac{Q_{e-h} (m_e m_h)^{\frac{1}{2}} v_{e-h}}{e^2}$$

Q_{e-h} is the electron-hole scattering cross-section and v_{e-h} the relative approach velocity. When $\gamma = 1$ the second term in the denominator represents scattering of the ionized imurity type. When $\gamma \neq 1$ the third term in the numerator accounts for drag of electrons by holes and holes by electrons.

The difficulty in evaluating the type of expression for graphite is the lack of information on the absolute value of the scattering cross-section Q_{e-h} . The Born approximation may be applied to calculate Q_{e-h} when equation (3.41) is satisfied. That is, when the electron wavelength is much smaller than the Debye length. When conduction in graphite is non-

degenerate this criterion becomes

$$\left(\frac{\xi k_B T}{4\pi n e^2}\right)^{\frac{1}{2}} \frac{m_h m_e}{m_e + m_h} \cdot \frac{0.73}{\hbar} \left(\frac{8 k_B T}{\pi \left(\frac{m_e m_R}{m_e + m_R}\right)}\right)^{\frac{1}{2}} \gg 1 . \quad \dots (3.50)$$

Electron and hole effective masses of $0.057 m_0$ and $0.039 m_0$ are known to represent good averages for the range of effective masses contributing to basal plane conduction. Substituting in the above formula leads to a value of 0.09 for the LHS. Perpendicular to the basal plane effective masses are orders of magnitude greater and values of $m_e = 14 m_0$ and $m_h = 5.7 m_0$ are consistent with experimental observation (SPAIN et al (1967); SPAIN (1971)). The LHS of equation (3.50) is in this case equal to 1.20.

The criterion for application of the Born approximation is therefore not strictly satisfied for carriers propagating either perpendicular or parallel to the basal plane of graphite. Models of carrier-carrier scattering based on the Born approximation are thus expected to provide only order of magnitude estimates for carrier-carrier relaxation times and mean free paths for carriers propagating along the c-axis and to be less applicable to basal plane conduction.

In view of the uncertainty in the absolute value of the scattering cross-section, the analysis of Chapter VII outlines a comparative study of the influence of carrier-carrier scattering on basal plane and c-axis conduction. To this end we assume that an average total scattering cross-section Q_{c-c} can be specified for transport in the basal plane and c-axis directions. For this situation APPEL (1963) and ABRAHAM (1954) have defined an average relaxation time for carrier-carrier collisions:

$$\tau_{c-c} = \frac{1}{N Q_{c-c}} \cdot \left(\frac{k_B T}{E_f}\right)^2 \frac{1}{v_R} .$$

v_R is the average relative approach velocity and N the number of electrons/holes. Q_{c-c} the total scattering cross-section is inversely proportional to the square of the total kinetic energy of the colliding

particles, such that the average mean free path between carrier collisions is given by

$$\lambda_{c-c} \propto \frac{1}{N|W|^{-2}} \left(\frac{k_B T}{E_f} \right)^2 \dots \dots (3.51)$$

The factor $(k_B T/E_f)^2$ will become dominant at temperatures well below the degeneracy temperature of 220 K.

3.6 CONDUCTION AT HELIUM TEMPERATURES

It is well known that in the presence of a magnetic field the motion of an electron transverse to the field is quantized with cyclotron frequency $\omega_c = eB/m^*c$. Parallel to the field electron motion is unaffected. In this section the quantization occurring at low temperatures, when $\omega_c \tau > 1$, is shown to result in oscillations in the density of states at the Fermi surface which are manifest in the electrical conductivity as a function of increasing magnetic field.

The Hamiltonian for an electron of mass m^* takes the form

$$H = \frac{1}{2m^*} \left(p + \frac{e\mathbf{A}}{c} \right)^2.$$

$\mathbf{A}$ is the vector potential defining the field and for a magnetic field in the z direction is described by the gauge $(0, B_x, 0) = (A_x, A_y, A_z)$. Substitution of the Hamiltonian into Schrodinger's equation leads to the equation of an harmonic oscillator of angular frequency ω_c centred at the point $\hbar k_y/eB$ and with a force constant $e^2 B^2/m$.

The electron eigenvalue excluding spin, are in this case

$$E_n = \left(n + \frac{1}{2} \right) \hbar \omega_c + \frac{\hbar^2 k_z^2}{2m^*},$$

where n is the oscillator quantum number. Electron kinetic energies along the field represented by the second term are unaffected, but the motion in a plane normal to B is quantized with $\hbar \omega_c$ as the energy quanta.

In section 3.1 we showed that the force experienced by an electron in a lattice is $\hbar \dot{\underline{k}}$. In the presence of a magnetic field the force is given by the Lorentz formula

$$\text{Force} = \frac{e}{c} \underline{B} \times \underline{v} = \frac{e}{c} \underline{B} \times \dot{\underline{r}} = \hbar \dot{\underline{k}}.$$

Thus $\hbar \dot{\underline{k}} = e/c \underline{B} \times \dot{\underline{r}} \dots (3.52)$

The path of an electron in real space is then the same as the path of the representative point in $\underline{k}$ space multiplied by $e\hbar/cB$ and rotated by $\pi/2$ about the magnetic field.

The density of states function $N(E)$ is completely altered in the presence of a magnetic field and for unit range of wave number k_z

$$N(E) = \frac{dN}{dE} = \left(\frac{2m^*}{\hbar^2} \right)^{\frac{1}{2}} \cdot \frac{1}{(2\pi)^2} \frac{eB}{\hbar c} \sum_n \left[E - (n + \frac{1}{2}) \hbar \omega_c \right]^{-\frac{1}{2}} \dots (3.53)$$

where $\frac{1}{(2\pi)^2} \cdot \frac{eB}{\hbar c}$ is the density of states with a given quantum number n . A singularity occurs whenever $E = (n + \frac{1}{2}) \hbar \omega_c$, the density of states takes on infinite values and we can no longer speak of a mean value. In practical cases the occupation of states is determined by the Fermi-Dirac distribution function, and it is the inclusion of this term which introduces a thermal damping factor

$$\frac{2\pi r^2 k_B T}{\hbar \omega_o} \bigg/ \sinh \left(\frac{2\pi^2 r k_B T}{\hbar \omega_o} \right)$$

which limits the singularities of equation (3.53).

In this work, at the lowest temperature employed, namely 1.6 K, and at the maximum magnetic field of 40 kG, the cyclotron frequency corresponds to 14.08×10^{12} hertz and the thermal damping factor reduces the amplitude of the fundamental oscillation by a factor of 0.98.

Oscillations in transport properties are a direct consequence of the inverse relation between carrier relaxation times and the density of states, equation (3.38). The proportionality changes for each collision process but PIPPARD (1965) has shown that oscillations in a general relaxation time

τ are limited to a relative amplitude

$$\frac{\text{Amp } \tau}{\tau} = \frac{1}{(2n)^{\frac{1}{2}}},$$

where n , the order of the oscillation, is defined by $n = E_f / \hbar \omega_c$. The low Fermi energy in graphite of 0.019 eV leads at 40 kG to a value for n equal approximately to 1.3. Large amplitude oscillations are therefore to be expected in transport properties of graphite, and this is confirmed by Fig.5.1, illustrating SdH oscillations in single crystal and pyrolytic graphite.

The physical interpretation of oscillations in the density states was greatly facilitated by the work of ONSAGER (1952) and LIFSHITZ (1957) who applied the Bohr-Sommerfeld phase integral formula to a magnetized electron distribution:

$$\oint \underline{p} \cdot d\underline{r} = (n + \gamma) 2\pi\hbar$$

where γ is a phase correction equal one-half for free electrons.

Quantization of the phase integral means that whatever the shape of the electron orbit in real space, the flux enclosed by each orbit is quantized such that permitted areas are given by $(n + \gamma) 2\pi\hbar / eB$. Orbits in real space are related to orbits in $\underline{k}$ space by equation (3.52) and therefore the area of the permitted orbit in $\underline{k}$ space ' A_n ' is quantized:

$$A_n = \frac{2\pi e \hbar}{c} (n + \gamma).$$

Different slices of the Fermi surface normal to the applied field have different orbit areas, but when the sum over all slices is evaluated the integral is of the Fresnel type, such that major contributions arise only from regions where the phase $\frac{\partial A(E_f, k_z)}{\partial k_z}$ is stationary. The resulting period of oscillation, as a function of reciprocal magnetic field, gives directly the external area of cross-section normal to the applied magnetic field

$$P\left(\frac{1}{H}\right) = \frac{2\pi e}{\hbar A_{\text{extremal}}}.$$

In addition to thermal damping, the amplitude of oscillations in a given field is determined by several other factors, the most important of which are the curvature $\partial^2 A / \partial k_z^2$ at the extremum and the collision broadening of levels. The curvature term, introduced by LIFZHITZ and KOSEVICH (1956) appears in the denominator of a general expression describing oscillations in the density of states. Surfaces having small curvature at the extremum result in large amplitude oscillations. BENDER and YOUNG (1973) have included this term in a discussion of the change in amplitude of SdH oscillations in graphite as the angle θ between the applied field and the c-axis varies. For fixed θ the effect of curvature is usually absorbed into a general amplitude term.

Collision broadening of Landau levels has recently received a good deal of attention. An extensive review of this subject, together with its application to single crystal and pyrolytic graphite is contained in the work by BENDER (1972). Briefly, the lifetimes of electronic states in graphite, at helium temperatures, are determined by the frequency of collisions with impurities and lattice imperfections. DINGLE (1952) assumed that energy levels are broadened by elastic collisions of electrons with impurities and that the level is described by a Lorentzian line profile of the form

$$dN = \frac{h}{\pi \tau} \frac{dE}{(E - E_n)^2 + \left(\frac{h}{\tau}\right)^2} .$$

In the free electron approximation each harmonic of the oscillatory component is reduced by an exponential damping factor $\exp(-2\pi r / \omega_c \tau)$. BRAILSFORD (1966) has subsequently shown that the relaxation time used by Dingle is twice the lifetime of a state at the Fermi level and the half-width of the Lorentzian is, in fact, $h/2\tau$. An extension of Dingle's treatment to Fermi surfaces of arbitrary shape by WILLIAMSON, FONER and SMITH (1964) resulted in the same exponential damping of oscillatory terms. Recently attention has been drawn to the change in period resulting from

introducing impurities into a lattice and two quite separate treatments have evolved.

The first approach initiated by FRIEDEL (1954) assumed that the introduction of impurities displaced each energy level by an amount $\Delta(E)$ and the Fermi level in the impure specimen becomes $E_f + \Delta E_f$. HEINE (1956) used the rigid band model to show that ΔE_f is simply calculated from the change in the concentration of conduction electrons and the density of states at the Fermi level, such that the change in period on alloying is proportional to the relative valence of the solute atom and the concentration of solute atoms per atom of solvent. BRAILSFORD (1966) generalised this treatment to account for situations in which the energy shift $\Delta(E)$ is a function of energy and $\underline{k}$, and showed that a period shift can occur in the case of zero relative valence. The Friedel 'energy shift' approach leads directly to a change in oscillatory period proportional to the concentration of solute atoms. A small positive imaginary component of $\Delta(E)$ leads to an exponential damping factor of the sort described by Dingle.

The second attempt to interpret the nature of the relaxation time was by BYCHKOV (1961). Bychkov based his approach on the temperature independent Green's function of the perturbed crystal, and quantum field theory. Changes in the period were not considered and the treatment was restricted to free electrons and δ -function scattering potentials. MANN (1970) has generalised this method to Fermi surfaces of arbitrary shape and to generalized scattering potentials. A self energy parameter Σ was defined in terms of the Transition Matrix T_n associated with a defect or impurity:

$$\Sigma(k, z) = NC \langle k | T_0(z) | k \rangle_{B=0},$$

where N is the number of lattice sites, C the concentration of solute atoms per atom site, and $T_0(z)$ describe the scattering by an impurity at the site where $R = 0$.

Σ was decomposed into real and imaginary parts:

$$\Sigma = \Sigma' - i \Sigma''$$

where Σ'' is related to the transition probability through the equation

$$\Sigma''(k) = \frac{\hbar}{2} \frac{1}{\tau(k)}$$

and the half-width of the broadened Landau level is equal to the imaginary part of the self energy. The relative change in oscillation period was shown to be proportional to the real part of the self energy which can be positive or negative, but the imaginary part is positive definite, and is proportional to the damping factor such that $\langle \Sigma'' \rangle = \pi k_B T_D$.

Although Mann has questioned the validity of Brailsford's procedure the complex energy shift $\tilde{\Delta}(E)$ was shown to be identical to the complex self-energy $\tilde{\Sigma}$ to second order in the potential perturbation. Changes in the period of SdH oscillations in pyrolytic graphite on irradiation with fast neutrons are discussed in section 5.3.1 in terms of a depressed Fermi level, leading to an enlarged electron surface and a shrunken hole surface. Oscillatory amplitudes diminish with increasing irradiation corresponding to increased exponential damping of the singularities of equation (3.53).

Oscillations in the electrical conductivity, which are periodic in $1/H$ and damped by the presence of impurities and a non-zero temperature, may be described without prior knowledge of the scattering mechanisms by a generalised Landau formula introduced by SOULE, McCLURE and SMITH (1963).

$$G_i = H^n \sum_{r=1}^{\infty} W_i(r) \cdot \frac{2\pi^2 r k_B T}{\hbar \omega_{ci} \cdot \sinh \left(\frac{2\pi^2 r k_B T}{\hbar \omega_{ci}} \right)} \exp - \left(\frac{r u_i \Delta T_{Di}}{T} \right) \cos \left(\frac{2\pi r}{P_i H} - \psi_i(r) \right) \dots (3.54)$$

where r refers to the harmonic, and i to a particular carrier. In section 5.2.2 this formula is fitted to SdH oscillations in single crystal and pyrolytic graphite by allowing the amplitude term $w_i(r)$, the phase factor $\psi_i(r)$, the Dingle temperature ΔT_{Di} and the period P_i to take arbitrary values.

At this juncture we should consider whether the smearing of oscillation periods in pyrolytic graphite will permit the observation of changes in period due to application of the rather low pressures used in this work. BENDER and YOUNG (1973) have shown that, to a good approximation, the dependence of electron and hole periods on the angle θ between the magnetic field and the $\underline{c}$ -axis follows a cosine law:

$$P_{\theta} = P_{(0)} \cos \theta .$$

Pyrolytic graphite used in this work has an angular spread of crystallite $\underline{c}$ -axes which is $\pm 0.5^{\circ}$ to the basal plane normal, resulting in a period spread of $\sim 0.015\%$ and setting one limit on the period resolution.

As θ increases from zero, the extremal area of cross-section of the electron and hole surfaces normal to the magnetic field, varies with the angle ' α ' of Fig.3.1(b). At $\theta = 65^{\circ}$ the electron period varies by 6% with changing ' α ' and the hole period by 5% (BENDER and YOUNG (1973)) with sixfold symmetry about the $\underline{c}$ -axis. In pyrolytic graphite the $\underline{a}$ axes of the basal plane crystallites are distributed at random in a plane normal to the $\underline{c}$ -axis. But the crystallite $\underline{c}$ -axes have an angular distribution $\Delta\theta$ with respect to a fixed plane and the complete range of ' α ' values present in this material will cause a period smearing which is absent for material in which $\Delta\theta = 0$. A $\underline{c}$ -axis misalignment of $\pm 0.5^{\circ}$ will cause a corresponding period smearing of $\sim 0.001\%$ due to random orientation of crystallites within a basal plane.

Application of pressure to the pyrolytic graphite used in this work cannot therefore determine changes in oscillation period to a resolution of better than 0.015%.

CHAPTER IV

EXPERIMENTAL

4.1 MATERIALS

Samples were cut from two single crystal specimens and from specimens of pyrolytic graphite from four separate preparations with each preparation following the depositing and annealing procedures described in Chapter I. Measurements were made on pristine pyrolytic and single crystal graphite, and on pyrolytic graphite irradiated by fast neutrons at a temperature of 30°C in the belt stringer of the BEPO reactor at AERE, Harwell.

4.2 SAMPLE PREPARATION

Because of the weak interplanar bonding, discs of pyrolytic graphite could readily be cleaved from the bulk specimen revealing surfaces of high perfection and exhibiting specular reflection. The very anisotropic nature of conduction in graphite, with σ_a reaching values 10^4 times σ_c requires that at the edges of a sample the high c-axis resistance should not be short circuited by mis-aligned high conductivity basal planes. An air abrasion unit was used to cut the graphite discs with a narrow jet of alumina dust, and the resulting slow cutting process minimised the tendency for the graphite layers to rip and bend at the edges of the sample. It was essential to ensure that all planes had been electrically bonded at the current and voltage terminals, in the case of samples with current flow in the basal planes, so that isopotential lines should be straight and the sample measurements truly represent the electrical dimensions. Similarly for c-axis samples it was important to avoid electrical bonding between layers. A new sample geometry was developed for samples with current along the c-axis to minimize errors in sample measurement and to provide a robust sample suitable for experiments at high pressure.

4.2.1 Basal Plane Samples

A stainless steel cutting mask was used to cut samples into a bridge geometry suitable for basal plane measurements of conductivity, Hall coefficient and magnetoresistance. PUTLEY (1960) has pointed out that a short wide sample would exhibit a Hall voltage less than the value intrinsic to the material, since the current electrodes tend to short circuit the Hall field. To eliminate this effect the ratio l/W of Fig.4.1 should be $> 3-4$, a condition satisfied in the samples used in this work.

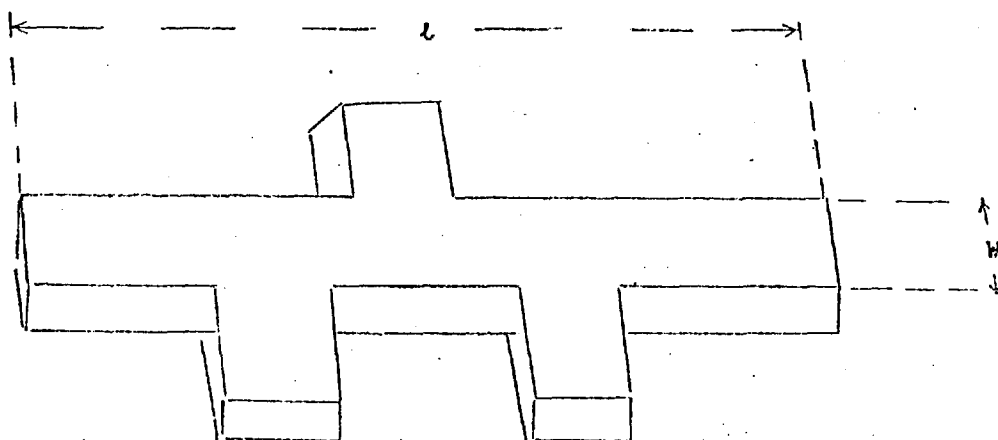


Fig.4.1
Sample geometry for basal plane measurements

Shortcircuiting of the Hall voltage by currents flowing between the Hall probes can occur in material with a large Hall angle. In graphite the Hall angle, equal to $\tan^{-1} \sigma_{xy}(H) / \sigma_{xx}(H)$ can be shown to reach a maximum of 4° and shortcircuiting is negligible in this material. Inhomogeneities in the sample or magnetic field can affect measurement of the magnetoresistance by producing unequal Hall fields at the two potential probes. The small Hall angle reduces this effect in graphite, and SPAIN, UBBELOHDE and YOUNG (1967) have estimated a 1% inhomogeneity to be within the error of measurement.

WOORE (1969) photographed actual samples cut in the configuration of Fig.4.1, and used paper coated with an almost uniform conducting layer of

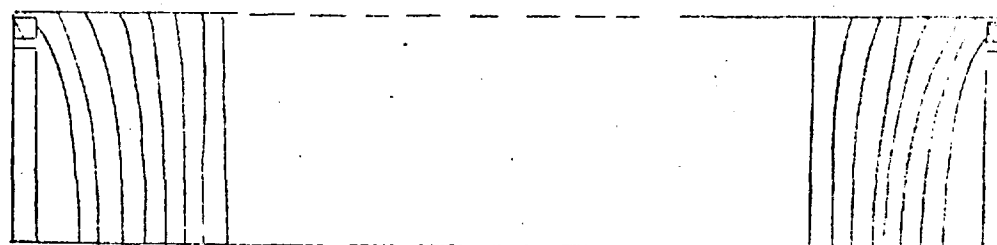
graphite to form an enlarged two-dimensional analogue of the sample. Corrections to the electrical length of the sample due to isopotential lines not being straight, or to not being situated at the centre of the probes were shown by this technique to be less than one percent.

Current and potential leads were attached to samples of pyrolytic graphite by copper plating the probe tips in a slightly acid solution of copper sulphate at a current of 1 ma/cm^2 . Copper deposits preferentially at the edge of a basal plane but after roughening the top and bottom surfaces of the probes with the air abrasive unit, an even layer of copper formed about the probe tip, while the rest of the sample was protected by several layers of plastic varnish. Leads of 45 gauge copper wire were fixed to the copper plated tips with conducting silver dag cement. A second coating overplated the cement and formed a continuous copper contact between the lead and the graphite sample. Finally the plastic varnish was dissolved with acetone. The single crystals used in this work were too fragile to support copper plated probes, and copper leads were attached in situ to the sample, with conducting silver dag cement, with the sample in position in the cryostat.

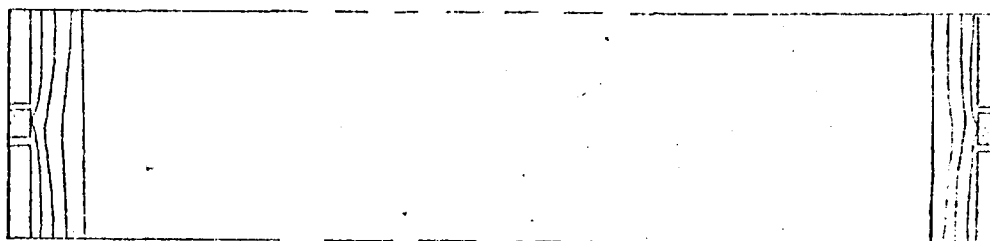
4.2.2 c-Axis Samples

Before this work was begun there existed no satisfactory method for attaching contacts to samples with current along the c-axis. Pressure contacts had been tried (PRIMAK and FUCHS (1954)) but this method gave irreproducible results, and is unsuitable for use over a large range of temperature and pressure. SPAIN et al (1967) used samples with large c-axis dimensions, typically 10 mm, and either cut grooves in the four corners of a rectangular specimen to take both current and potential probes, or employed a bridge geometry similar to that used for basal plane samples. Tapered potential probes reduced the short-circuiting of the current path through the copper plated contacts but resulted in a fragile specimen whose c-axis dimensions could not accurately be measured.

Analogue experiments with conducting paper were begun to examine several probe geometries, and one was found which was suitable for c-axis samples 1-3mm thick and which produced a robust sample whose true electrical length could be determined to within 1%. The two dimensional analogue of a c-axis sample in isotropic conducting paper is long and thin (SPAIN et al (1967)) and is illustrated diagrammatically in Fig.4.2. The configuration consisting of a spot current, and a spot potential contact was shown to be the worse electrode arrangement producing curved isopotential lines for more than 10% of the sample length. Fig.4.2(a) illustrates the case of a large current contact over the face of the sample and a small potential probe at one end. Isopotential lines ending at the potential probe still substantially reduces the sample length. The optimum probe geometry appears to be one with a large current contact enclosing a spot potential probe and shown in Fig.4.2(b). Isopotential lines are straight and the electrical length is within 1% of the sample thickness.



(a)



(b)

Fig.4.2

Two dimensional analogue of a c-axis sample

- (a) Current probe covering sample surface potential probe at one end.
- (b) Central potential probe enclosed by current contact.

c-axis samples were prepared with the analogue experiments in mind. The top and bottom of a rectangular slab of graphite typically 3 mm wide, 8 mm long and 2-3 mm thick, were roughened with the air abrasive unit. Copper was deposited directly onto this surface leaving a spot 2 mm in diameter at the centre of the face which although plated was separated from the rest of the plated surface by an annulus of unplated graphite. Two 45 swg copper wires served as potential and current leads, and were fixed with conducting silver dag to the centre spot and surrounding plated area respectively. Over-plating with deposited copper provided a direct copper link between probe wire and the graphite surface. During the plating process the sides of the sample which display basal plane edges to the depositing copper were protected with several layers of plastic varnish to avoid shortcircuiting the c-axis resistance.

4.3 APPARATUS AND PROCEDURE - NON-OSCILLATORY GALVANOMAGNETIC MEASUREMENTS

The non-oscillatory electrical conductivity of pristine and irradiated samples of pyrolytic graphite was measured as a function of applied pressure with a point-by-point potentiometric technique. At liquid helium temperatures where quantum effects occur, an automatic digital voltmeter recorded resistance as a function of applied magnetic field. A description of the apparatus employed falls conveniently into two categories; namely that used for measuring classical galvanomagnetic effects and secondly, the system employed near the absolute zero of temperature, with some of the apparatus common to both high and low temperature measurements.

4.3.1 Cryostats and Constant Temperature Baths

All the measurements on galvanomagnetic effects in graphite were conducted at or below room temperature, and several dewar systems were employed. A Monax glass dewar was used with a short tail designed to take the pressure vessel described in section 4.3.4, and to fit between the poles

of a water cooled electromagnet. Early measurement of the pressure coefficient of resistance in graphite at 4.2 K was made using a cryostat of very simple construction and consisting of the Monax glass inner dewar and an outer dewar of polystyrene foam. Since the dewar was of short construction the cryostat had the novel feature of a top plate cooled with liquid nitrogen. However, a boil-off rate of three litres an hour restricted the use of the cryostat to short twenty minute runs.

Galvanomagnetic effects were measured at temperatures maintained constant by immersing the pressure vessel containing the sample into; water at its melting point, nitrogen at its boiling point and nitrogen at its melting point, liquid helium at its boiling point at atmospheric pressure (4.2K), and liquid helium at reduced pressure (1.6K).

Later measurements employed the Oxford Instruments cryostat, described in section 4.4.1, at 77K, 52K and at liquid helium temperatures. The results obtained with this cryostat confirmed earlier measurements with the Monax glass/polystyrene system.

4.3.2 Electromagnet

The magnetic field for magnetoresistance and Hall coefficient measurements was provided by a water cooled Newport magnet with a 25kW motor generator and sweep speeds varying from a kilogauss a second to less than a kilogauss an hour. Pole pieces were used to attain a maximum field of 17.5kG, a field stability of one part in 10^5 and a resolution of two parts in 10^6 over a cylindrical sample 6mm diameter and 19mm long. The pole gap of 4.5cms dictated the width of the Monax dewar used in conjunction with this magnet. A turntable facility allowed the magnet to take any position to an accuracy of 0.1° in 360° , while permanently fixed rails enabled the magnet to roll out of the region of the cryostat. Fast sweep speeds resulted in sample heating and induced large stresses in the support frame. A sweep speed of about 17kG/hour was used throughout.

4.3.3 Electrical Measurement

The basal plane resistance of pyrolytic graphite changes by only $0.05 \times 10^{-6} \Omega$ over a pressure range of 10 bar at room temperature. In order to measure changes of this order, a system capable of detecting changes of 15 nV in a background voltage of $\sim 300 \mu\text{V}$ was needed. This requirement was met by a Cambridge microstep potentiometer with a Tinsley photocell galvanometer amplifier and zero indicator. A sensitivity of 10 cms deflection per $0.1 \mu\text{V}$ was obtainable with this system and voltages were recorded to an accuracy of 2-3 nV.

A Farnell TSV 70 constant voltage unit supplied the sample current. By first passing the output through a series resistance, large compared with the variable lead and sample resistance, constant current was supplied to the sample. Point-by-point monitoring of the current was affected by recording the voltage drop across a standard 1 ohm Cropico resistance in series with the graphite sample.

Hall coefficients were measured as a function of pressure with a Pye microvolt vernier potentiometer and the Tinsley photocell galvanometer amplifier and zero indicator used for resistance measurements. Voltages could be read to $0.1 \mu\text{V}$ with this instrument, which also served to monitor the voltage across an InSb Hall probe employed to measure the magnetic field. The resistive component of the Hall probe was balanced to provide zero output in zero field, with a simple potentiometer circuit. This proved to be important at low fields but had little effect on the Hall voltage at high fields.

4.3.4 High Pressure System

A non-magnetic pressure vessel was designed, capable of withstanding pressures of 1000 bar with a safety factor of 2 over a temperature range of 300 K. The bomb, shown in Fig. 4.3, was fabricated from a rod of Mallory 73

beryllium-copper in the annealed state. Heat treatment in air at 300°C for two hours raised the Vickers hardness number from 242 to 420 but also produced a dark brown layer of oxide on the heat treated components. A 10% sulphuric acid solution at 60°C removed the oxide without difficulty and final pickling was affected with a solution of sodium dichromate in sulphuric acid. The

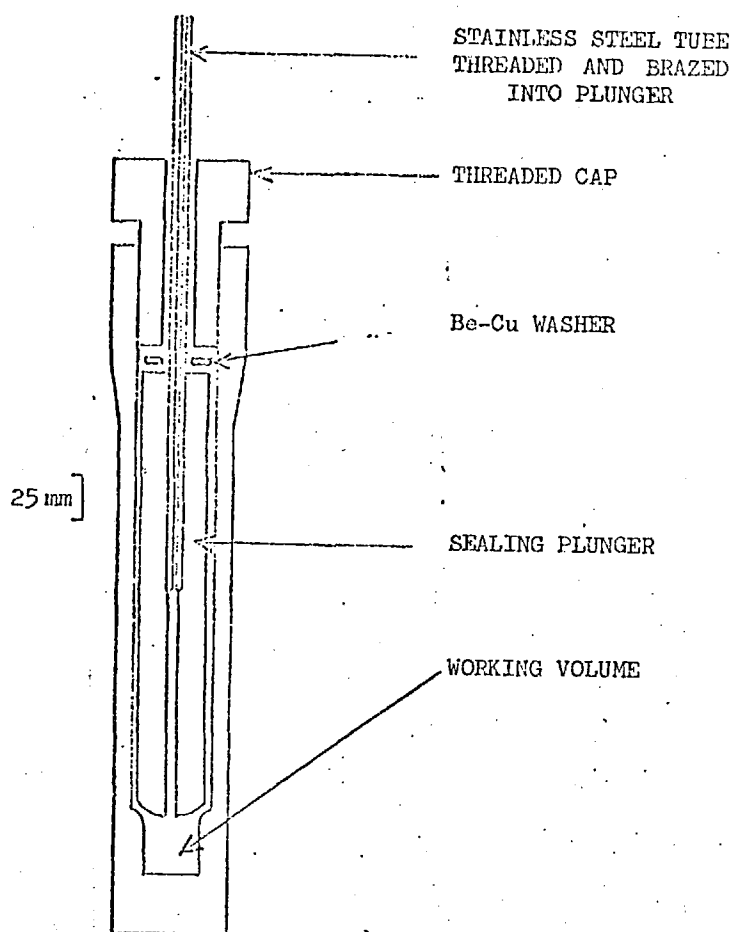


Fig. 4.3
PRESSURE VESSEL

pressure seal between the working volume and bomb insert was of the simple metal-to-metal type and was found to work well over the whole temperature range of 300K. Into the male section was hard soldered a $\frac{1}{8}$ " O/D stainless steel tube which had previously been threaded and screwed into the beryllium-copper insert. Brazing was carried out with the material in the annealed state as the elastic strength of heat treated Be-Cu is impaired rapidly by temperatures about 600°C. The pressure vessel was suspended on the stainless steel tube which served to conduct the pressure and electrical wires a distance of almost 1½ metres to the working volume. A four-way PPI junction introduced the rest of the pressure system to the stainless steel tube and provided one arm for an araldite pressure seal through which electrical wires passed from the high pressure environment to the ambient pressure outside.

The araldite seal consisted of a short length of standard $\frac{1}{4}$ " O/D pressure tubing tapped at both ends to provide grip for the epoxy resin. Insulated 40 swg copper wires were glued in position by a little seccotine at one end of the tube and casting araldite poured in as a liquid mass of low viscosity. Care was taken to ensure that there were no air pockets trapped beneath or within the setting araldite. At room temperature the resin took between one and two days to set and of the eight seals made not one was found to fail or leak up to the highest pressure used. However, on setting, araldite can break individual 40 gauge wires. This was avoided by twisting the leads to form a robust composite wire which was led from the araldite junction around a thin copper rod, the end of which was covered in a plastic varnish. The araldite-plastic junction so formed proved to be robust and flexible and overcame difficulties encountered with sharp brittle junctions formed by taking the wires directly into the araldite seal.

Helium or nitrogen gas from a high pressure cylinder was led, as in Fig.4.4, into the stainless steel tube and hence the pressure vessel by standard PPI pressure tubing. A Budenberg 0-500 bar pressure gauge monitored the applied pressure which could be controlled with a two way needle valve for pressure increase, and three-way needle valve for pressure decrease. Very fine pressure control was possible with this system and changes of one atmosphere were easily affected.

4.3.5 Procedure

The pressure dependence of the resistance, oscillatory magneto-resistance and Hall coefficient were measured at fixed points in the temperature range 1.6 to 300 K using the isothermal baths described in section 4.3.1. Pressure was increased slowly in 10 bar steps in the range 1-500 bar. Thermal voltages were allowed to subside and readings were taken when the voltage reached a stability of better than 1 part in 10^6 corresponding to a jitter of $< \pm 2$ nV. A copper conduit was used to lead the strain free copper,

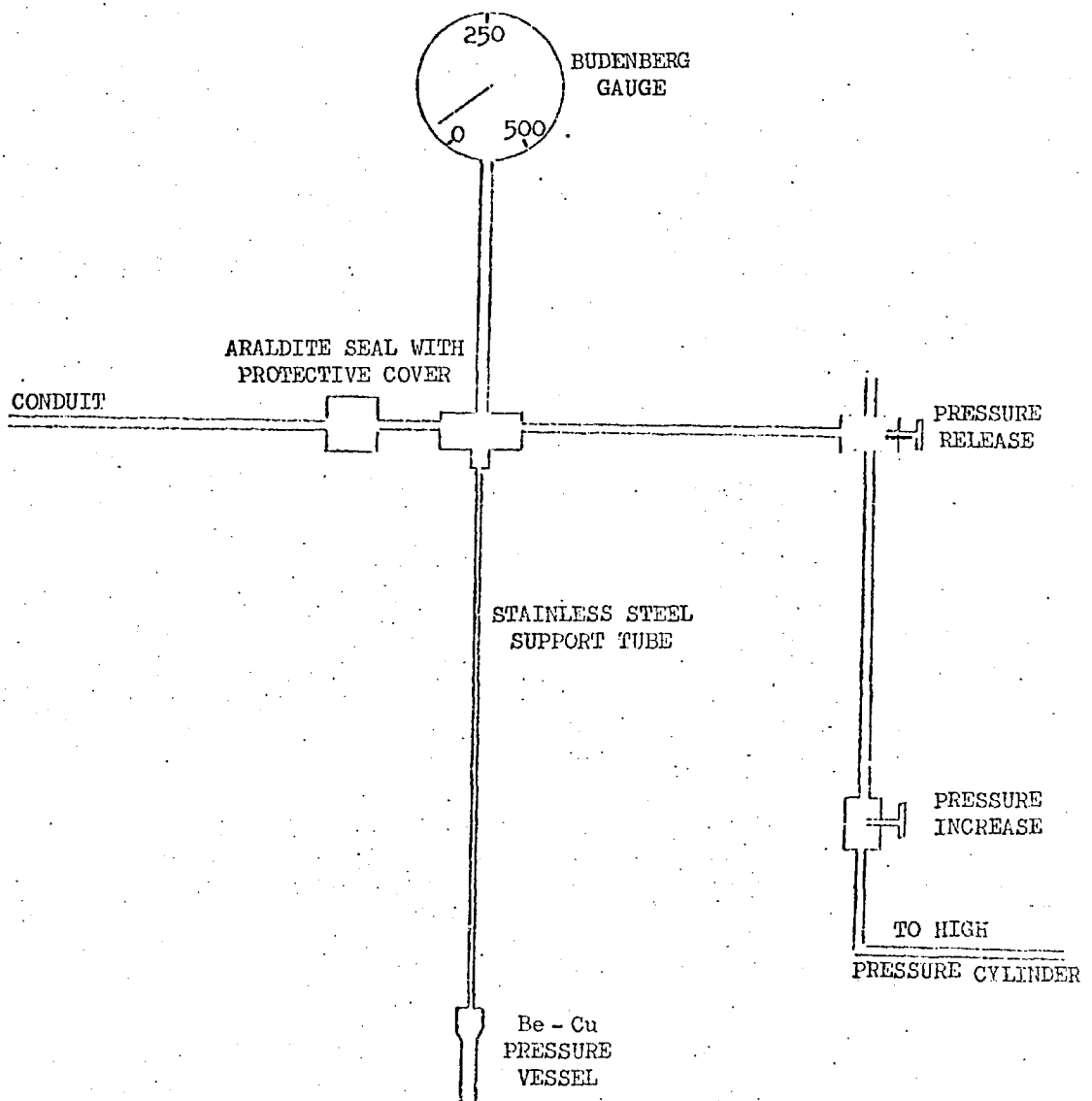


Fig. 4.4
PRESSURE SYSTEM

current and voltage, wires from the pressure junctions to the potentiometer. Thermal voltages in the leads, measuring $\sim 0.9\mu\text{V}$ with the sample at 4.2K and $\sim 0.6\mu\text{V}$ with the sample at 77 K were accounted for by reversing the direction of current through the sample and taking the mean of the two readings.

c-axis and basal plane samples were located in the pressure vessel by gluing the sample with plastic varnish to a Tufnol plate which was aligned parallel to the inset plunger of the pressure bomb with a travelling microscope, and finally glued to the bottom of the plunger. The c-axis of the sample was located by detecting the sharp minimum in the magnetoresistance which occurs when the magnetic field is directed at right-angles to the c-axis.

When measuring Hall coefficients in graphite, it is not possible to eliminate the perturbing influence of the Righi-Leduc-Seebeck, the Ettinghausen-Seebeck or the Nernst effects by magnetic field and current reversal. WOORE (1969) has shown that a non-isothermal temperature distribution which is caused by the Ettinghausen transverse heat flow and the Peltier effect at the contacts, will in fact lead to transverse voltages produced by the Nernst, Righi-Leduc-Seebeck and Ettinghausen-Seebeck effects which can only be accounted for by a field reversal, together with a current reversal so fast that thermal gradients do not have time to alter. The high basal plane conductivity in graphite prevents a fast current reversal but also acts to keep perturbing voltages due to non-isothermal effects to very low values. Thus, SPAIN et al (1967) have used the expressions of PUTLEY (1960) to estimate $0.1\mu\text{V}$ for the Nernst effect at 5000 G and a current of 200 mA, while Righi-Leduc-Seebeck and Ettinghausen-Seebeck produce perturbing voltages of less than a nanovolt.

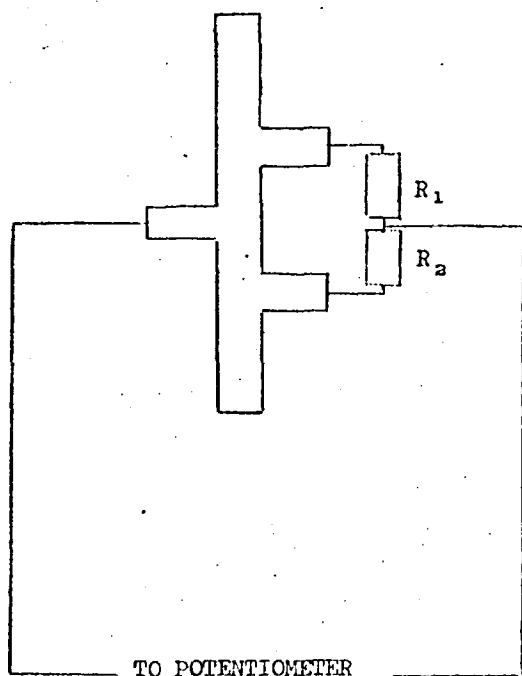


Fig.4.5
Lead arrangement for Hall
coefficient measurements

The sample configuration used to measure Hall coefficients is shown in Fig.4.5. Because of the difficulty in cutting Hall probes which lie on the same equipotential line, a bridge circuit was used to balance the magnetoresistance contribution. Resistances R_1 and R_2 were typically 28 and 32 Ω respectively, and were adjusted to give zero Hall voltage at zero field. However, on reversing the magnetic field a 3% difference in Hall voltage was measured at low fields while at high

fields no appreciable difference was detected. Thus at low magnetic field strengths, current and magnetic fields were reversed and the mean of the four readings taken as the true voltage.

4.4 APPARATUS AND PROCEDURE - OSCILLATORY MAGNETORESISTANCE

Shubnikov de Haas oscillations were recorded in the magnetoresistance of pyrolytic and single crystal graphite with the aid of a niobium-titanium superconducting magnet. The magnetic field was continuously variable up to a maximum field of 40 kG and enabled at least fourteen nodes in the oscillatory magnetoresistance to be recorded with an automatic digital voltmeter and typewriter print-out. Apart from heater coils wound about the Be-Cu pressure bomb, the pressure system was the same as that used at higher temperatures and described in section 4.3.4.

4.4.1 Oxford Instruments Cryostat

Some of the point-by-point measurements of the pressure coefficient of resistance at 4.2K and all of the Shubnikov de Haas oscillations were

recorded with the sample in the low temperature environment of a variable temperature cryostat supplied by the Oxford Instrument Company. The outer dewar, shown in Fig.4.6, consists of a liquid helium reservoir cooled by a liquid nitrogen jacket, and isolated from ambient temperatures by a vacuum spaced pump to 10^{-6} torr. A superconducting solenoid was suspended by thin walled stainless steel tubes from the dewar base-plate and located in the tail section of the liquid helium reservoir. The insert dewar, shown in Fig.4.7, itself has a tail section which was a sliding fit into the magnet bore, and included as a special design feature, a one inch stainless steel specimen tube which allowed access to the pressure bomb and tubing described in section 4.3.4. A second helium reservoir, the He II pot, was isolated from the main helium bath by a vacuum jacket, but was in good thermal contact with the one inch specimen tube. Helium was transferred from the outer dewar to the He II pot through a thin walled filling tube, and control of the transfer rate was via a needle valve fitted to the filling tube and adjusted from the top plate of the cryostat.

A three-phase rotary pump with a capacity of 450 litres/min. was connected as in Fig.4.8, through a four inch pumping line and butterfly valve to the insert dewar, and thereafter through tapered pumping lines to the He II pot. Smaller pumps of 250 litres/min. capacity were used to pump the one inch specimen tube and to rough pump the outer dewar before transfer of liquid helium. Metal bellows placed in series with the pumping lines helped to prevent pump vibrations from reaching the low temperature parts of the cryostat, and thus reduced the heat leak to the liquid helium. Speedivac 0-760 mm and 0.20 mm pressure gauges were fitted to pumping lines to the He II pot and the one inch specimen tube, and thus served as vapour pressure thermometers on condensed gaseous helium introduced into the specimen tube, and on superfluid helium in the He II pot. A rotameter reading from 0.3 to 3 litres/minute, and connected to the helium gas exhaust

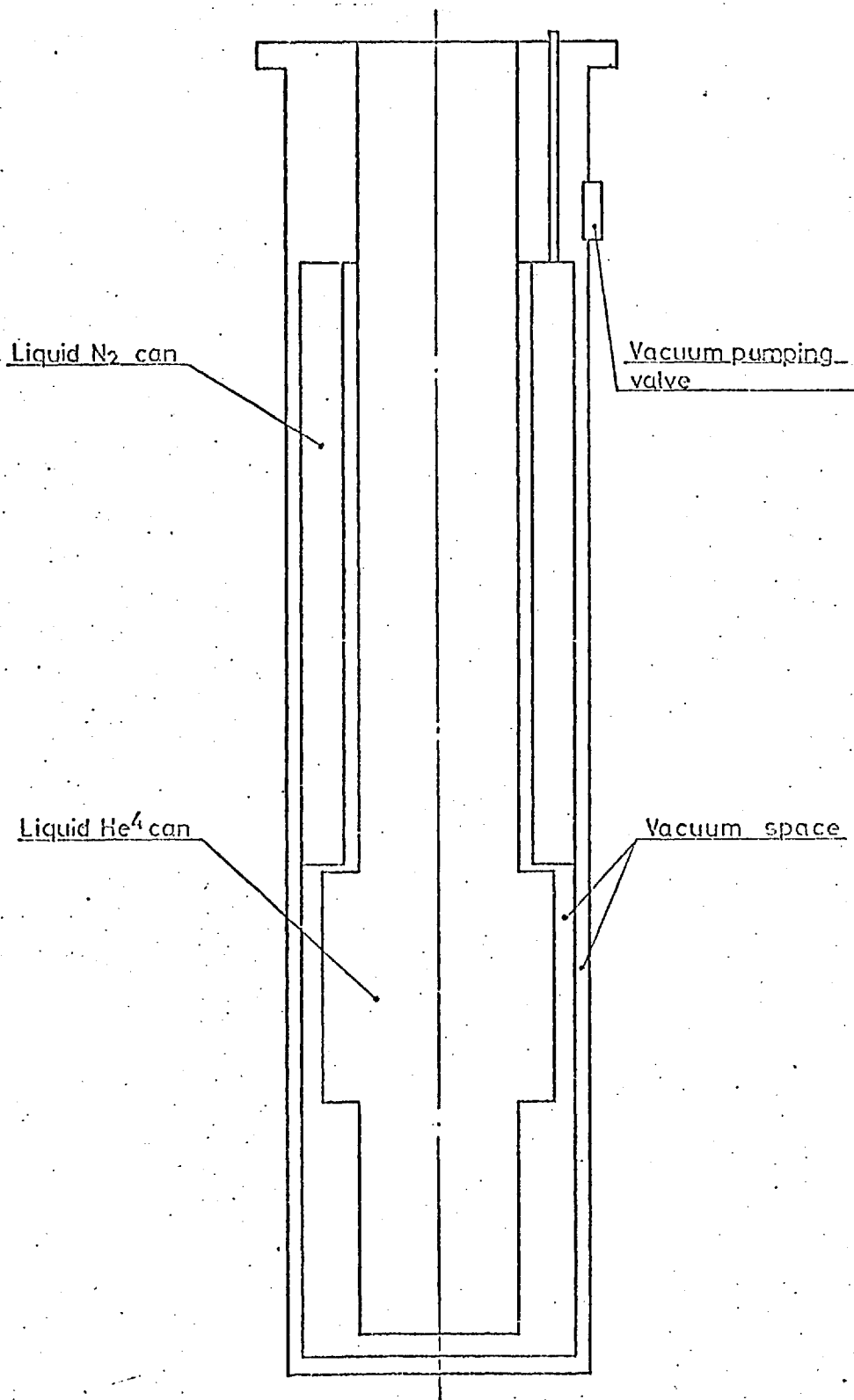


Fig.4.6
Oxford Instruments Cryostat - Outer Dewar

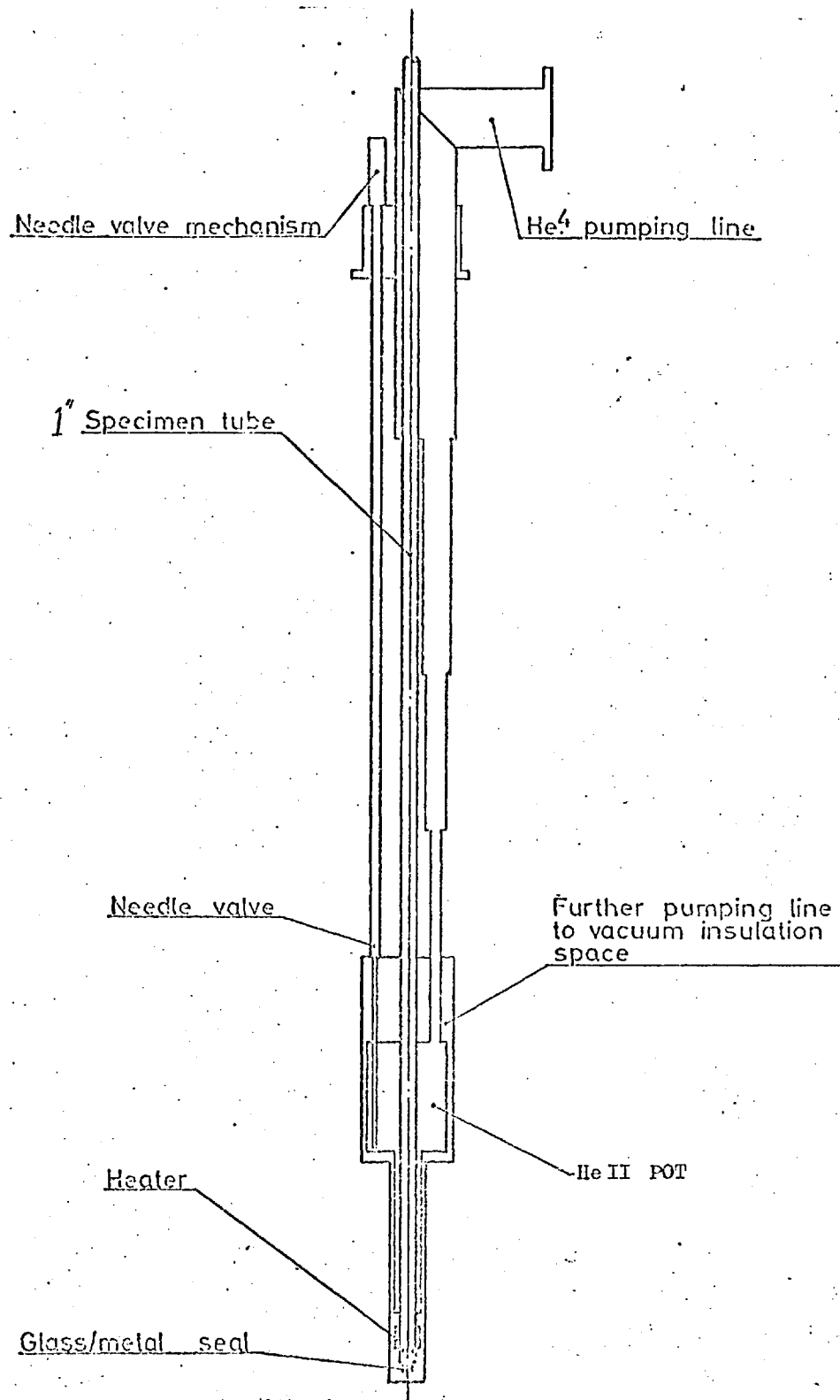


Fig.4.7

Oxford Instruments Cryostat - Insert Dewar

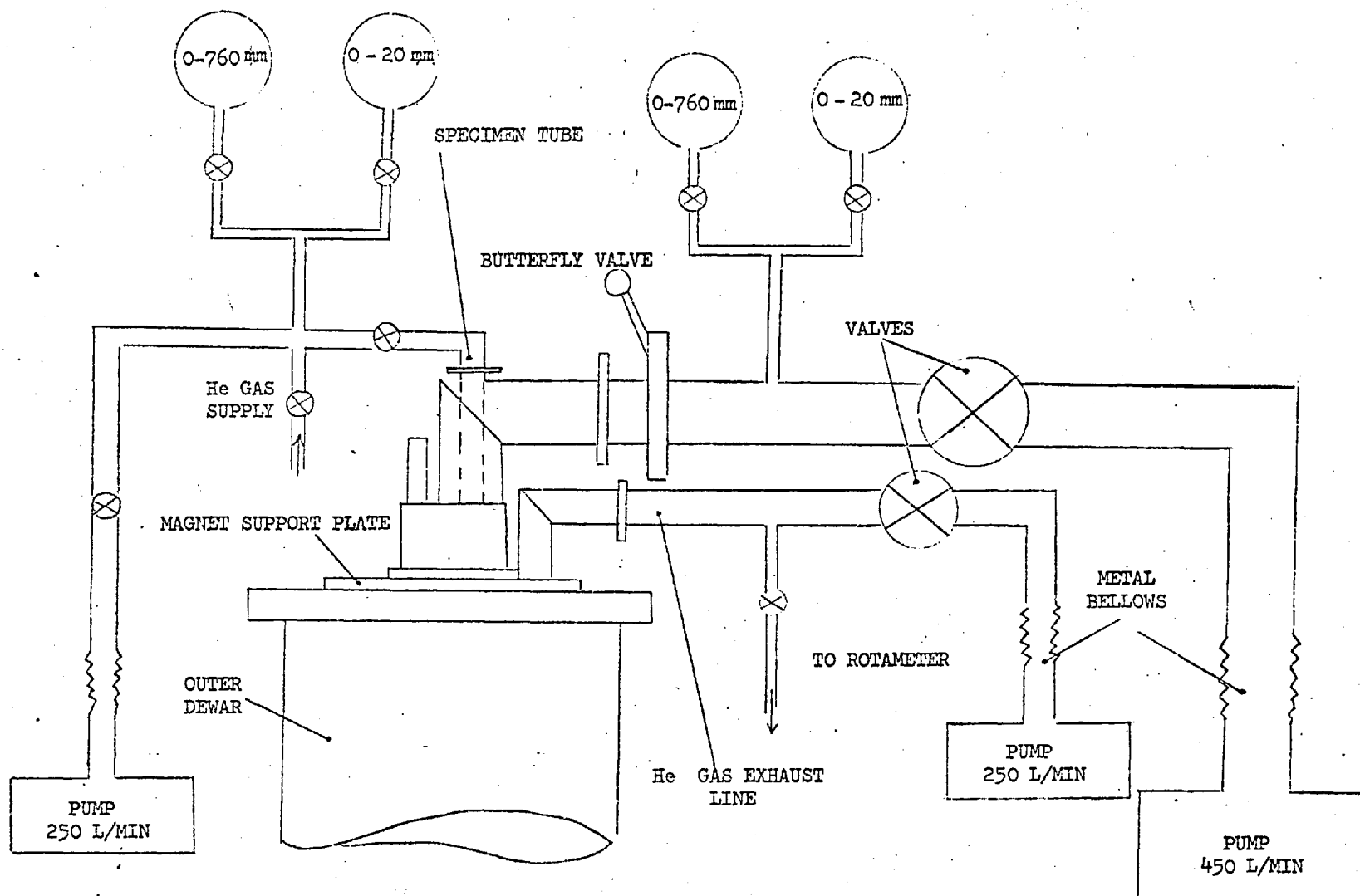


Fig.4.8
Pump Connections to Cryostat

line proved to be a useful monitor of the boil-off rate and a sensitive indicator in the transfer of liquid helium from the storage dewar to the cryostat.

4.4.2 Isobaric Freezing of Liquid Helium

Solid helium occurs in at least three different structures; body centred cubic, hexagonal close packed, and face central cubic. The phase diagram is shown for the isotope ^4He in Fig.4.9.

(DUGDALE & FRANCK (1963)).

At the pressure and temperature used in this work, namely ~ 400 bar and 4.2K , the solid exists in a hexagonal close packed structure, and with a compressibility of $70.1 \times 10^5 \text{ cm}^2/\text{kG}$. is the most

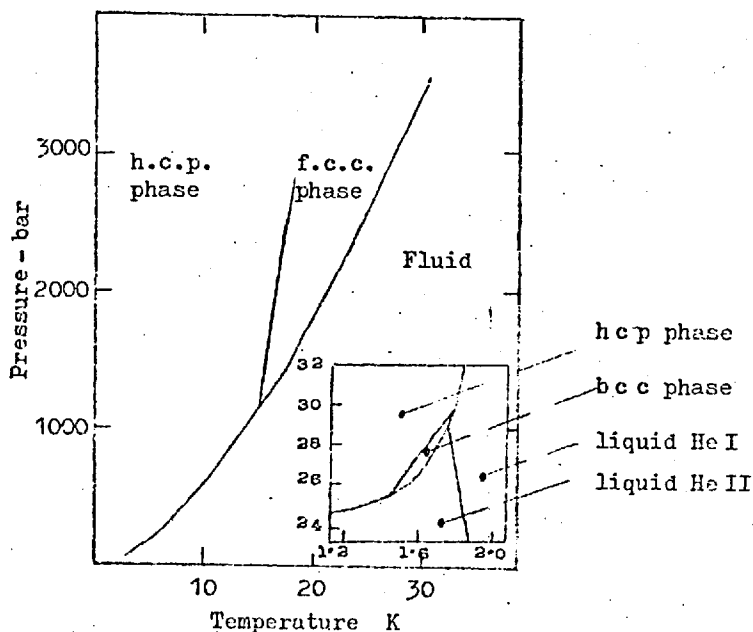


Fig.4.9
Phase diagram of ^4He

compressible of solids. Even so the sudden change in pressure coefficient of resistance which occurred at the helium melting pressure, as shown in Fig.6.1, indicates that at pressures above the triple point little pressure is transmitted to the graphite sample when the gas pressure above the solid helium is increased. Because of this difficulty and the possibility of damaging the crystal on rapid solidification of helium, an isobaric freezing technique was developed.

Three independent heater coils consisting of 36 swg chromel wire were wound about the outside of the pressure bomb, and along a ten inch length of the stainless steel pressure tubing connecting the bomb to the four way pressure junction. Copper-Constantan thermocouples were attached to the pressure tubing and bomb with tissue paper to provide good thermal contact while remaining electrically insulated. By controlling the current

to the heater coils the temperature could be raised from the 4.2K of liquid helium to 10 K where the melting pressure for solid ^4He is 650 bar.

The Be-Cu pressure vessel, supported by the stainless steel pressure tubing, was positioned in the specimen tube of the Oxford Instruments Cryostat, so that samples in the high pressure chamber were at the centre of the superconducting solenoid. A brass flange and pumping line were soldered to the pressure tubing and bolted, as shown in Fig.4.8, to the flange top of the specimen tube with a vacuum seal. This enabled the specimen tube to be filled with helium gas and provide good thermal contact between the pressure bomb and the He II pot or to be evacuated to thermally insulate the sample from the liquid helium environment.

With a seven bar pressure of helium in the pressure bomb and exchange gas in the specimen tube, the cryostat was cooled to 4.2K. Liquid helium was transferred from the main helium chamber to the He II pot and the pressure bomb cooled through thermal contact to 4.2K. After evacuating the specimen tube, the three heaters on the pressure vessel were used to raise the bomb temperature to 10K. During this period the temperature rise of ~ 6 K was matched by a rise in the pressure of gas in the pressure vessel from 7 to 12 bar. With the pressure bomb and cold region of the support tubing at 10 K the gas pressure was raised to over 400 bar. Helium gas was then introduced slowly to the specimen tube and the current to the bottom heater reduced. Thermal contact through the exchange gas cooled the lower section of the pressure bomb to the temperature of the He II pot. Current to the second heater was then reduced, permitting more of the pressure bomb to reach 4.2K. Finally, current to the top heater was slowly reduced and the helium in the pressure bomb and tubing allowed to solidify. During the cooling process the gas pressure was maintained constant with the two-way pressure valve of Fig.4.4, and solidification occurred upwards from the bottom of the pressure chamber under isobaric conditions.

4.4.3 Superconducting Magnet

To observe Shubnikov de Haas oscillations without serious smearing, a field homogeneity of better than 1 part in 10^3 over the sample area is required. The superconducting solenoid, wound from a copper clad alloy of niobium and titanium on a stainless steel former, easily met the requirements with a field homogeneity at the magnet centre of 1 part in 10^5 over a spherical volume of 1 cc. A five volt current stabilised power supply provided the magnet current at sweep times ranging from five seconds to two hours, and the peak current of 25.6 amps produced a maximum field of 40 kG at the magnet centre, with a current stability of 1 part in 10^4 . As a precaution against the superconducting windings suddenly becoming normal, an automatic trip disconnected the current supply when a potential difference greater than one volt appeared across the magnet terminals. Operation in a continuous or a persistent mode was possible through a switch of niobium-zirconium fitted across the coil terminals and shown in Fig.4.10. In the normal mode of operation the magnet was run continuously, with a heater circuit raising the temperature of the Nb-Zr above its transition temperature, resulting in a resistance of 6Ω appearing across the magnet terminals. In the persistent mode, the magnet winding and switch formed a complete superconducting circuit, no further increase in current was possible, and the supply from the stabilizing current unit could be discontinued leaving a stable fixed magnetic field. A 0.01 ohm standard Crompton resistance was connected in series with the current leads to the magnet windings, and the magnet current monitored by measuring the voltage developed across this resistance with one channel of a digital voltmeter. The magnetic field at the centre of the solenoid was linearly related to the current and supplied at a rate quoted as 1568.37 gauss/amp. However, experiments at different sweep rates showed the actual magnetic field to be a function of the sweep rate employed. The relation between sweep rate and magnetic field is examined in section 4.4.5.

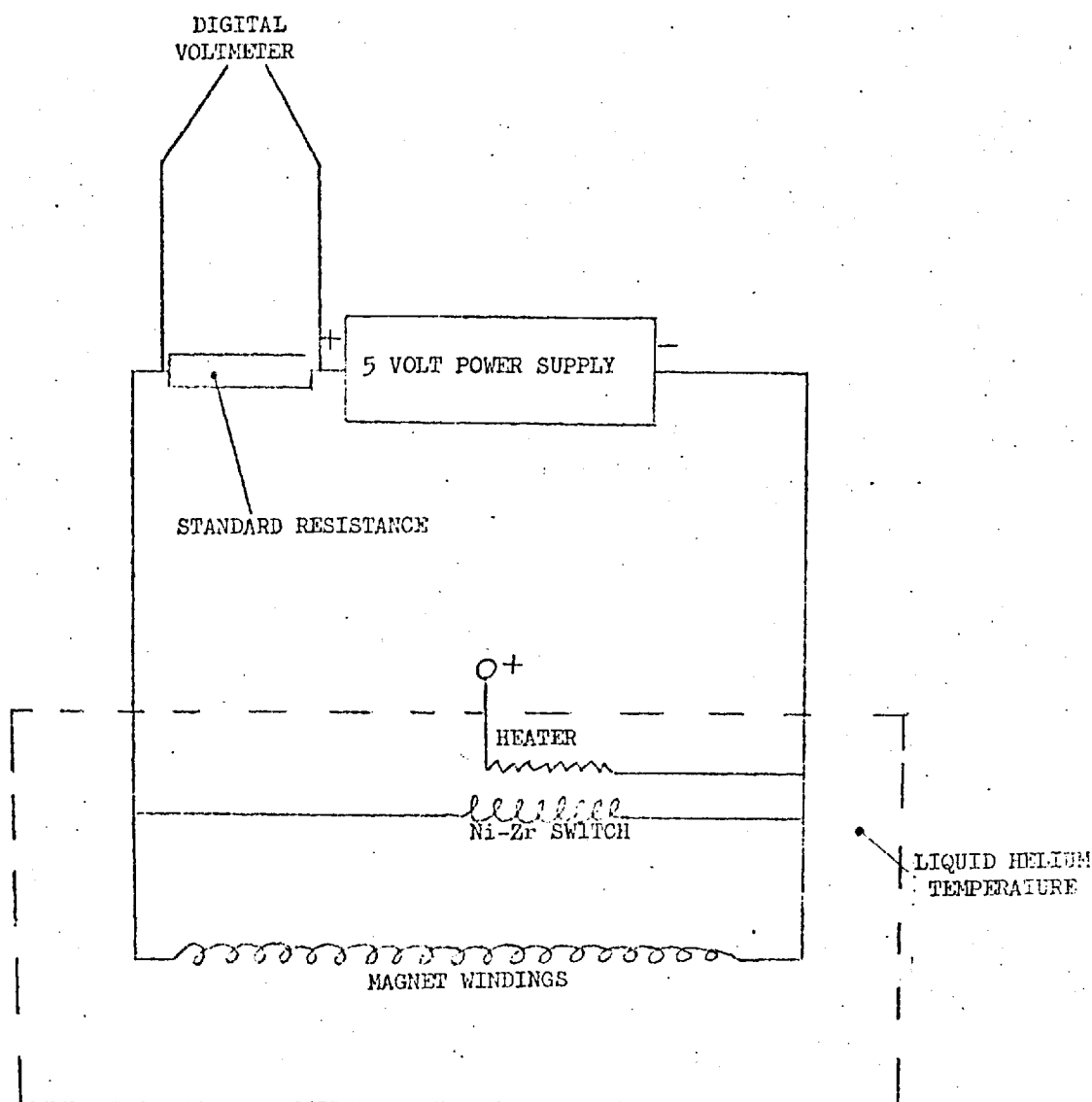


Fig.4.10
Superconducting switch and magnet

4.4.4 Digital Voltmeter

A two channel integrating digital voltmeter (DVM) with two D2 model preamplifiers recorded simultaneously the sample magnetoresistance and the current to the superconducting magnet. The DVM measures an unknown voltage by applying it to a capacitor for a fixed period, and comparing that period with the time taken to discharge the capacitor when a reference voltage of opposite polarity is applied. An input voltage is applied to the capacitor of the integrator for a period determined by an internal counter completing a cycle of 10^4 pulses. On the ten thousandth pulse the capacitor is isolated from the input voltage and transferred to the precisely defined

reference voltage of opposite polarity. The capacitor discharges linearly while the counter continues on its second cycle. As the voltage across the capacitor falls a zero detecting circuit operates, and on reaching zero produces a signal disconnecting the counter from the oscillator. The reading, an accurate measure of the input voltage, is transferred to cold cathode number tubes providing a visual display, and is simultaneously converted by code changers to provide an output for an external electronic typewriter. The typewriter was set to print out alternatively the sample magnetoresistance and magnet current at a maximum rate of one line per second. With the D 2 module preamplifiers, a maximum sensitivity of $10\mu\text{V}$ was obtainable with this instrument. In the sample circuit this was improved by a Hewlett Packard times ten preamplifier placed in front of the DVM which thus enabled the sample voltage to be read with a $1\mu\text{V}$ sensitivity.

4.4.5 Procedure

At liquid helium temperatures the magnetoresistance of unirradiated pyrolytic graphite has an oscillatory component superimposed on the classical magnetoresistance. Before this study, oscillations had not been observed in material irradiated with fast neutrons. Galvanomagnetic measurements at room and liquid nitrogen temperatures had shown that irradiation reduced the relaxation time with a resulting increase in the Dingle temperature. Measurements of the oscillatory magnetoresistance in irradiated specimens were therefore made at the lowest temperature available, namely 1.6 K, while in single crystal and pristine pyrolytic graphite oscillations were readily observed at 4.2 K.

Specimens were cut in the basal plane configuration of section 4.2.1 and mounted horizontally in the high pressure bomb on a tufnol bridge shown schematically in Fig. 4.11. Two samples were placed inside the pressure bomb, one above and one below the bridge cross piece, and a further two samples were placed on the bottom flat outside surface of the bomb. The bridge legs

were glued to the bottom of the bomb insert with seccotine, and the base of the bridge lined up parallel to the bottom of the insert with a travelling microscope. Seccotine was found to retain its adhesive properties at low temperatures, the plastic varnish mentioned earlier was here used to anchor samples to the bridge and bottom surface of the bomb. Soft solder, typically the lead-tin eutectic is known to superconduct at liquid helium temperatures. To avoid magnetic field perturbations all soldered junctions were kept at least 4 cm from the sample.

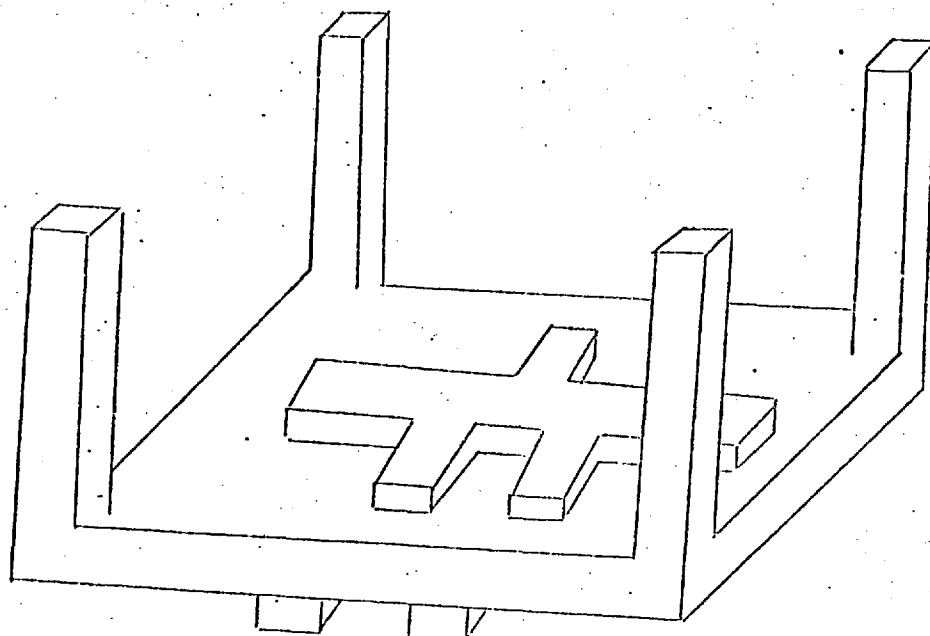


Fig.4.11
Tufnol bridge with samples

The cryostat was rough pumped to remove traces of water and then pre-cooled with liquid nitrogen, both in the nitrogen jacket and the main helium chamber.

When the inside of the crystal had cooled to 77K excess liquid nitrogen was driven off with high pressure nitrogen gas, liquid helium was then transferred to the main bath, cooling both superconducting magnet and the insert dewar to 4.2K. During the transfer the He II pot was pumped and the needle valve opened occasionally to suck cold gas through, thus cooling the pot and specimen tube to 4.2K. Once sufficient helium had

been transferred to the main helium chamber, the insert dewar was filled by opening the needle valve for a few minutes and momentarily opening the butterfly valve on the pumping line to assist the transfer. By isolating the He II pot from the main bath and pumping with the butterfly valve fully open, a low temperature of 1.6K was reached.

Shubnikov de Haas oscillations were recorded for each sample in turn with the two-channel DVM and automatic print-out. Constant current was supplied by the method described in section 4.3.5, and was monitored by measuring the voltage developed across a standard resistance with the Cambridge potentiometer and Tinsley photocell galvanometer amplifier.

4.4.6 Calibration of the Superconducting Magnet

Pyrolytic graphite with its very large magnetoresistance at helium temperatures is a sensitive monitor of the applied magnetic field. It was noted that values of the magnetoresistance of a typical sample at a given magnet current were not the same for different magnet sweep rates. In Fig.4.12, the resistance of a specimen from the IFP 37 series is plotted as a function of magnet current for four magnet sweep rates ranging from 0.3 amps/minute to 3 amps/minute. The phase lag between magnetic field and applied current increases with increasing sweep rate. When the rise in current was brought to a halt, the field continued to rise, reaching a steady state after about forty readings of the DVM. The final field value was independent of the sweep rate employed.

Since the magnetic field fell to zero with zero applied current, resonant currents circulating permanently in the superconductor were absent in this magnet, but the resistive copper present between and about the magnet windings results in a large magnet self induction. In Fig.4.13 lines of constant sample resistance and therefore constant magnetic field are plotted as a function of the sweep rate and magnet current. The phase lag between magnetic field and applied current is proportional to the sweep

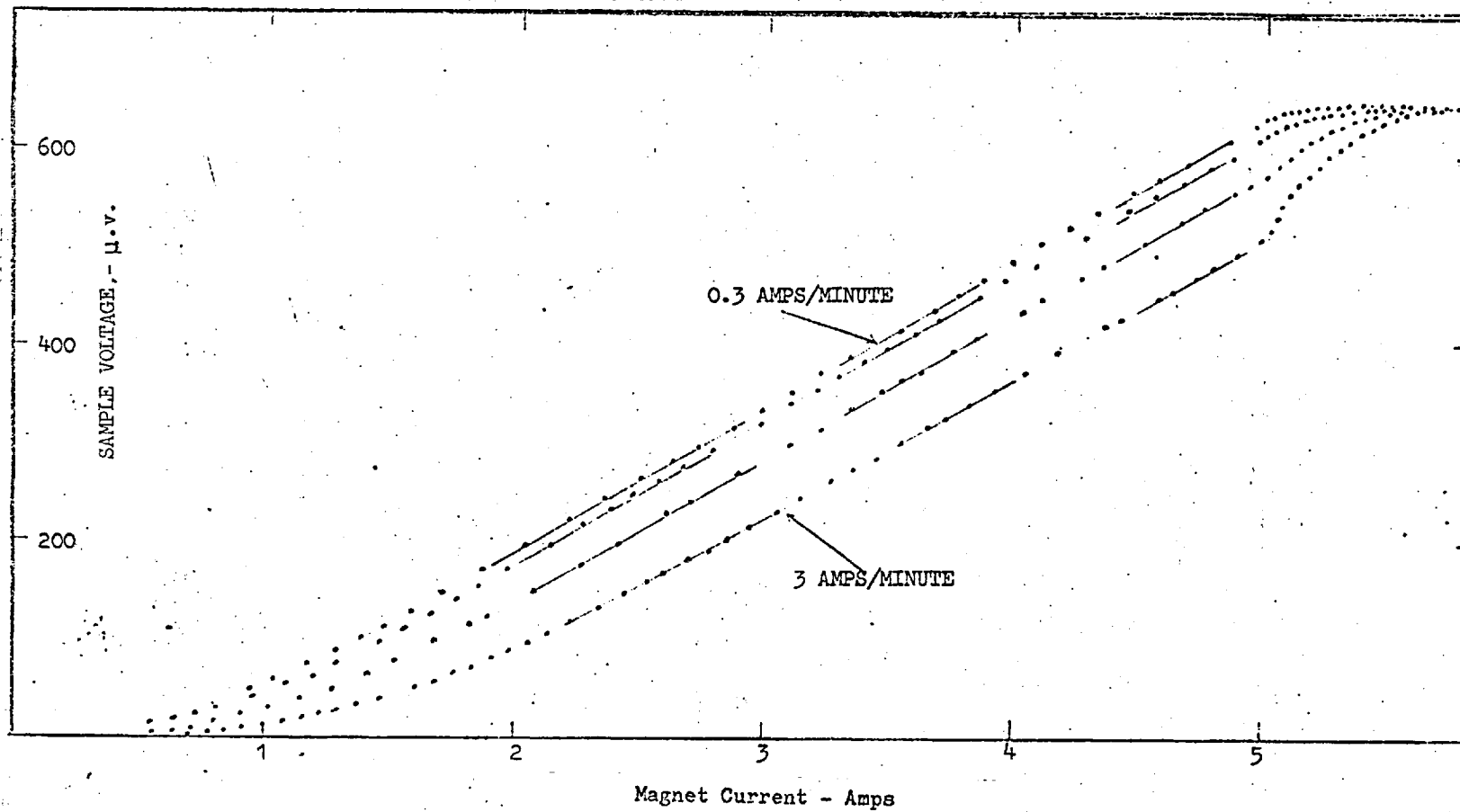


Fig. 4.12

Magneto resistance of graphite sample
at different sweep rates

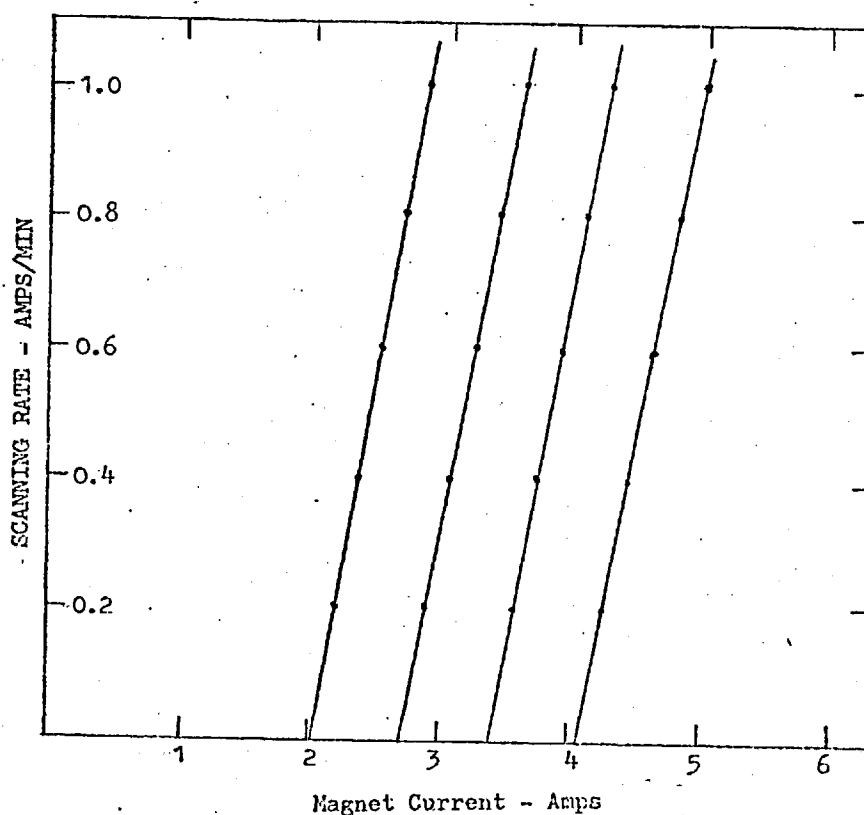


Fig. 4.13
Constant magnetic field lines

rate, and the constant of proportionality is seen to be independent of the magnetic field. In this work a sweep rate of 0.6 amps/minute corresponding to a phase lag of 0.2 amperes was used throughout, and the magnetic field at the sample was equal to $B = I \cdot 1568 - 315$ Gauss.

CHAPTER V

EXPERIMENTAL AND DERIVED RESULTS - OSCILLATORY

5.1 OSCILLATORY DATA

Shubnikov de Haas oscillations were observed in samples of pyrolytic graphite from three separate preparations, two single crystal specimens and, for the first time, in pyrolytic graphite irradiated with fast neutrons. Two fixed temperatures, namely 4.2K and 1.6K were employed and pressures ranging from 1 to 407 bar was applied as described in Chapter IV. The oscillatory results are labelled with run numbers 1, 2 ..., 14 and are listed in Table 5.1. with the experimental conditions. SCG refers to single crystal graphite while HaT, IFP 37 and JHTM 3 are code names for preparations of pyrolytic graphite. Adjacent run numbers of the same material refer to measurements on a single sample and the out of sequence runs 10 and 14 are low pressure and high pressure runs on the same sample.

TABLE 5.1

Run Number	Material	Temperature K	Pressure-Bar	Irradiation Dose - nvt
1	S.C.G.	1.6	1	3.96×10^{15} 1.18×10^{16} 1.18×10^{16}
2	S.C.G.	4.2	1	
3	HaT	1.6	1	
4	HaT	1.6	1	
5	HaT	1.6	117	
6	IFP 37	1.6	5	
7	IFP 37	4.2	4	
8	IFP 37	4.2	407.2	
9	JHTM 3	4.2	1	
10	IFP 37	1.6	122	
11	S.C.G.	4.2	1	
12	HaT	1.6	9	
13	HaT	1.6	124	
14	IFP 37	1.6	5	

Graphite has a magnetoresistance at low temperatures which for good specimens of pyrolytic material approaches very large values. In consequence the quantum oscillations which are observed at liquid helium temperatures are superimposed upon a classical midline rising approximately as $H^{1.79}$, and showing signs of saturation at ~ 25 kG. The effect of temperature on the Shubnikov de Haas oscillations is shown in Fig.5.1 for runs 6 and 7. Thermal broadening of the quantized energy levels, as discussed in section 3.6 is seen to reduce the oscillation amplitude. At the low temperature of 1.6 K evidence for more than one period can clearly be seen in the marked structure of the quantum oscillations of run 1. Irradiation with fast neutrons is known to reduce the carrier mean free path, but oscillations can still be seen in the raw data, and are illustrated in Fig.5.1 for run 3.

5.2 DATA FITTING

The oscillatory data were processed for nine of the fourteen runs with three computer programs initiated by WOORE (1969), developed by COOPER (1971) and modified for the present analysis into a form suitable for use interactively on an ICL 470 computer with teletype printout. As a first step the monotonically rising midline was subtracted graphically according to the procedure described in Appendix A3. The experimental data in the form of punched cards were processed together with the graphical midline by the program 'DVMOUT'. A three-term polynomial fitted by DVMOUT to the midline was subtracted from the data points, and a card deck produced of data minus midline as a function of reciprocal magnetic field. A detailed discussion of the fitting process is included in Appendix A3. By plotting data processed by DVMOUT, direct comparison can be made of oscillatory amplitudes for changing run conditions. This is illustrated for runs 7, and 8 in Fig.5.2, and for runs 12, 3 and 4 in Fig.5.3. Application of pressure to ~ 130 bar has no effect on the oscillatory amplitude. But, the

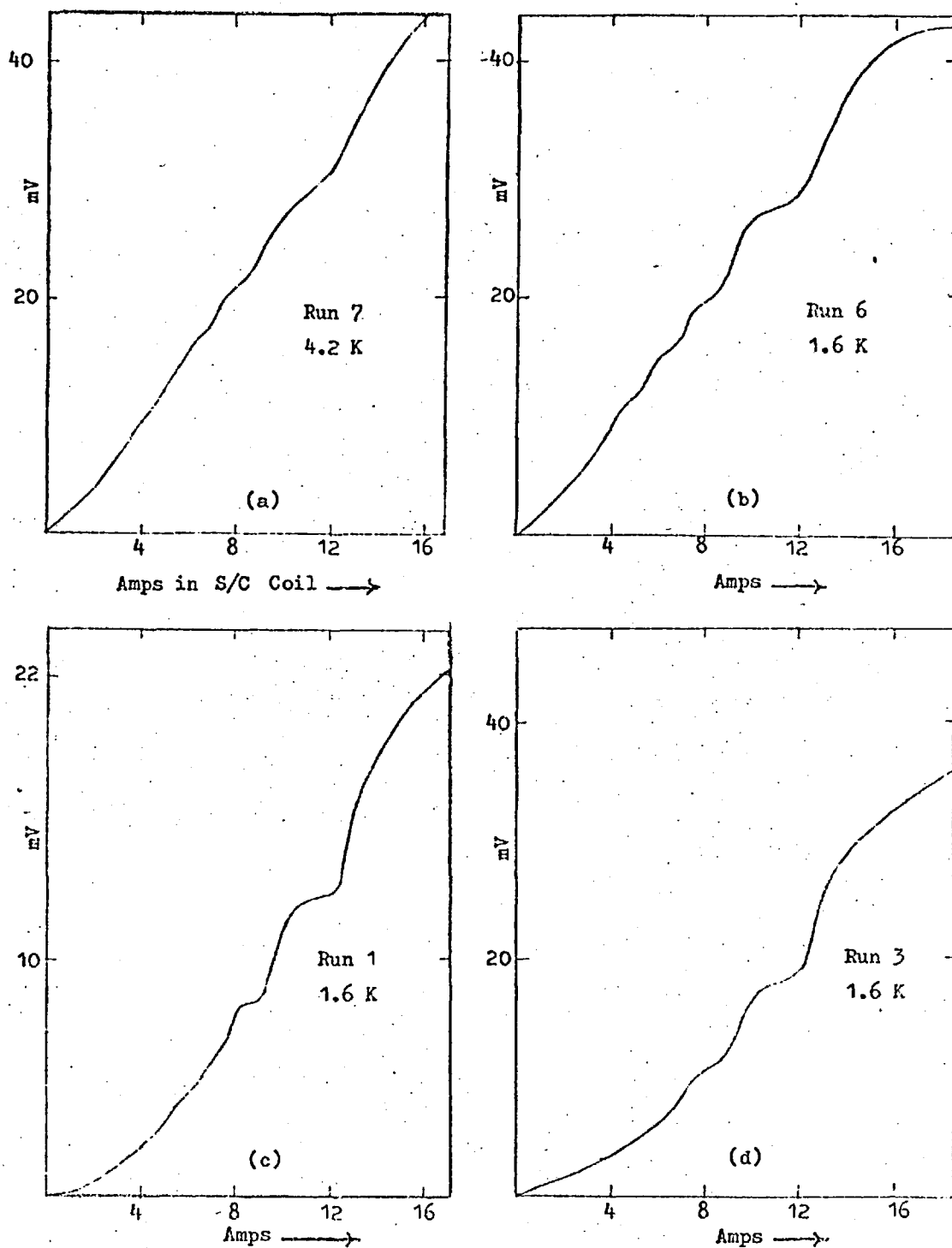


Fig.5.1

DATA - AS RECORDED

- (a),(b) Pristine Pyrolytic Graphite
- (c) Single Crystal Graphite
- (d) Irradiated Pyrolytic

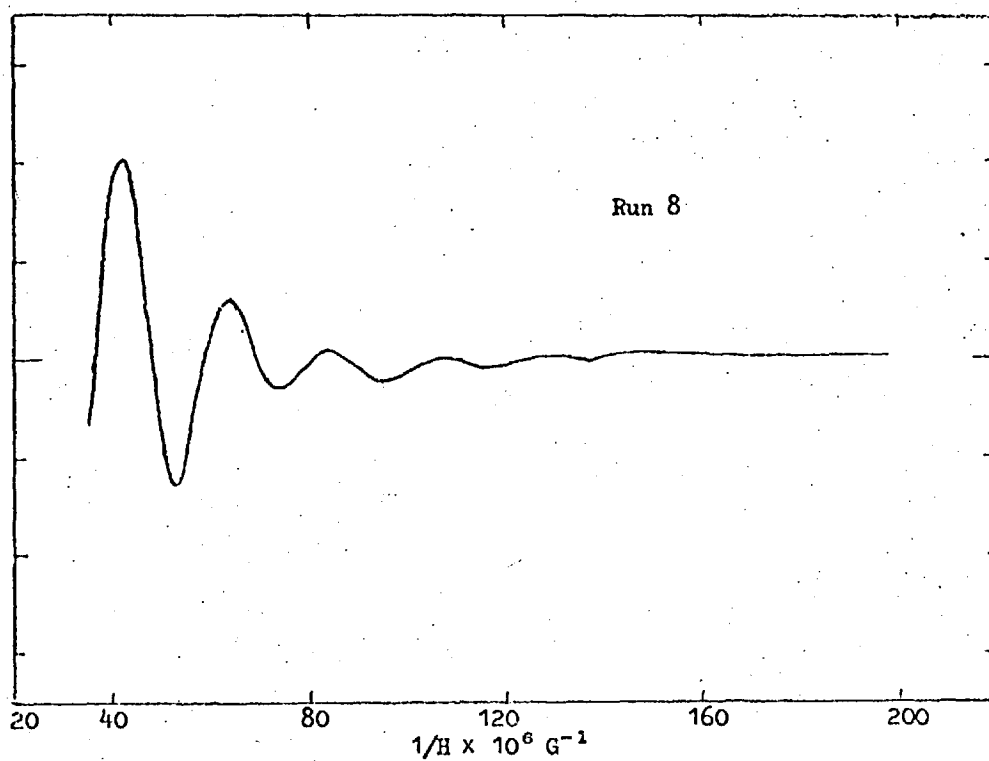
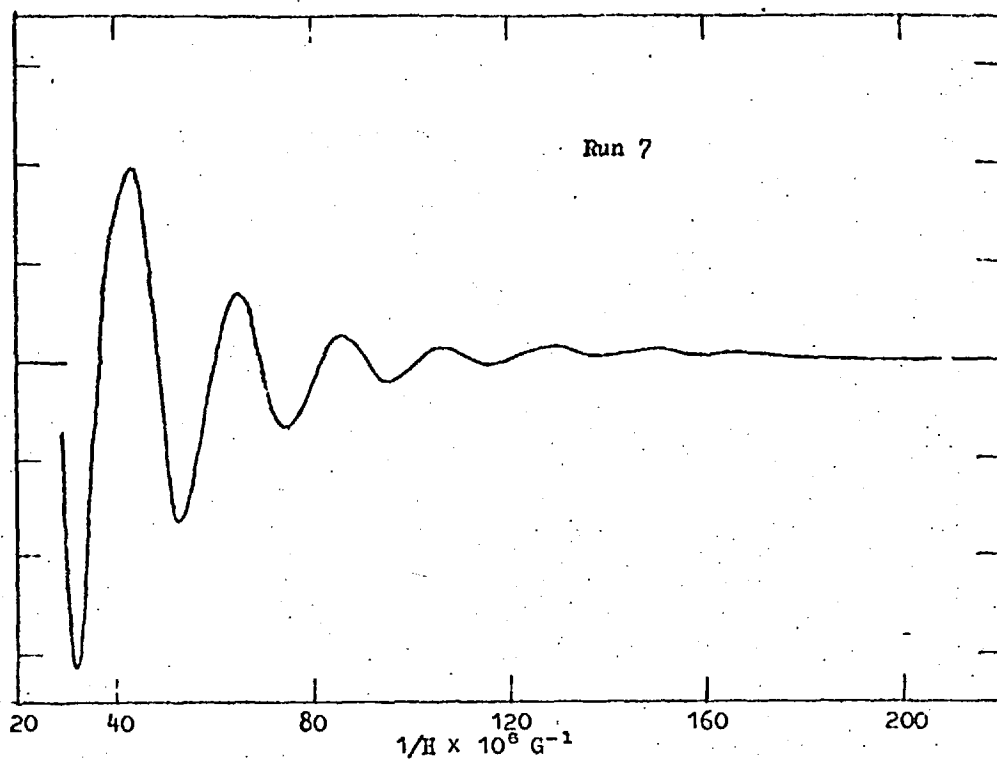


Fig.5.2

SdH Oscillations in Pyrolytic Graphite - DVMOUT Plots.

isobaric freezing technique of Chapter IV, which produced at the sample a pressure of 407 bar, caused a reduction in oscillation amplitude as shown in Fig.5.2, of $\sim 10\%$. Details of the method used to calculate pressure at the sample using solid helium as the transmitting medium, are given in section 5.3.2. The effect of irradiation on the amplitude of oscillation is illustrated in Fig.5.3 by plotting the magnetoresistance $\{\rho(H) - \rho(0)\} / \rho(0)$ against the reciprocal magnetic field for pristine graphite and two irradiation doses. Beats can clearly be seen in the irradiated material indicating the presence of at least two oscillating periods.

5.2.1 Integer Plots

An indication of the periods present in the oscillatory data produced by DVMOUNT can be obtained from integer plots; a technique used by SOULE 1958 in which equivalent points of a full oscillation period are numbered, and integers plotted against corresponding values of reciprocal magnetic field.

Integer plots for, pristine pyrolytic material - run 9, single crystal graphite - run 2, and irradiated pyrolytic - run 4 are shown in Fig. 5.4. The oscillation period, which must necessarily be an average of all the contributing periods, can be read directly from the graph as the gradient of a line connecting the integer points. The single crystal specimen of run 2 clearly has at least two periods present with a beat occurring after eight integer points or four complete cycles. Pyrolytic graphite, however, exhibits an integer plot which can be well represented by a single line without break, and indicates that oscillations in this material are monop periodic and are dominated by a period of about $2.1 \times 10^{-5} \text{ G}^{-1}$. In neutron irradiated graphite with its much reduced magnetoresistance, two periods can be identified, and for run 4 of Fig.5.4 beats again occur after four complete cycles. At high fields, a period of $1.8 \times 10^{-5} \text{ G}^{-1}$ appears to be dominant while at low fields the period is close to $1.4 \times 10^{-5} \text{ G}^{-1}$.

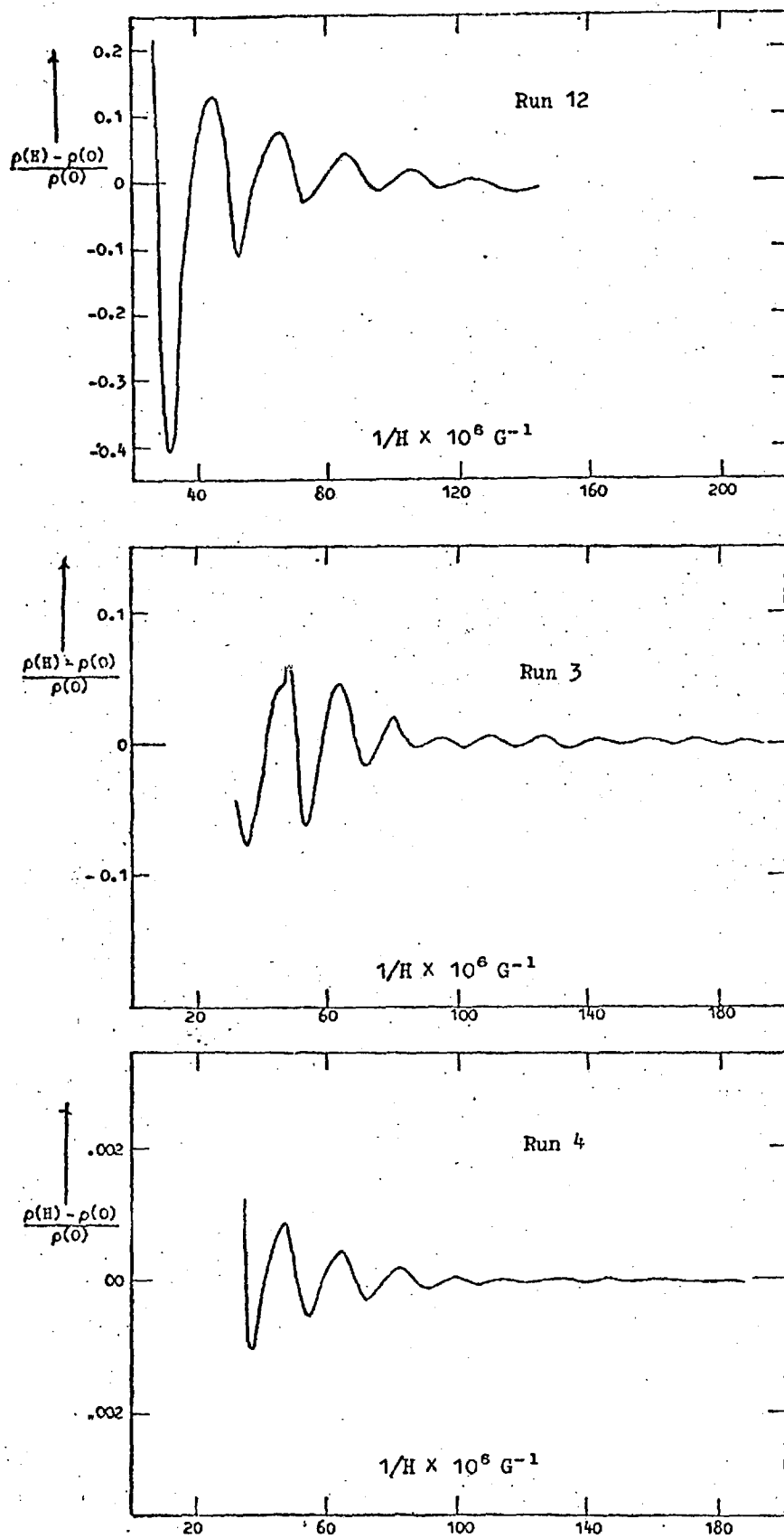


Fig.5.3

Amplitude variation of normalised SdH oscillations with changing run conditions

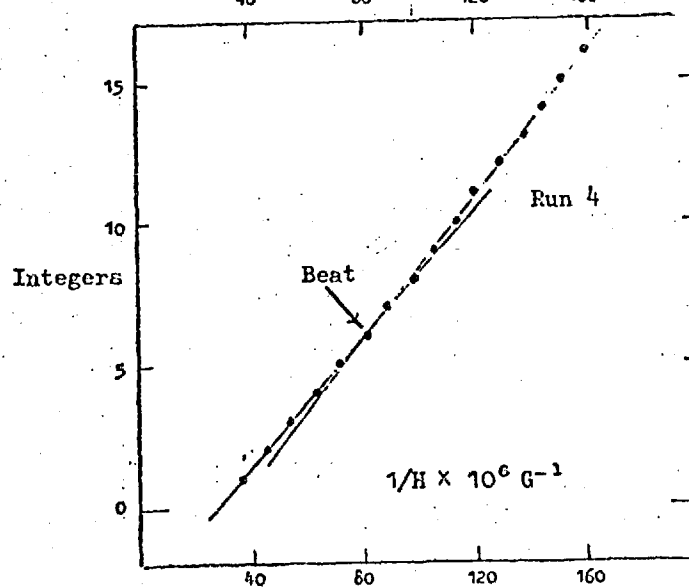
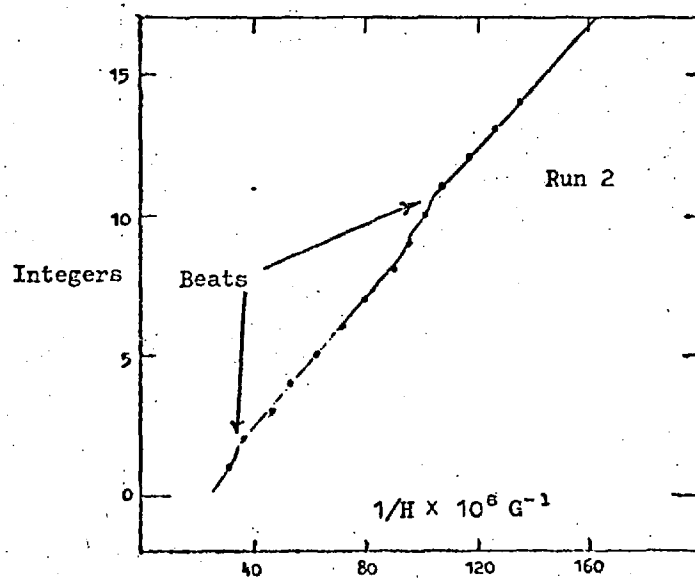
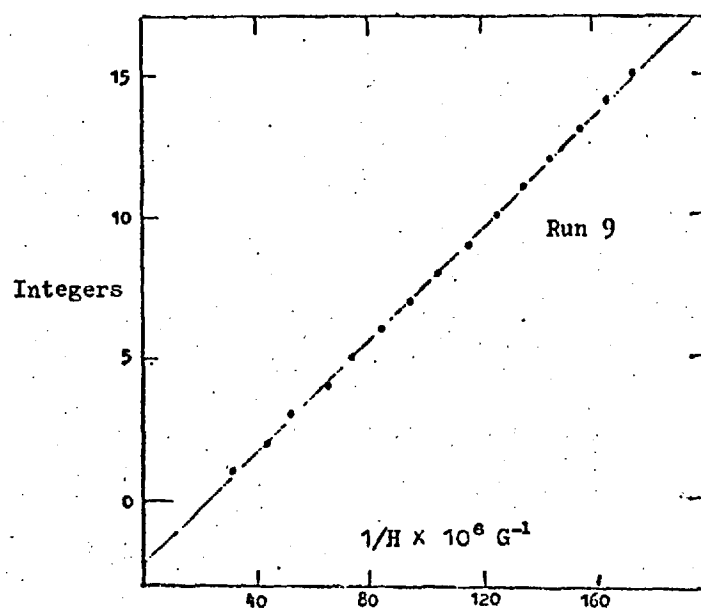


Fig. 5.4
Integer Plots

Extrapolating the integer plots to the abscissa zero is equivalent to applying an infinitely strong magnetic field. Run 9 of Fig.5.4 extrapolated in this way shows that only one more complete oscillation is possible after the 40kG maximum field used in this work, thus confirming the discussion of section 3.6, which predicted only two remaining filled quantum levels after 40kG. Further evidence for this approach to the quantum limit is provided by the changing shape of the oscillations at the highest fields employed. The cusp like shape at high magnetic field has been discussed in some detail by BIBISKIN (1957) and the asymmetry has been utilized by WOOLLAM (1971) in the identification of electron and hole terms contributing to the quantum oscillations.

Of the fourteen runs at liquid helium temperature only the single crystal specimen at 4.2K was too noisy for detailed analysis. The results of integer plots for the remaining thirteen runs are listed in Table 5.2.

TABLE 5.2

Run Number	Periods $\times 10^{-5} \text{ G}^{-1}$
1	1.63
2	1.70 , 1.81
3	1.78 , 1.54
4	1.79 , 1.39
5	1.71 , 1.47
6	2.09
7	2.16
8	2.07
9	2.06
<u>10</u>	2.10
11	—
12	2.08
13	2.08
<u>14</u>	2.13

Application of pressure appears to reduce the oscillation period when applied

through liquid helium, runs 10, 14, and through the isobaric freezing process employed in the pair of runs 7 and 8. Irradiation by fast neutrons in addition to reducing the magnetoresistance increases the oscillation frequency of monop periodic pristine graphite, resulting in a reduction of the $2.1 \times 10^{-5} \text{ G}^{-1}$ period to a value closer to $1.8 \times 10^{-5} \text{ G}^{-1}$. Although, the presence of two periods of comparable strength makes the latter figure an average value.

5.2.2 Iterative Fitting

The integer plots of Fig.5.4 and Table 5.2, although providing period values quite close to the accepted values for graphite, are not capable of selecting individual periods from material with more than one oscillatory component. For this purpose an iterative technique was used to fit data in the form of Fig.5.4 to the generalised Landau relation of section 3.6:

$$G_i(r) = H^n \sum_r W_i(r) \frac{r U_i}{\sinh(r U_i)} \cdot \exp(-\lambda_i r) \cos \left[\frac{2\pi r}{P_i H} - \psi_i(r) \right] \dots (5.1)$$

with $U_i = \frac{2\pi^2 k_B T}{h \omega_{ci}}$, $\lambda_i = \frac{U_i \Delta T_{Di}}{T}$, $W_i(r) = W_i(1) r^{-\frac{3}{2}} \cos \frac{r \pi m_i^*}{m_0}$

$\psi_i(r)$ is the phase factor, and

ΔT_{Di} the Dingle temperature equal to $\frac{h}{\pi k \tau_{coll}}$

where τ_{coll} is an average carrier collision time.

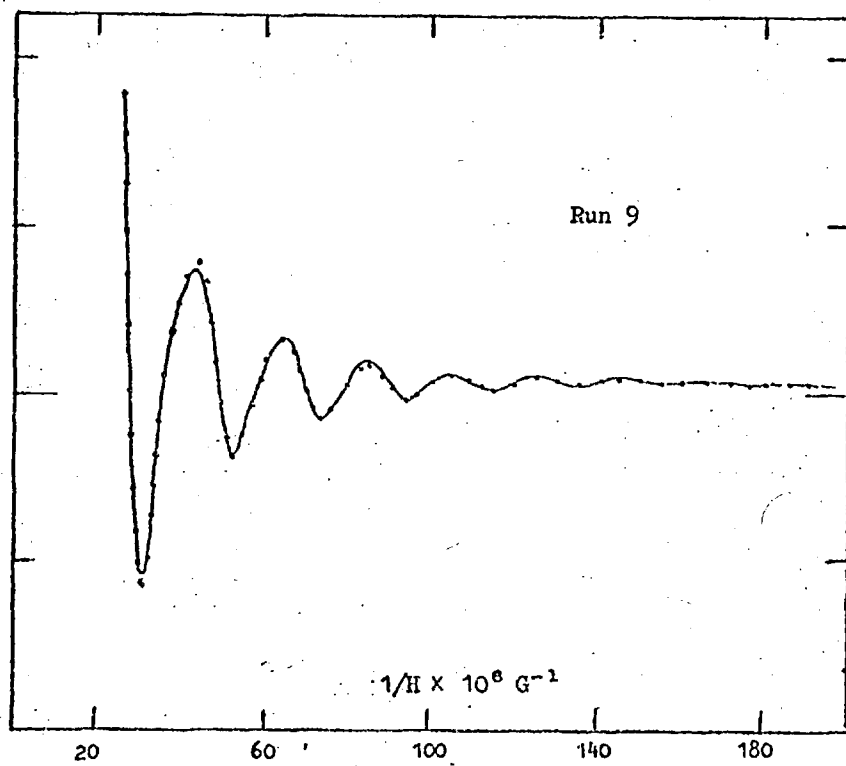
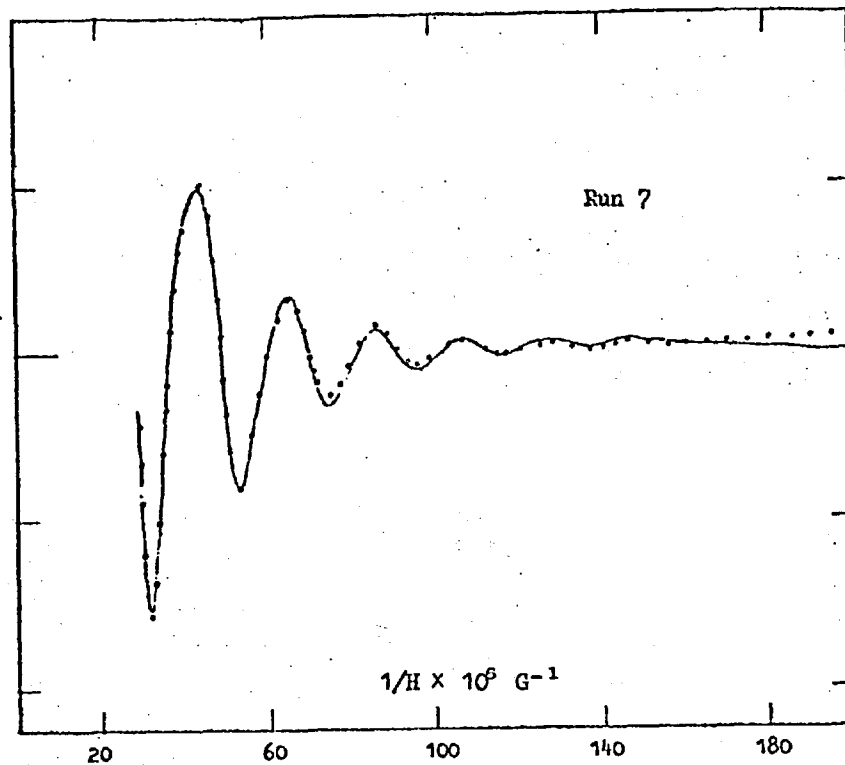
Details of the fitting procedure are given in Appendix A3. and briefly, involved the use of a program developed by POWELL (1964) and available as a subroutine VAO 4A on the ICL 470 computer used for the analysis. The subroutine finds the minimum of a function of several variables, and requires no derivatives while the user was required to provide a routine to evaluate the function for any value of the variables. In this case the function was the sum of the squares of the residuals between the experimental data and equation (5.1) evaluated for certain values of the variables P_i , ΔT_{Di} , n_i , $U_i H$, $W_i(r)$, $\psi_i(r)$, and the coefficients of a

sixth order polynomial describing the midline remaining in the DVMOUT plots of Fig.5.2.

The minimum was never found in less than N iterations, where N is the number of variables, and the subroutine calculates the function at least $2N$ times per iteration. A routine developed by WOORE (1969) was used to evaluate the function before and after each iteration by VAO 4A and enabled the user to free all of the variables for iteration or to lock some of the variables, namely P_0 , ΔT_i , n_i , $U_i H$ and the six polynomial coefficients at present values. Convergence was assumed when an iteration changed each variable by less than 10% of the stated accuracy, at which point subroutine VAO 4A printed out final values for all of the N variables together with the minimum value of the function.

A third program reconstructed the plots of Fig.5.2 from the Landau expression of equation (5.1) for values of the N variable produced by VAO 4A, and proved to be a useful monitor on the fitting progress. Exemplary fits to the experimental data are shown in Fig.5.5 for runs 7 and 9.

Although we are concerned in this work principally with the change of period with changing experimental conditions, BENDER and YOUNG (1972b, 1973) have shown how the oscillatory amplitudes can be interpreted as a guide to the scattering mechanisms present, at low temperatures, in single crystal and pyrolytic graphite. The present finding of hole dominated oscillations in pristine pyrolytic graphite is in complete agreement with the previous work of WILLIAMSON et al (1965), ANDERSON et al (1967) and WOORE (1969). In fact all pure material whether single crystal or pyrolytic has been found to be hole dominated with the exception of the synthetic single crystals of ITSKEVICH and FISCHER (1967), which are now thought to have contained negatively charged point defects, and the pyrolytic material of obscure origin examined briefly by ANDERSON et al (1967). In Chapter III



— Experiment
 o Iterative Fit

Fig.5.5

Measured SdH oscillations reproduced by computational fit to the generalised Landau expression

details of the graphite band structure are outlined together with factors affecting the amplitude of Shubnikov de Haas oscillations. It is clear that the presence of twice as many hole as electron extrema in the Brillouin zone, and the higher effective mass of the electron will reduce the electron contribution compared to that of the hole. The effective masses of the electron ($0.059 m_0$) and hole ($0.037 m_0$) enter the Landau expression through the amplitude term $W_i(r)$ but, more importantly, through the two damping factors $U_i/\sinh U_i$ (temperature damping) and the Dingle factor $e^{-U_i \Delta T_i / T}$ (impurity damping). As the magnetic field increases, the damping falls off at a rate which is greater for carriers of lighter mass (holes) than for the heavier carriers, namely the electrons. Thus the neutron irradiated graphite of run 4 and Fig.5.4 has an electron contribution with a period close to $1.5 \times 10^{-5} \text{ G}^{-1}$ at low field which tends towards the hole period of $2.1 \times 10^{-5} \text{ G}^{-1}$ at high magnetic field.

The curvature of the Fermi surface extremum, expressed through the term $(d^2 A_0 / dk_z^2)^{-1/2}$ is a measure of the Landau state degeneracy and has been included in equation (5.1) by LIFSHITZ and KOSEVICH (1956). The greater this term, the larger the oscillation amplitude (PIPPARD (1965)). In graphite the curvature of the hole extremal area of cross-section is slightly less than that of the electron, thus further enhancing the hole contribution to the oscillatory amplitude.

In the SdH effect a scattering event sufficient only to dephase the cyclotron orbit will catastrophically reduce the oscillation amplitude. Low angle scattering, which is unable to randomise the carrier momentum, and thus to influence D/C conductivity, has a controlling influence on the amplitude of quantum oscillations. The band parameter γ_3 produces in graphite a trigonal warping of the Fermi surface which is zero at point H at the zone edge, but rises to a maximum at K. Low angle scattering will therefore deflect electrons through higher angles than holes. Finally,

scattering by charged impurities, as argued by BENDER and YOUNG (1972b), will scatter with a cross section which for an attractive potential is twice the value for scattering via a repulsive potential. Selective scattering will consequently occur at charged impurities and in neutron irradiated material, having negatively charged point defects, electrons will be weakly and holes strongly scattered by the Coulombic potential. The electron oscillation can in these circumstances reach a strength comparable with the hole oscillation and beats will occur if sufficient cycles are recorded. This behaviour is exemplified in the present work in runs 9 and 4 of Fig.5.4.

5.3 DERIVED RESULTS

The aim of the low temperature measurements is to obtain a value for $d \ln n / dP$, the rate of change of carrier density with increasing pressure, and to assess the acceptor yield on irradiating pyrolytic graphite with fast neutrons.

Two periods were identified in the present work corresponding to the three elongated surfaces at the corner of the Brillouin zone. At the commencement of this work it was generally accepted that the Fermi surface of graphite consisted of holes located around the point $K(K')$ on the zone corner and electrons as the two outer surfaces around point $H(H')$. This assignment was based on $dHvA$ and cyclotron resonance measurements together with the band structure requirements of SLONCZEWSKI and WEISS (1955) and McCLURE (1957). However the location of the hole and electron Fermi surface was a matter of some debate until SOULE (1964), lowered the Fermi level by introducing boron into the graphite lattice. The interpretation of this experiment led to the erroneous belief that γ_2 was positive, and holes were located at the centre of the zone corner. The observation, in this study, of SdH oscillations in neutron irradiated graphite provides an independent method for establishing the position of the two component bodies

of the Fermi surface. A detailed investigation of this technique has subsequently been made by COOPER, SMITH, WOORE and YOUNG (1971).

Irradiation with fast neutrons is known to depress the Fermi level in graphite resulting in a positive, almost field independent, Hall coefficient and a large positive thermoelectric power (SPAIN, UBBELOHDE and YOUNG (1967); REYNOLDS (1968)). The hole surface will therefore expand and the electron surface contract on irradiation. If the short period is properly attributed to holes at K the two periods will diverge with increasing irradiation dose, but if electrons are located at K the periods will converge.

The results of the computational analysis described above and applied to unirradiated pyrolytic graphite in the form of run 12, and to irradiated graphite from the same preparation, runs 3 and 4, are listed in Table 5.4. Irradiation is seen to reduce the long period which was the only period which could clearly be identified in pristine pyrolytic graphite while further irradiation increased the short period. In Fig.5.6 the short and long periods are plotted

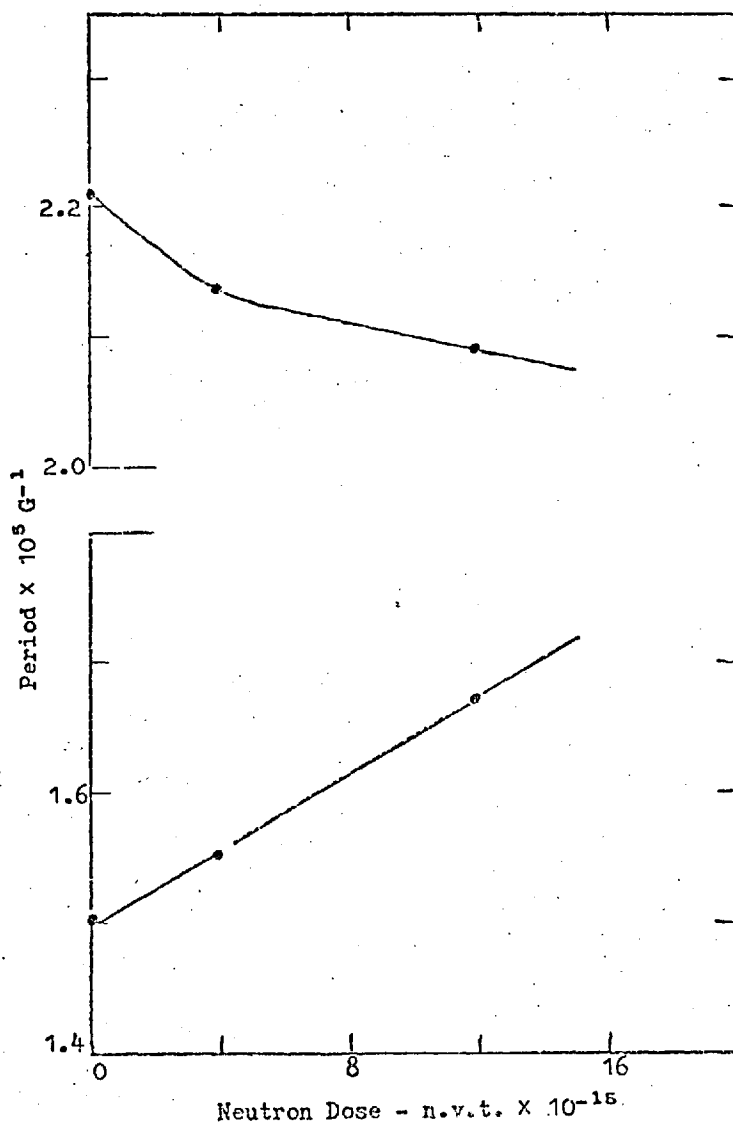


Fig.5.6

SdH periods converging with increasing irradiation

against irradiation dose and are seen to converge. The short period for pristine pyrolytic graphite included in this diagram, was calculated using the acceptor concentration for pristine material found by COOPER et al (1971), and the analysis of section 5.4. Electrons are therefore located at the centre of the Brillouin zone edge with the Fermi surface having two outer hole bodies. This finding confirms the magneto-optical reflection data of SCHROEDER et al (1968), and the oscillatory Hall and thermoelectric power measurements of WOOLLAM (1971).

5.3.1 Acceptor Density

Expressions for the external cross-sectional areas and Fermi surface volumes, as derived in Chapter III in terms of the band parameters, may be written within the $\gamma_3 = \gamma_4 = \gamma_5 = 0$ approximation in the form:

$$A_e = \frac{4\pi}{3a_o^2\gamma_o^2} (2\gamma_2 - E_f)(2\gamma_1 - E_f + \Delta)$$

$$A_h = \frac{4\pi}{3a_o^2\gamma_o^2} \left(E_f - \frac{\gamma_2\Gamma_E^2}{2}\right) (E_f + \gamma_1\Gamma_E - \Delta)$$

$$V_e = \frac{4}{3} A_e \cdot \frac{4}{c_o} \cos^{-1} \left(\frac{E_f}{2\gamma_2}\right)^{\frac{1}{2}}$$

$$V_h = \frac{8}{3} A_h \cdot \frac{4}{c_o} \left\{ \cos^{-1} \frac{\Gamma_E}{2} - \cos^{-1} \left(\frac{E_f}{2\gamma_2}\right)^{\frac{1}{2}} \right\}$$

where

$$\Gamma_E = \frac{1}{3\gamma_1} \left(\Delta - E_f - \sqrt{(\Delta - E_f)^2 + \frac{6\gamma_1^2 E_f}{\gamma_2}} \right)$$

Δ , γ_2 and E_f are all at least an order of magnitude smaller than γ_1 and we may write Γ_E , following AOSS, as:

$$\Gamma_E = \sqrt{\frac{2}{3} \frac{E_f}{\gamma_2}}.$$

Since the density of states in $\underline{k}$ space is $1/4\pi^3$ per unit volume, the electron and hole densities are obtained by evaluating the expressions

$$n_e = \frac{1}{4\pi^3} \cdot \frac{4}{3} A_e \cdot \frac{4}{c_o} \cos^{-1} \left(\frac{E_f}{\gamma_2}\right)^{\frac{1}{2}} \quad \dots (5.2)$$

$$n_h = \frac{1}{4\pi^3} \cdot \frac{8}{3} A_h \cdot \frac{4}{c_0} \left\{ \cos^{-1} \left(\frac{E_f}{6\gamma_2} \right)^{\frac{1}{2}} - \cos^{-1} \left(\frac{E_f}{2\gamma_2} \right)^{\frac{1}{2}} \right\} \dots (5.3)$$

The ratio E_f/γ_2 turns out to be a very stable parameter, e.g. irradiation with fast neutrons to a dose of 2.2×10^{16} nvt increases the value by less than 0.8% (COOPER et al (1971)). Application of pressure to 4 kbar left the value unchanged according to ANDERSON et al (1967), while ITSKEVICH and FISCHER (1967) estimate a change of 0.5% over a pressure range of 8 kbar. Moreover, the absolute value measured for this parameter on a wide range of materials is remarkably constant. The values listed in Table 5.3 of a number of independent assessments differ by less than 5%.

TABLE 5.3

Source	E_f/γ_2
Itskevich & Fischer (1967)	1.3265
Cooper et al (1971)	1.3380
Anderson et al (1967)	1.3000
Bender and Young (1972)	1.3588
Likhter & Kechin (1964)	1.3500

It is therefore a good approximation to assume that E_f/γ_2 is independent of applied pressure and neutron irradiation to levels in excess of the highest pressure and longest irradiation dose used in this work. The most recent estimate of E_f/γ_2 , namely that obtained by BENDER and YOUNG (1972a), has a greater degree of consistency than that achieved by previous authors, e.g. COOPER et al (1971), and is the value adopted here.

The external cross-sectional areas of the electron and hole surface, A_e and A_h respectively, are related to the SdH periods P_e and P_h through the expression

$$A_i = \frac{2\pi e}{ch} \cdot \frac{1}{P_i} \quad i = e, h.$$

Then

$$A_i = 9.548 \times 10^7 \cdot \frac{1}{P_i} \text{ cm}^{-2}$$

and the electron and hole densities are linearly related to the oscillation frequency:

$$n_e = 3.862 \times 10^5 \times 9.548 \times 10^7 \cdot \frac{1}{P_e} \text{ cm}^{-3}$$

$$n_h = 6.0715 \times 10^5 \times 9.548 \times 10^7 \cdot \frac{1}{P_h} \text{ cm}^{-3}$$

with P_e and P_h expressed in G^{-1} .

Electron and hole densities calculated with the above formulae are listed with other relevant quantities for the nine fully analyzed runs in Table 5.4. Irradiated graphite has a hole excess which increases as in Fig.5.7 with increasing irradiation dose. If we assume that each damage site accepts a single electron, then the acceptor yield is found to be 23.7 acceptors/nvt. This is three times the value estimated by COOPER et al (1971).

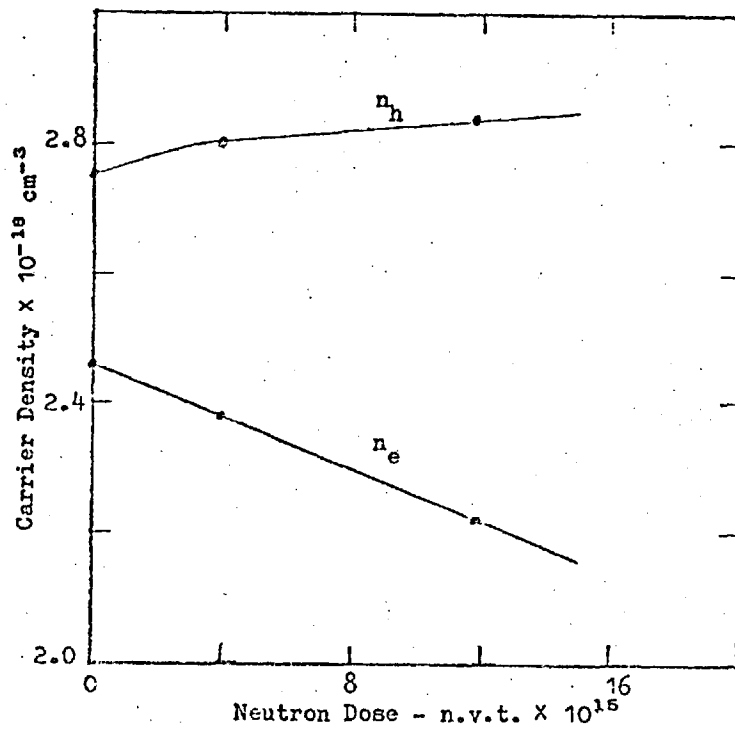


Fig.5.7
Carrier concentrations diverging with increasing irradiation

TABLE 5.4

Run No.	Periods $G^{-1} \times 10^5$		Extremal Area $\text{cm}^{-2} \times 10^{-12}$ of cross-section		Fermi Surface Volumes $\text{cm}^{-3} \times 10^{18}$		Carrier Density $\text{cm}^{-3} \times 10^{18}$		Dingle Temperature K	
	h	e	A_h	A_e	V_h	V_e	n_h	n_e	h	e
1	2.0753	1.5939	4.6007	5.9903	173.2935	287.0287	2.7934	2.3133	4.3939	2.0289
3	2.0675	1.5509	4.6181	6.1564	173.9475	294.0987	2.8039	2.3775	10.1800	3.6586
4	2.0451	1.6615	4.6687	5.7466	175.8527	275.3507	2.8346	2.2193	4.2044	3.5957
7	2.1278	-	4.4872	-	169.0178	-	2.7244	-	4.9934	-
8	2.0999	-	4.5468	-	171.2634	-	2.7606	-	6.7441	-
9	2.1025	-	4.5412	-	171.0516	-	2.7572	-	4.0217	-
10	2.0766	-	4.5979	-	173.1850	-	2.7916	-	2.9342	-
12	2.1056	-	4.5345	-	170.7998	-	2.7532	-	4.500	-
14	2.0839	-	4.5817	-	172.5784	-	2.7818	-	2.2698	-

5.3.2 Pressure Dependence of Carrier Density

In order to estimate the rate of increase of electron and hole density with pressure, normalised to the density at zero pressure, we take the logarithm of equations (5.2) and (5.3) and differentiate wrt the applied pressure.

$$\frac{d \ln n_e}{dP} = \frac{d \ln A_e}{dP} - \frac{d \ln c_o}{dP} + \frac{d \ln \cos^{-1} \left(\frac{E_f}{2\gamma_2} \right)^{\frac{1}{2}}}{dP}$$

$$\frac{d \ln n_h}{dP} = \frac{d \ln A_h}{dP} - \frac{d \ln c_o}{dP} + \frac{d \ln \left\{ \cos^{-1} \left(\frac{E_f}{6\gamma_2} \right)^{\frac{1}{2}} - \cos^{-1} \left(\frac{E_f}{2\gamma_2} \right)^{\frac{1}{2}} \right\}}{dP}$$

Then

$$\frac{d \ln n_i}{dP} = \frac{d \ln A_i}{dP} + 2.85 \times 10^{-6} \quad i = e, h.$$

Since the pyrolytic graphite used for the pressure measurements was monophasic we have no way of measuring $d \ln n_e / dP$, but we may infer a value from measurements on the hole period. Application of pressure increases the band overlap and results in an increase of both electron and hole densities. Graphite itself is not compensated, usually exhibiting an excess of holes, but the departure from compensation may be considered independent of pressure such that:

$$\frac{d(n_e - n_h)}{dP} = 0 \quad \text{then} \quad \frac{dV_e}{dP} = \frac{dV_h}{dP}$$

and

$$\frac{d \ln n_e}{dP} = \frac{V_h}{V_e} \frac{d \ln n_h}{dP}.$$

Substituting for V_h and V_e from equations (5.2) and (5.3)

$$\frac{d \ln n_e}{dP} = \frac{2A_h}{A_e} \frac{\left\{ \cos^{-1} \left(\frac{E_f}{6\gamma_2} \right)^{\frac{1}{2}} - \cos^{-1} \left(\frac{E_f}{2\gamma_2} \right)^{\frac{1}{2}} \right\}}{\cos^{-1} \left(\frac{E_f}{2\gamma_2} \right)^{\frac{1}{2}}} \cdot \frac{d \ln n_h}{dP}.$$

An acceptor concentration of $0.292 \times 10^{18}/\text{cc}$ found by COOPER et al (1971) in pristine pyrolytic graphite, together with the hole period of $2.1278 \times 10^{-5} \text{ G}^{-1}$ measured for pristine graphite in run 7 predicts an electron period of $1.516 \times 10^{-5} \text{ G}^{-1}$. Then:

$$\frac{d \ln n_e}{dP} = 1.09 \frac{d \ln n_h}{dP} .$$

Before applying the above formulae to the data of Table 5.4, the pressure exerted through the isobaric freezing technique of run 8 must be calculated from the known isochores of solid helium. At the applied pressure of 418.5 bar, helium 4 melts at a temperature of 7.8 K. As the temperature falls, pressure at the sample is reduced according to Fig.5.8. In this figure the tabulated results of DUGDALE and FRANCK (1964) are plotted and extrapolated to higher temperatures. A temperature drop of 3.6 K reduces the applied pressure by 2.7%, and at the sample the final pressure at a working temperature of 4.2 K is 407.2 bar.

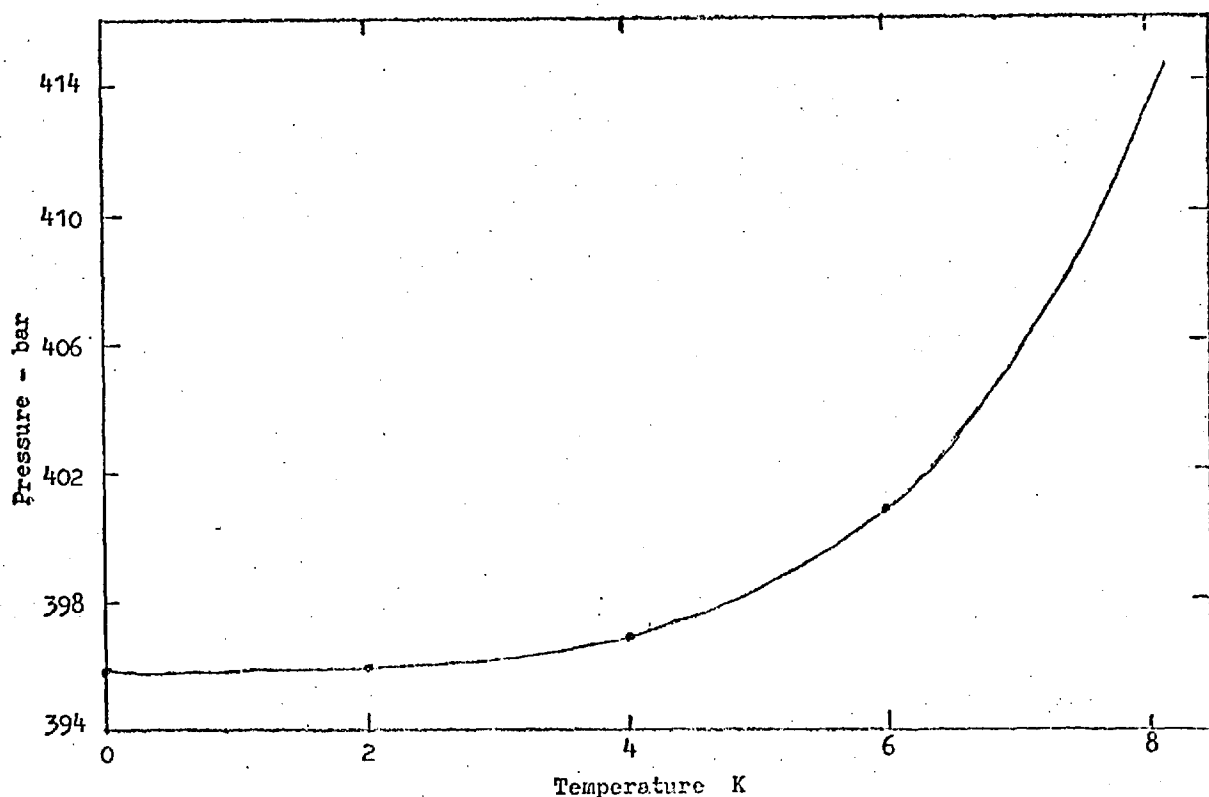


Fig.5.8

Isochore of solid ^4He

A pressure differential of 403.2 bar between runs 7 and 8 increases the carrier density resulting in a change in hole period of $0.0279 \times 10^{-5} \text{ G}^{-1}$, so that for the isobaric freezing technique

$$\frac{d \ln p_h}{dP} = 32.47 \times 10^{-6} \text{ bar}^{-1}.$$

Liquid helium assumed to be perfectly incompressible transmits all of the 122 bar applied in run 10, resulting in a period change of $0.0073 \times 10^{-5} \text{ G}^{-1}$ and a value of $29.94 \pm 1.5 \times 10^{-6} \text{ bar}^{-1}$ for the pressure dependence of the hole period. A mean value of $31.21 \pm 1.5 \times 10^{-6} \text{ bar}^{-1}$ is therefore obtained for material IFP 37.

Then:

$$\frac{d \ln n_h}{dP} = (31.21 + 2.85) \times 10^{-6} = 34.06 \pm 1.5 \times 10^{-6} \text{ bar}^{-1}.$$

A value for the pressure dependence of the electron density may be obtained using equation (5.4)

$$\frac{d \ln n_e}{dP} = 1.09 \frac{d \ln n_h}{dP} = 37.12 \times 10^{-6} \text{ bar}^{-1}.$$

The rate of increase of carrier density with applied pressure has thus a mean value of:

$$\frac{d \ln n}{dP} = 35.59 \pm 1.5 \times 10^{-6} \text{ bar}^{-1}.$$

ANDERSON et al (1967) measured a value of $39.9 \times 10^{-6} \text{ bar}^{-1}$ for this quantity on single crystals of naturally occurring graphite at pressures up to 4 k bar. ITSKEVICH and FISCHER (1967) working at 4.8 and 8.0 k bar on single crystals of synthetic graphite were able to identify only the electron period, and obtained a value of $37.2 \times 10^{-6} \text{ bar}^{-1}$ for $d \ln n_e / dP$.

However, there is good agreement between the measured pressure dependence of the electron density in this work ($37.12 \times 10^{-6} \text{ bar}^{-1}$) and both that of ITSKEVICH and FISCHER ($37.2 \times 10^{-6} \text{ bar}^{-1}$) and AOSS at $36.88 \times 10^{-6} \text{ bar}^{-1}$. The electron dominated pyrolytic graphite examined by AOSS produced a pressure derivative which agreed with their single crystal majority electron

result and is therefore in excellent quantitative agreement with that measured in this work. But, they appear to have been unable to measure the hole period in pyrolytic graphite and thus the pressure dependence of $34.06 \pm 1.5 \times 10^{-6} \text{ bar}^{-1}$ estimated here is the first measurement of the pressure derivative for the majority holes in material other than natural single crystals.

5.3.3 Relaxation Times

Table 5.4 includes values of the Dingle temperatures estimated by program VAO 4A. This factor is related to an average relaxation time through the expression:

$$\Delta T_i = \frac{h}{\pi k_B \tau_i(\text{coll})}$$

and may be used to estimate $\tau_i(\text{coll})$. However, in agreement with COOPER et al (1971) we find that there is no systematic dependence of Dingle temperature on acceptor concentration in pyrolytic graphite. Textural inhomogeneities in the pristine material are present in concentrations comparable to those introduced by the low level of irradiation used in this work.

It is clear from runs 12 and 4 of Fig.5.3 that the amplitude of hole oscillations in pristine graphite is reduced through collision broadening of Landau levels. Restricting attention to the hole term, we may use the figure of 23.7 acceptors per nvt estimated from the change in oscillation period on irradiation to calculate the change in resistivity per acceptor. The value of $(d\rho_{xx}/dN_A)_{H=0}$ where N_A is the acceptor concentration obtained from runs 12 and 4, is approximately $2 \times 10^{-23} \text{ ohm cm/acceptor}$. Assuming equal partial conductivities for electrons and holes, and substituting an average electron, hole concentration of $2.6 \times 10^{18} \text{ cm}^{-3}$ and an average mass of $0.05 m_0$ into equation (3.21); a reciprocal relaxation time $\left(\frac{1}{\tau_h}\right)_{\text{coll}}$ resistivity of $5.8 \times 10^{-7} N_A$ is obtained. BOARDMAN and

GRAHAM (1969) have considered the problem of charged point defect scattering in graphite and have obtained a theoretical estimate for $(d\rho_{xx}/dN_i)_{H=0}$ of 1.1×10^{-23} ohm cm/ionized impurity for electron, hole concentrations of $\sim 10^{19} \text{ cm}^{-3}$, leading to a reciprocal relaxation time $\left(\frac{1}{\tau_h}\right)^{\text{Theor.}}$ of $12.3 \times 10^{-7} N_i$. This value is within an order of magnitude of that estimated for acceptor scattering in irradiated graphite and lends support to the original assumption of singly ionized acceptor point defects.

CHAPTER VI

EXPERIMENTAL AND DERIVED RESULTS -- NON-OSCILLATORY

6.1 PRESSURE EFFECTS IN PYROLYTIC GRAPHITE

Section 1.2 of Chapter I has outlined the few measurements on the pressure coefficient of resistance (p c r) in pyrolytic and single crystal graphite which have appeared in the literature. PAUL and SOULE (1963) omitted to publish detailed results, but in this laboratory SPAIN (1964) made preliminary measurements at room temperature and showed that the normalised differential conductivity is directly proportional to the applied pressure :

$$\frac{\sigma_p - \sigma_0}{\sigma_0} = a \cdot P$$

with the constant of proportionality equal to $25.4 \times 10^{-6} \text{ bar}^{-1}$ for c-axis conduction. Basal plane conductivity was found to be insensitive to pressures applied to 2 kbar with a p c r which could be marginally positive or negative, such that $a < \pm 2 \times 10^{-6} \text{ bar}^{-1}$.

Application of pressure increases the carrier density with, according to section 5.3.2, a mean pressure coefficient of $35.59 \times 10^{-6} \text{ bar}^{-1}$. A linear increase in conductivity will conceivably result through the density term of equation (3.26).

$$\sigma = \sum_{i=e,h} n_i e \mu_i = \sum_{i=e,h} \frac{n_i e^2 \lambda_i}{m_i^* v_i} \quad \dots (6.1)$$

When discussing conductivity, it is sufficient to replace the electron/hole velocity and effective mass spectrum with an effective carrier having a mean free path λ , effective mass m^* and velocity v .

The pressure dependence of the conductivity is then :

$$\frac{d \ln \sigma}{dP} = \frac{d \ln n}{dP} + \frac{d \ln \lambda}{dP} - \frac{d \ln m^*}{dP} - \frac{d \ln v}{dP}.$$

A carrier's effective mass and velocity spectrum are determined by the Fermi surface curvature ($\partial^2 E / \partial k^2$), and the gradient of the energy

spectrum in $\underline{k}$ space ($\partial E_k / \partial k$). As such, changes with applied pressure are second order effects when compared with the large change in density and concomitant swelling of the electron and hole Fermi surfaces, resulting from the increase in band overlap. But the mean free path $\lambda(P)$ is a composite of those scattering mechanisms affecting carrier transport, such that:

$$\frac{1}{\lambda} = \sum_{i=1}^N \frac{1}{\lambda_i}.$$

Of the possible scattering processes, some, with a mean free path (mfp) λ_1 , may be pressure independent, e.g. neutral impurity scattering, and, as discussed in section 3.5.8, others with a mfp λ_2 may change with applied pressure. Then

$$\frac{d\lambda(P)}{dP} = \frac{\lambda_1 + \lambda_2 \left\{ \lambda_1 \frac{d\lambda_2}{dP} + \lambda_2 \frac{d\lambda_1}{dP} \right\} - \lambda_1 \lambda_2 \left\{ \frac{d\lambda_1}{dP} + \frac{d\lambda_2}{dP} \right\}}{(\lambda_1 + \lambda_2)^2}$$

which reduces to

$$\frac{d \ln \lambda}{dP} = \frac{\lambda_1}{\lambda_1 + \lambda_2} \frac{d \ln \lambda_2}{dP}$$

and

$$\frac{d \ln \sigma}{dP} = \frac{d \ln n}{dP} + \frac{d \ln \mu_c}{dP} = \frac{d \ln n}{dP} + \frac{\lambda_1}{\lambda_1 + \lambda_2} \frac{d \ln \lambda_2}{dP}, \quad \dots (6.2)$$

where μ_c is the conductivity mobility.

A value of $25.4 \times 10^{-6} \text{ bar}^{-1}$ found by SPAIN for $d \ln \sigma / dP$, together with the pressure dependence of carrier density, estimated in section 5.3.3, lead to a figure of $-10.19 \times 10^{-6} \text{ bar}^{-1}$ for the pressure coefficient of $\underline{c}$ -axis mobility at room temperature. However, the same procedure leads to a decrease of basal plane mobility which is almost exactly matched by the increase in carrier density, the net change in $(d(\ln \sigma) / dP)_{300 \text{ K}}$ being virtually zero.

The Hall mobility μ_H defined as R/ρ is related for a Maxwell Boltzmann distribution (which applies to graphite at temperatures in excess of the degeneracy temperature, 220 K) and parabolic energy bands to the mobility μ_c by the equation:

$$\frac{\mu_H}{\mu_c} = \frac{\langle v^2 \tau^2 \rangle}{\langle v^2 \rangle} \bigg/ \left(\frac{\langle v^2 \tau \rangle}{\langle v^2 \rangle} \right)^2 .$$

(Shockley (1950))

That is by the weighted average of τ^2 divided by the square of the weighted average of τ . A velocity dependent relaxation time results in the ratio μ_H/μ_c deviating from unity. McCLURE (1958) has applied the Kramers-Kronig relation to the graphite magnetoconductivity tensor to separate electron and hole terms. Using the expressions for individual conductivities, the ratio of Hall mobility to conductivity mobility that each carrier would have if present alone, was found to range from 1.2 to 1.6, demonstrating the presence in graphite of an energy dependent relaxation time. Clearly data concerning the pressure dependence of the Hall mobility can be utilized in evaluating scattering processes in graphite.

Then

$$\frac{d \ln \mu_H}{dP} = \frac{d \ln R_H}{dP} + \frac{d \ln \sigma}{dP} .$$

In graphite the minority carrier contributes but 2.3% to the total conductivity (SPAIN et al (1967)) and the material may, to a good approximation, be considered as a two-band conductor when:

$$R_H = \frac{a - b^2}{n_1 e c (a + b)^2} \quad a = \frac{n_h}{n_e}, \quad b = \frac{\mu_e}{\mu_h} .$$

The results of Chapter V show that the ratio of hole to electron densities is not pressure independent. But, there is no evidence to show that application of pressure selectively affects the mobility of one carrier more than the other, and we assume that b is pressure independent. Then

$$\frac{d \ln R_H}{dP} = \frac{1}{a - b^2} \frac{da}{dP} ,$$

and

$$\frac{d \ln \mu_H}{dP} = \frac{1}{a - b^2} \frac{da}{dP} + \frac{d \ln \sigma}{dP} .$$

From section 5.3.2:

$$\frac{da}{dP} = -3.06 \times 10^{-6} \text{ bar}^{-1} .$$

WOORE (1969) has listed values for a and b over a range of temperatures for good pyrolytic graphite, and these, together with Spain's estimate of $d \ln \sigma / dP$, are used to estimate the values of $d \ln \mu_H / dP$ listed in Table 6.1. Because of the fine balance of the electron/hole density and mobility, the measured low field Hall voltage in pyrolytic graphite is at most $\sim 5 \mu V$; changes listed in Table 6.1 are, for pressures attainable in this work, smaller than the experimental error.

TABLE 6.1

$d \ln \mu_H / dP$	T K
$- 24.6 \times 10^{-6} \text{ bar}^{-1}$	298
$- 11.0 \times 10^{-6}$	77

The above analysis is borne out in Fig.6.1, where the Hall coefficient is plotted as a function of magnetic field for a sample of IFP 64T graphite. At 77 K the coefficient has a magnetic field dependence with at low fields, an upwards trend to more positive values. This is now known to be due to positive minority carriers giving further support to the conclusions of Chapter V that electrons are located at point K in the Brillouin zone. Application of hydrostatic pressure to 100 bar has no discernable effect over a magnetic field range of 4 kG.

6.2 PRESSURE COEFFICIENT OF RESISTANCE

X-ray measurements of the compressibility of Ceylon natural graphite by KABALKINA and VERESHAGIN (1960) have shown that the c-axis compressibility is well represented by a quadratic of the form:

$$-\frac{\Delta c}{c_0} = 28.5 \times 10^{-7} P - 10^{-12} P^2,$$

where P is the pressure in bar. Accordingly, the highest pressure employed in this work will result in a decrease of the interplanar spacing by 0.14%. Kabalkina and Vereshagin were not able to estimate the change

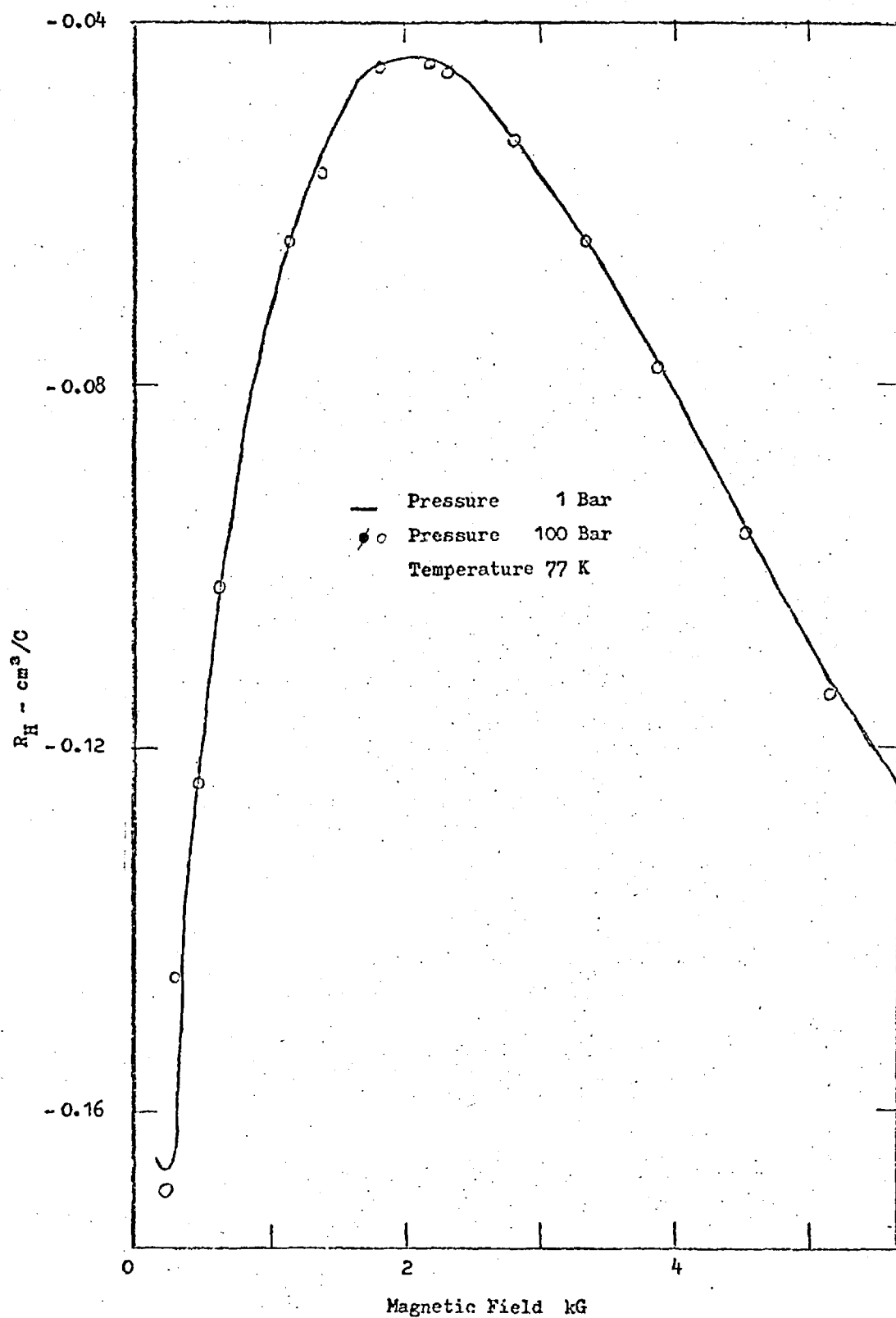


Fig.6.1
Low field Hall coefficient in pyrolytic
graphite at low and high pressure

of a_0 with pressure, but on substituting the compliance constants S_{11} , S_{12} and S_{13} of Table 2.2 into equation (2.1) we obtain for the basal plane compressibility a value of $2.8 \times 10^{-6} \text{ bar}^{-1}$ which is ten times less than that perpendicular to the basal planes. Application of hydrostatic pressure to graphite may thus, to a good approximation, be considered as a uniaxial stress applied along the c-axis. The large change of interplanar spacing with increasing pressure, leads to an increase of carrier concentration as determined in Chapter V. Since the band overlap is dictated by γ_2 representing overlap of B atoms on next nearest neighbour planes the differential conductivity on application of pressure is less than may be expected for a material of this compressibility.

Helium was employed as the pressure transmitting medium as discussed in Chapter IV to ensure a hydrostatic stress at all temperatures down to 4.2K where the maximum pressure attainable with liquid helium was limited to 138 bar by the helium melting line. This avoids the use of the isobaric freezing technique and the problem of pressure transmission through a solid medium where a reliable hydrostatic pressure is difficult to achieve. In fact it is evident from Fig.6.2, where resistance is plotted at 4.2K to pressures in excess of 138 bar, that little pressure is transmitted through the solid helium.

6.3 PRISTINE MATERIAL - PRESSURE COEFFICIENT OF RESISTANCE

Samples from four separate preparations were examined for their p.c.r. Three of the four materials were those used for measurement of the SdH effect, while the fourth, code named IFP 64T, is a well documented graphite (SPAIN, UBBELOHDE and YOUNG (1967)) of density 2.26 gms cm^{-3} . A convenient measure of the material perfection is the ratio of basal plane resistivities at 295 and 4.2K. These are listed in Table 6.2 for samples from the four preparations, together with the sample resistivities.

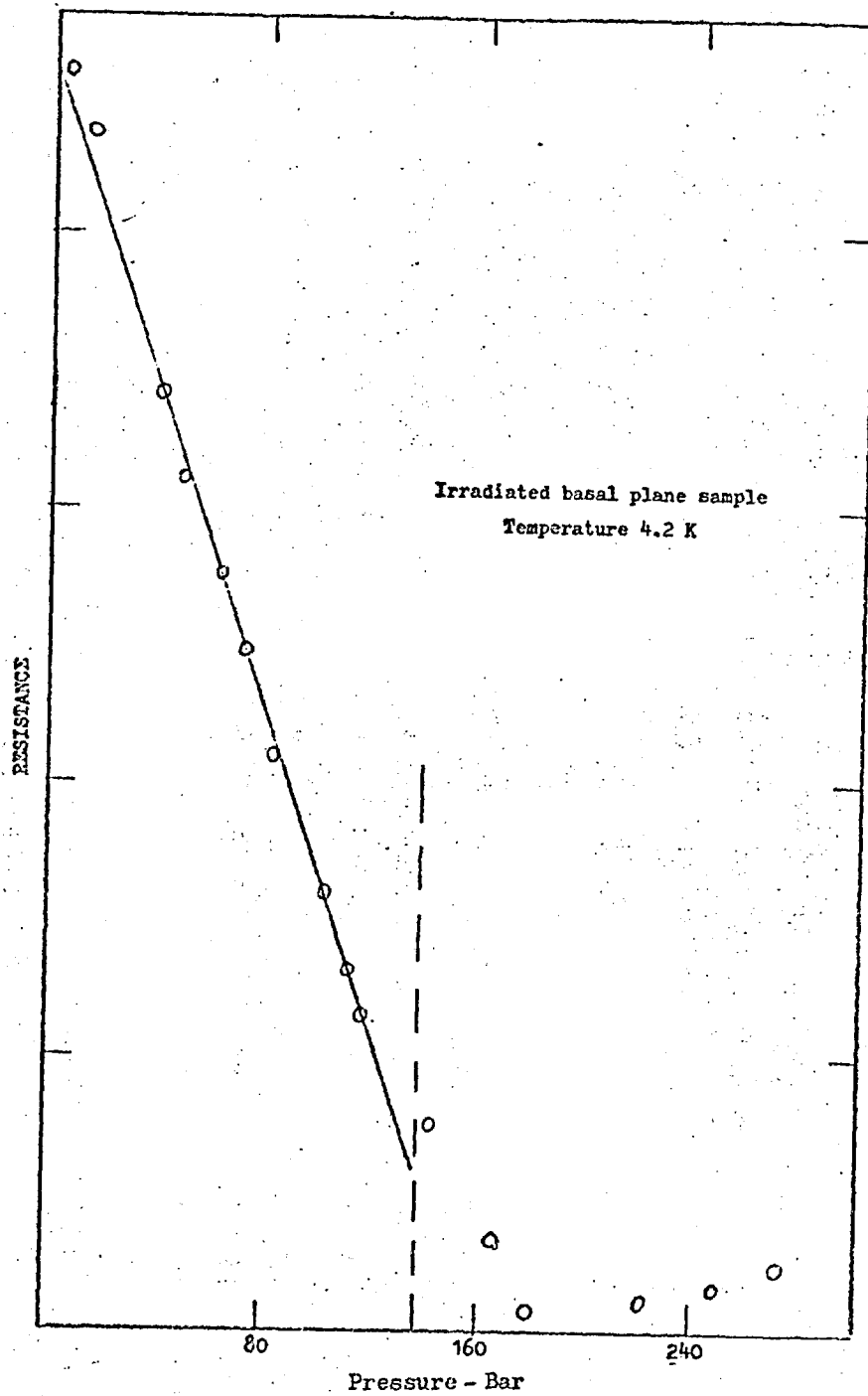


Fig.6.2
Hydrostatic pressure not transmitted
through solid helium

TABLE 6.2

Material	$\rho_{77} \text{ basal} / \rho_{295} \text{ basal}$	$\rho_{295} \text{ basal} \times 10^7 \Omega \text{ cm}$
IFP 37	0.615	4.03
JHTM 3	0.693	4.43
HaT	0.72	5.90
IFP 64 T	0.625	3.59

SPAIN et al (1967) have shown that best quality pyrolytic graphite has a value of $\rho(\text{basal})_{77} / \rho(\text{basal})_{295}$ around 0.56, thus the present material is not of top quality, and is inferior to that studied by WOORE (1968). However, large amplitude SdH oscillations and the magnetoresistance and Hall effect properties known to be typical of high quality pyrolytic graphite could readily be observed.

6.3.1 c-axis Conduction

c-axis resistance was found to be very sensitive to the application of pressure, an increase of 5 bar corresponding to a voltage change of $\sim 0.2 \mu\text{V}$ at 18 mA current could easily be detected. As the temperature was reduced the p.c.r. slowly increased from $25.5 \times 10^{-6} \text{ bar}^{-1}$ at 273 K to $28.2 \times 10^{-6} \text{ bar}^{-1}$ at 4.2 K. A typical set of results are shown in Fig. 6.3 to 6.5 for c-axis samples of HaT material. The curves are noteworthy for their complete lack of structure on pressure cycling to 140 bar.

A room temperature pressure coefficient of $25.5 \times 10^{-6} \text{ bar}^{-1}$ confirms the result of SPAIN (1964) using oil as the pressure medium to 1700 bar, and shows the pressure coefficient to be independent of the pressurising medium employed. This was further checked by pressurising with gaseous and liquid nitrogen; the results obtained were identical to those recorded using gaseous helium as the pressurising agent.

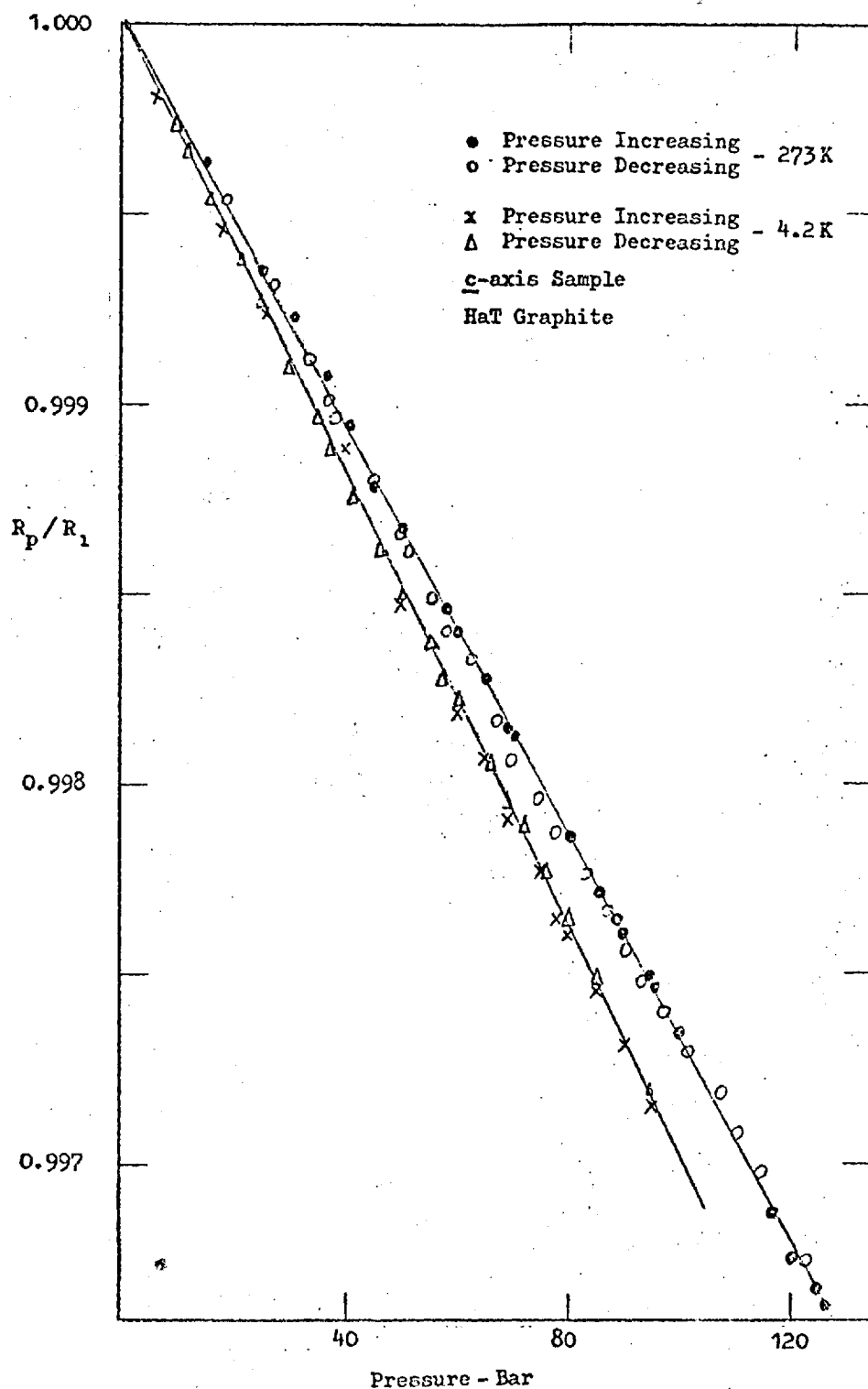


Fig.6.3

Pressure dependence of normalised c-axis resistance at low and high temperatures

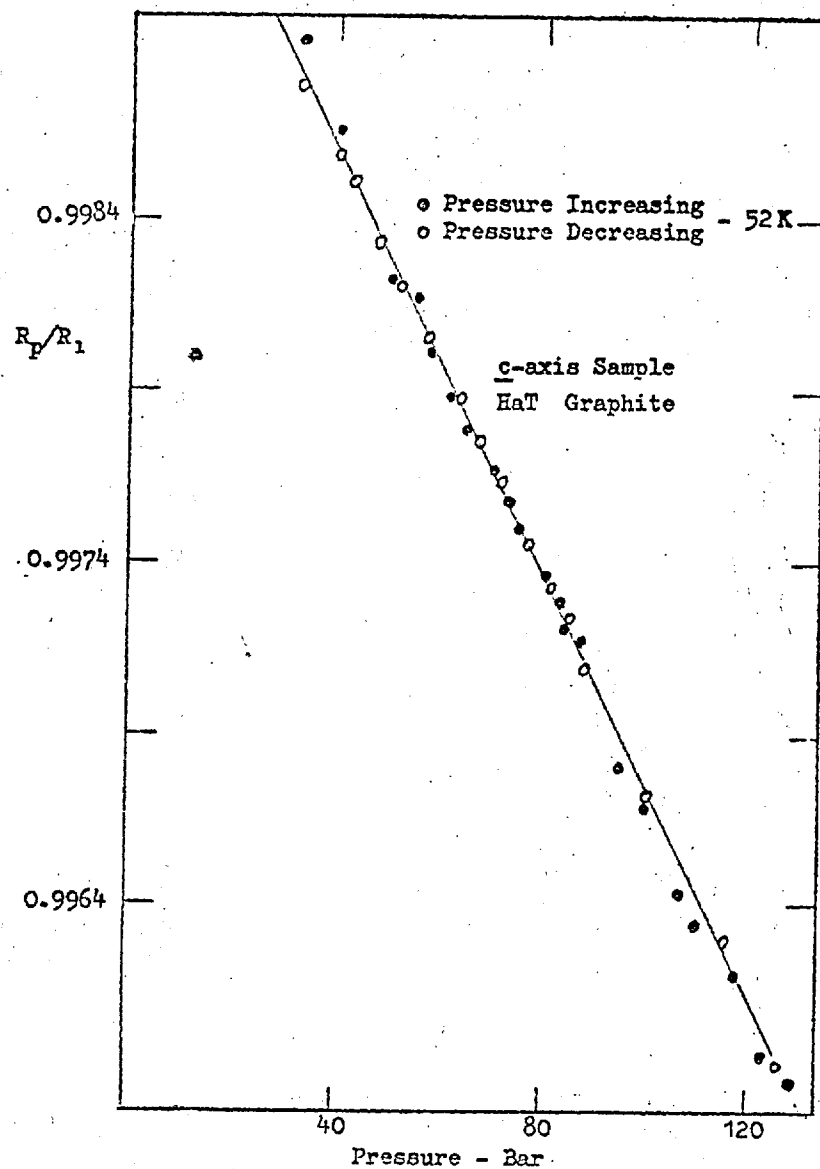


Fig.6.4

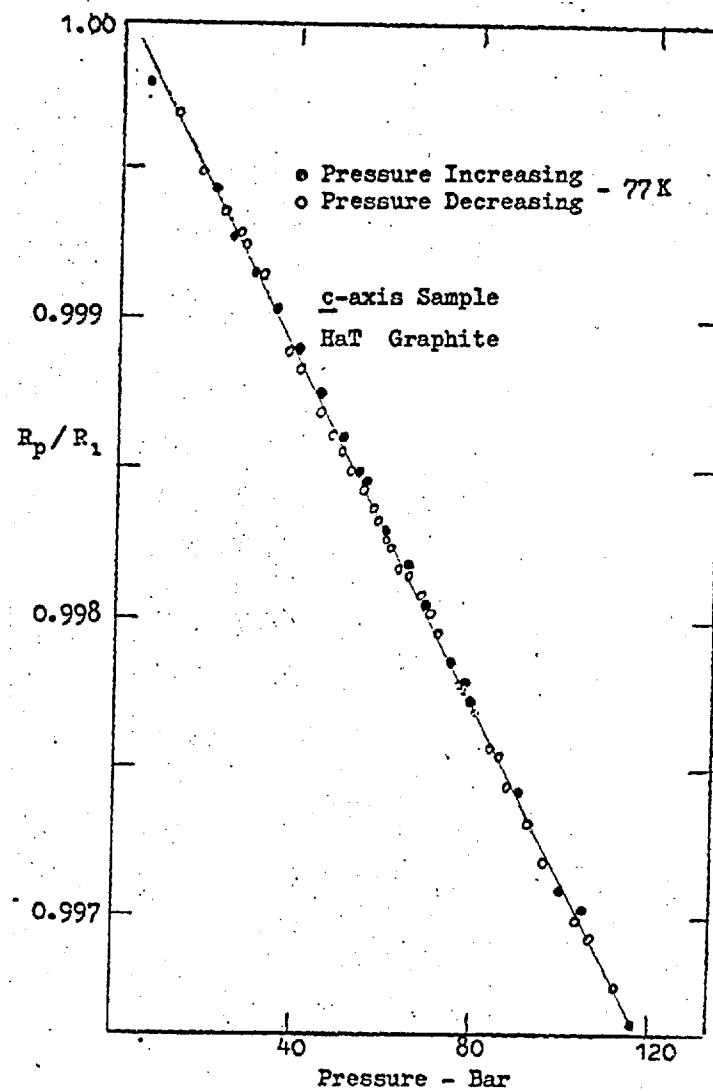


Fig.6.5

Pressure dependence of normalised c -axis resistance at intermediate temperatures

6.3.2 Basal Plane Conduction

At room temperatures the p c r for samples with current in the basal plane was found to be so small that the working pressure range was increased to 500 bar , whereas pressure runs up to 100 bar were quite adequate for c-axis samples. Apart from the present work the only published measurement at a temperature other than 295 K is that of LIKHTER and KECHIN (1964). By taking points from a graph shown in their paper, we find the pressure coefficient for basal plane samples of single crystal graphite to decrease from $-4.3 \times 10^{-6} \text{ bar}^{-1}$ at 293K to $-3.1 \times 10^{-6} \text{ bar}^{-1}$ at 355 K.

Basal plane samples were found to exhibit a small positive or negative pressure coefficient at room temperature, with some initial curvature at low pressure and a slight hysteresis on pressure decrease. At 77K the structure at low pressure was absent and a large pressure coefficient of $13 \times 10^{-6} \text{ bar}^{-1}$ appeared, with again a small hysteresis on reducing pressure. Plots of the raw data showing resistance as a function of pressure are illustrated with material IFP 37 in Fig.6.6. The hysteresis is of the same sign, but is smaller than that recorded by Likhter and Kechin on basal plane samples of natural graphite.

As the temperature was lowered to 4.2K the large temperature coefficient of basal plane resistance reduced the resistivity from typically 4.4 ohm cm (295K) to 0.38 ohm cm (4.2K) . The maximum current which could be supplied to the sample was limited to 200mA by heating in the leads to the specimen, resulting in a voltage change on application of pressure which was so small that sets of readings were taken at 1 and 130 bar only. Higher pressures would have involved solid helium and so were avoided. In Fig.6.7, the resistance normalised to zero pressure resistance, is plotted as a function of pressure for a basal plane sample at temperatures ranging from 295 to 4.2K. At room temperature a slight drop in resistance on application of pressure is followed by a small positive pressure coefficient

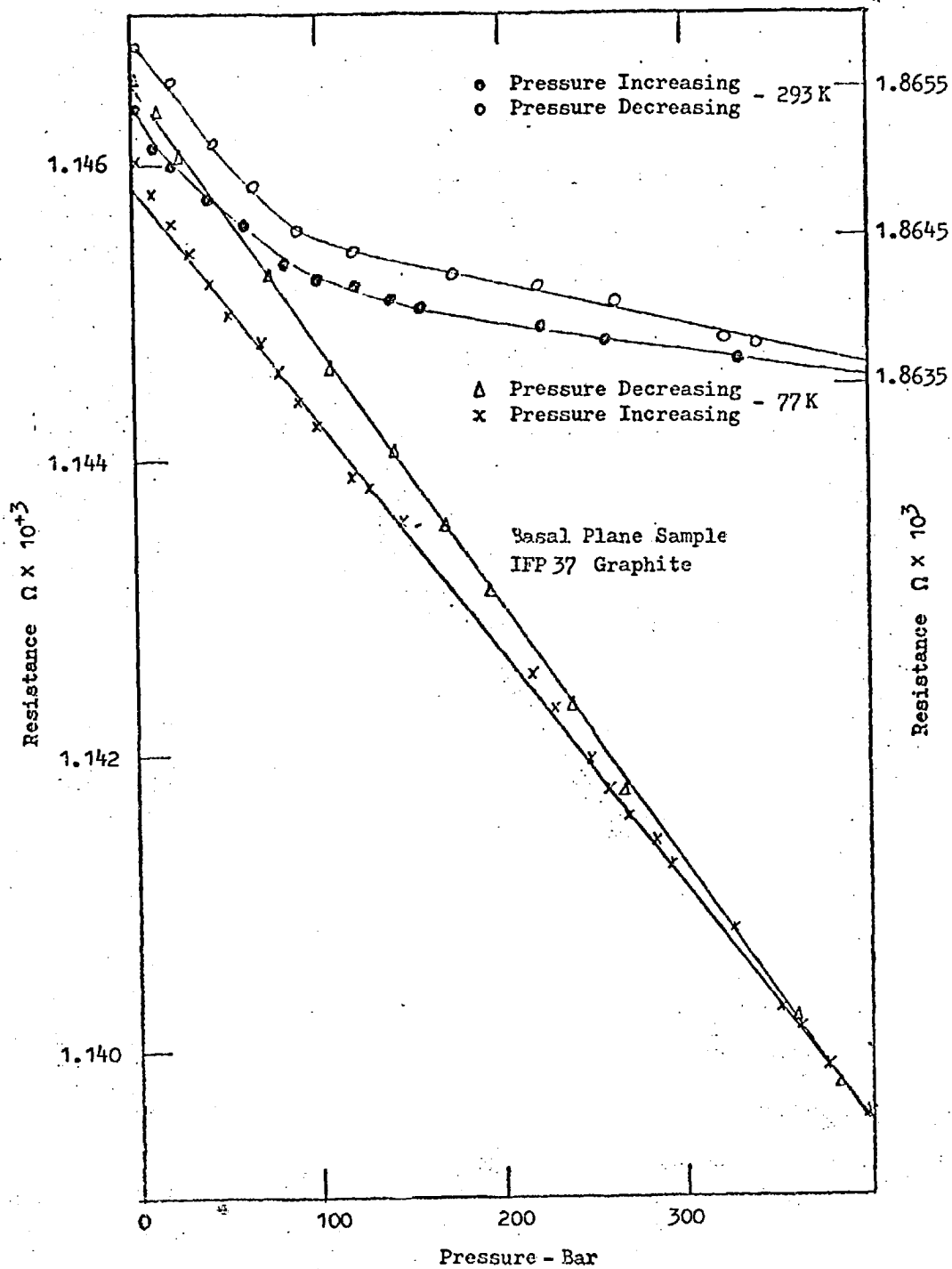


Fig.6.6
Basal plane resistance exhibiting
hysteresis on pressure cycling

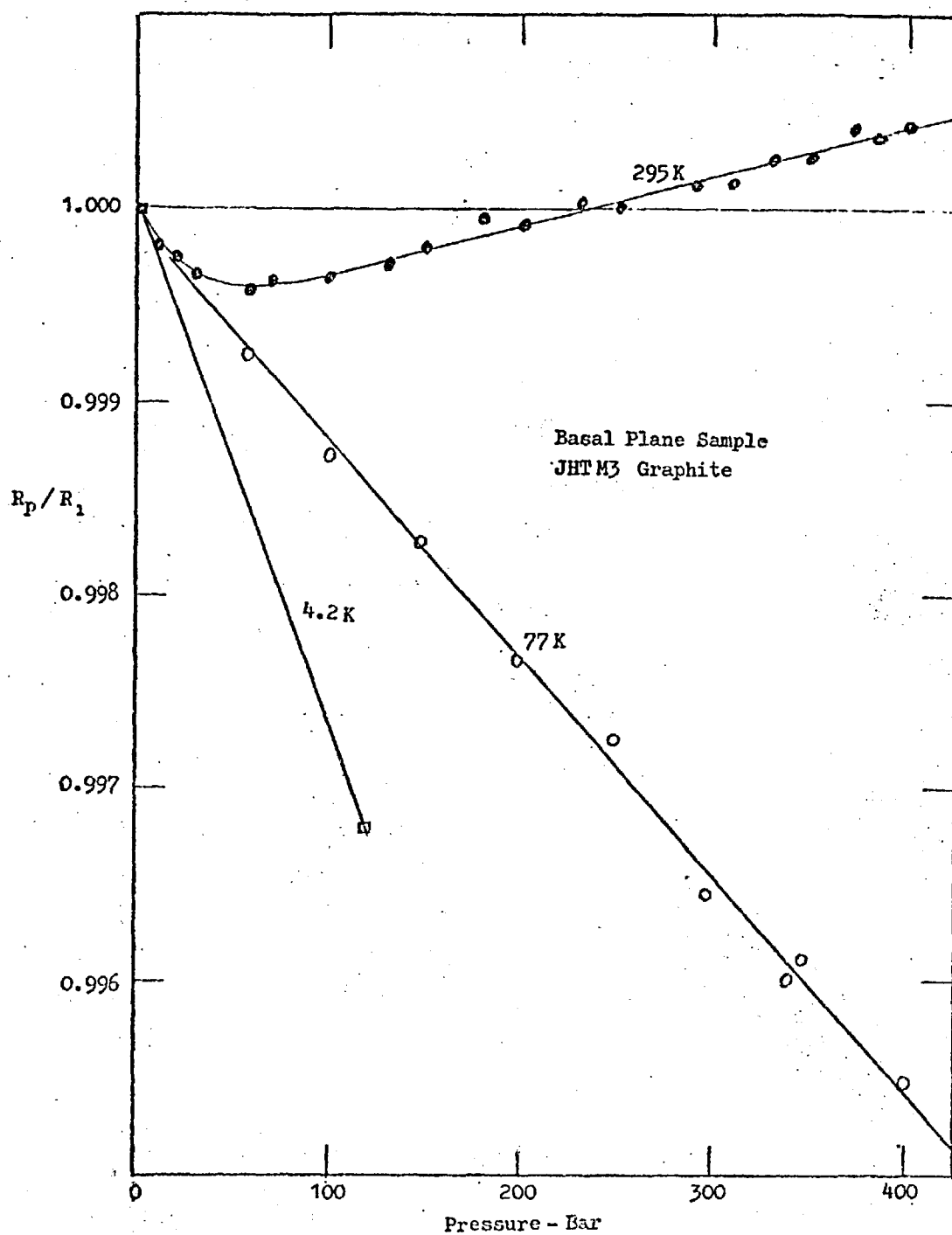


Fig.6.7
Basal plane p c r increasing with
decreasing temperature

of $0.9 \times 10^{-6} \text{ bar}^{-1}$. As the temperature is reduced, the low pressure transients disappear and the negative pressure coefficient of resistance increases monotonically reaching a value of $-27.8 \times 10^{-6} \text{ bar}^{-1}$ at 4.2K.

6.4 IRRADIATED GRAPHITE-PRESSURE COEFFICIENT OF RESISTANCE

Samples of pyrolytic graphite were irradiated with fast neutrons as described in Chapter V. In Table 6.3, the code name and irradiation dose are listed for the range of samples examined. Irradiation of pyrolytic graphite with fast neutrons to the moderate levels of irradiation used in this study, has no appreciable affect on the elastic moduli which determine a and c-axis compressibility (section 2.3). However, the results of Chapter V confirm the finding of other workers (GOGGIN and REYNOLDS (1960). SPAIN et al (1967)) that even light irradiation will have a marked affect on the electrical properties.

TABLE 6.3

Sample	Fast Neutron Dose at 30 C
	n v t
HaT/3	1.2×10^{16}
HaT/4	1.2×10^{17}
HaT/N	1.0×10^{18}

The introduction of charged acceptors lowers the Fermi level causing the hole surface to expand and the electron surface to contract, with a net increase in the carrier concentration. At the same time scattering at charged defects reduces the mean free path and causes the a-axis conductivity to decrease. Above $\sim 40\text{K}$, c-axis conduction has a mean free path apparently fixed by longitudinal acoustic phonons (SPAIN et al (1967), YOUNG (1968)), and for irradiation doses in excess of 10^{18} nvt the increase in carrier density on irradiation results in a decrease in c-axis resistivity.

The one previous measurement on the p c r of irradiated graphite was conducted at room temperature by SPAIN (1964); preliminary results showed the pressure coefficient of basal plane resistance to increase with pressure. This work provides the first detailed study of the pressure dependence of conductivity in irradiated graphite.

6.4.1 c-axis Conduction

In contrast to pristine material, the initial drop of resistance with pressure was anomalous, and consequently data was recorded up to pressures where the p c r became pressure independent. Irradiation was found to increase the negative pressure coefficient at all temperatures by an amount which increased with irradiation dose. At low pressures, typically < 25 bar, the c-axis resistance of irradiated samples rose rapidly with decreasing pressure. The effect was more pronounced at room temperature than below, and increased with irradiation until finally in sample HaT/CN, which had received the largest dose, the resistance reached a maximum at ^{8 bar} ~8 kbar decreasing at higher pressures, Fig.6.8.

Unirradiated c-axis samples showed no hysteresis on pressure cycling but the irradiated material exhibited a slight negative hysteresis. This is evident in Fig.6.8, and is further illustrated in Fig.6.9. The initial structure at low pressures is attributed to lenticular voids introduced during the irradiation and is ignored when calculating pressure coefficients. The mean of the pressure increasing and pressure decreasing results are listed in Table 6.4, for three doses of irradiation.

TABLE 6.4

Pressure Coefficients of Resistance		
Sample Material	Temperature	
	<u>273 K</u>	<u>77 K</u>
HaT/ C3	26.3	33
HaT/ C4	29.2	-
HaT/ CN	32.0	35.7

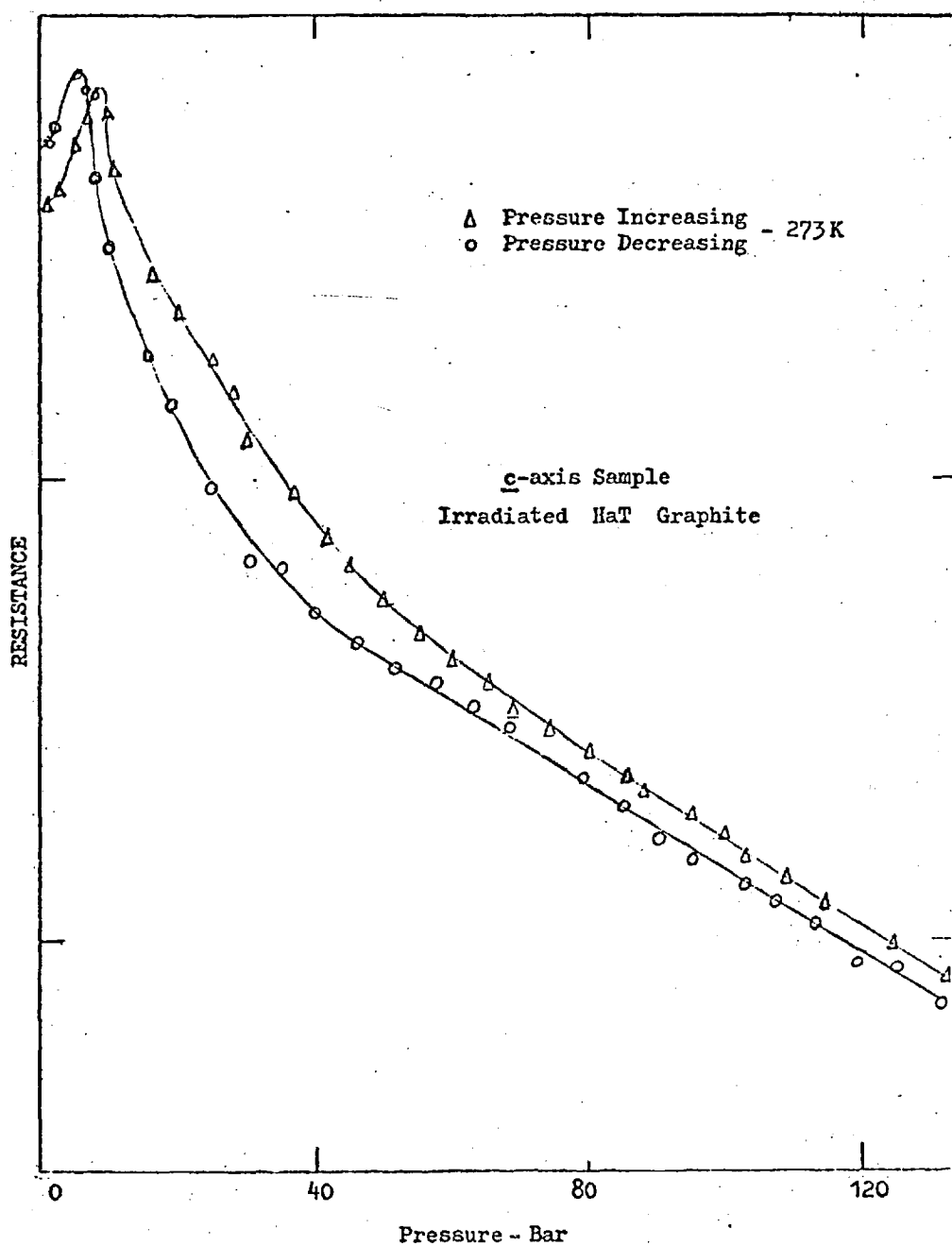


Fig.6.8
 Low pressure structure in the pcr of
 irradiated c-axis samples

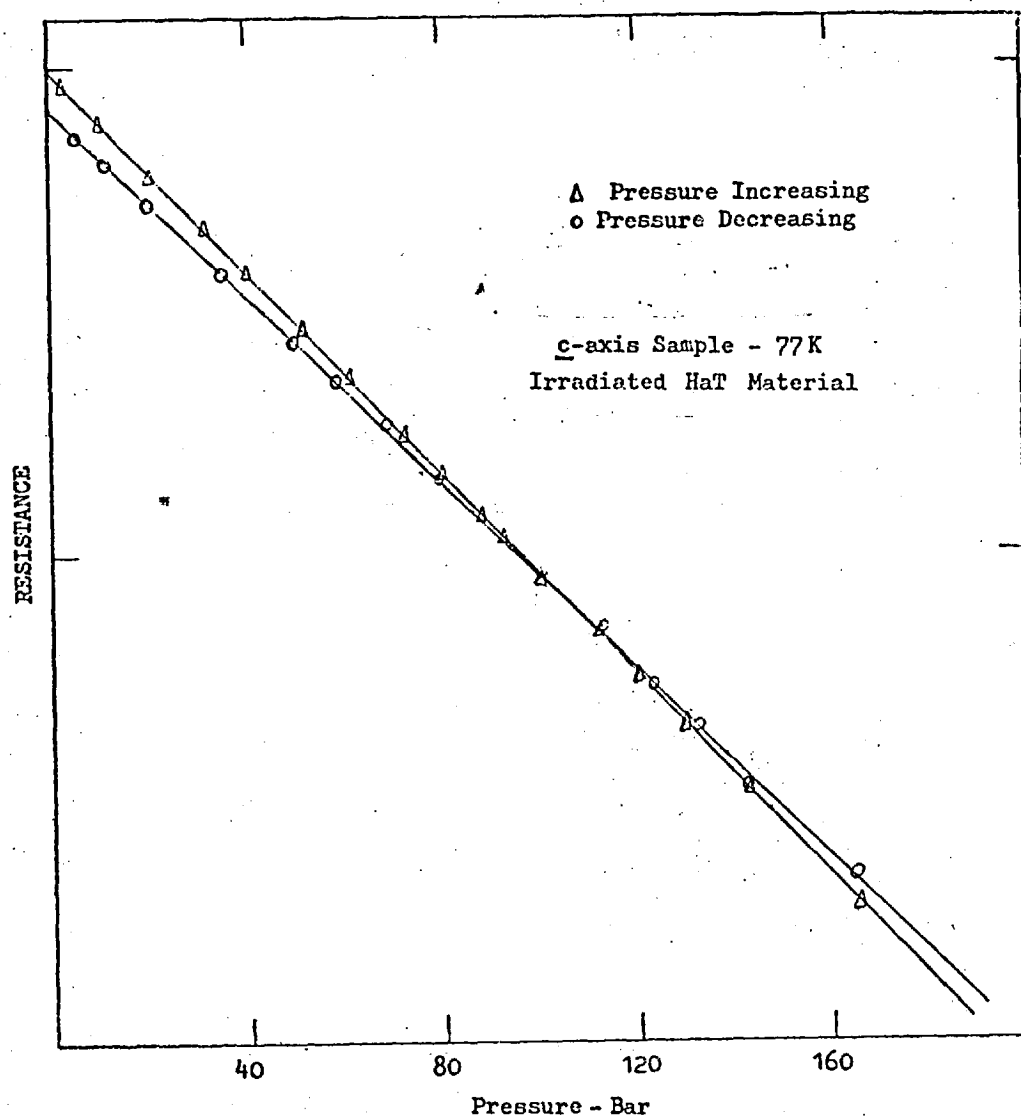


Fig.6.9
 c-axis resistance of irradiated graphite
 exhibiting hysteresis on pressure cycling

6.4.2 Basal Plane - Conduction

Irradiation by fast neutrons has a significant effect on the p c r of basal plane samples. At 295 K the coefficient rises from the near zero value of unirradiated graphite through 2.6 and $7.8 \times 10^{-6} \text{ bar}^{-1}$ for irradiation doses of 1.2 and $12 \times 10^{16} \text{ nvt}$ to $10.2 \times 10^{-6} \text{ bar}^{-1}$ for the most heavily irradiated sample HaT/AN. A slight rise of resistance occurs at low pressures, but the marked structure of the c-axis samples of corresponding dose is absent. On cooling, the low pressure transients decrease until at 4.2 K a linear fall of resistance with increasing pressure is observed over the whole pressure range. Resistance values could be measured at 10 bar intervals at this temperature in irradiated graphite, since the large temperature coefficient of pristine graphite is reduced almost to zero by irradiation. At 77 K the p c r rose with irradiation dose, the dependence was however weaker than at 295 K. Thus, HaT/A3 recorded a value of $16 \times 10^{-6} \text{ bar}^{-1}$ and HaT/A4 a value of $18.4 \times 10^{-6} \text{ bar}^{-1}$. Hysteresis was present and could be positive or negative, but in either sense was small. Fig.6.10 illustrates the positive hysteresis observed in HaT/A3 and the negative hysteresis recorded for HaT/AN at the same temperature. As with unirradiated material the p c r increased monotonically with decreasing temperature; at all temperatures larger values were observed for irradiated graphite. In Fig.6.11 the change of resistance with pressure is shown normalised to the zero pressure resistance for samples HaT/A3 and HaT/A4 at the four fixed temperature points. Low pressure structure which is evident at 273 K has disappeared by 52 K and the p c r increases steadily with decreasing temperature.

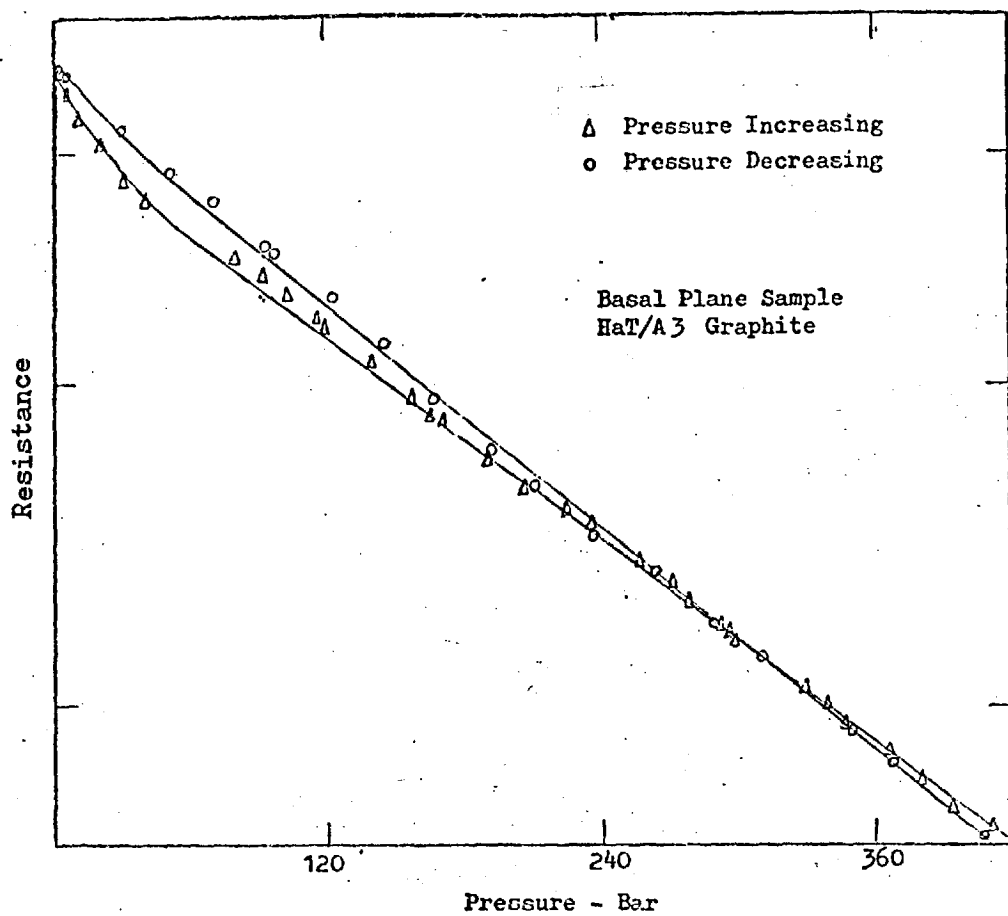


Fig.6.10(a)

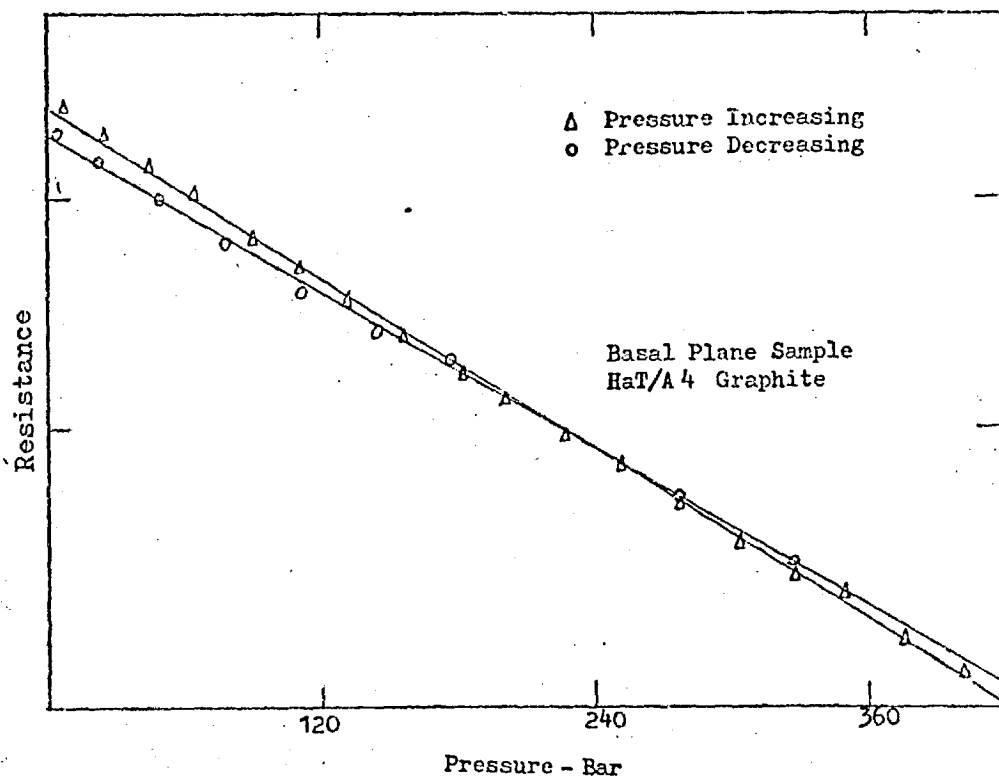


Fig.6.10

Positive and negative hysteresis in the pcr of irradiated basal plane samples at 77 K

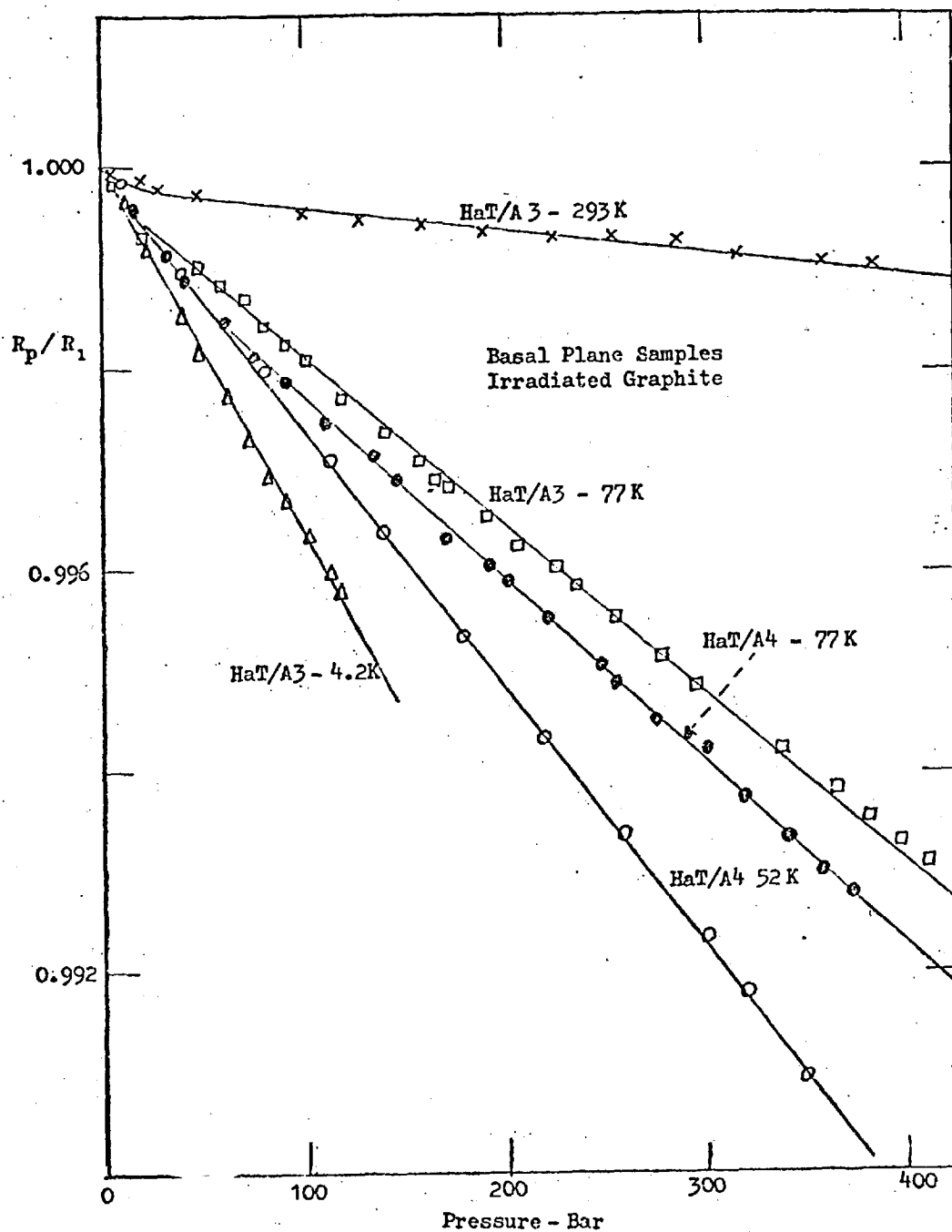


Fig.6.11
Basal plane pcr of irradiated graphite
increasing with decreasing temperature

6.5 DERIVED RESULTS

The application of equation 6.1 to the results described above, results in a pressure dependence of the conductivity mobility μ_c which is anisotropic and, in the case of basal plane mobility, a strong function of temperature.

In Fig.6.12 the pressure coefficient of c-axis and basal plane mobility is plotted as a function of temperature. No previous measurements are available for comparison, but results obtained independently by HOWELL (1969) of this laboratory at 90 K and 198 K are included in the diagram.

Irradiation with fast neutrons has a greater effect on basal plane than c-axis mobility, Fig.6.13. Here we may make some comparisons with the pressure dependence of mobility in samples known to contain a high concentration of textural defects, and the results obtained by Howell on carefully selected poor quality graphite are included.

As the temperature is reduced the pressure coefficient of mobility falls in the basal plane direction from a value almost equal to the pressure coefficient of the carrier density, reaching at 4.2 K the coefficient appropriate to c-axis conduction. The introduction of Coulombic scattering centres by pre-irradiation further unbalances electron/hole ratios by an estimated 23.7 acceptors/nv t and is seen to decrease the mobility coefficients throughout the temperature range. c-axis coefficients are much less sensitive to temperature and pre-irradiation than those with current in the basal plane, but values are increased by the introduction of radiation damage and the large anisotropy apparent at room temperature is removed at 4.2 K.

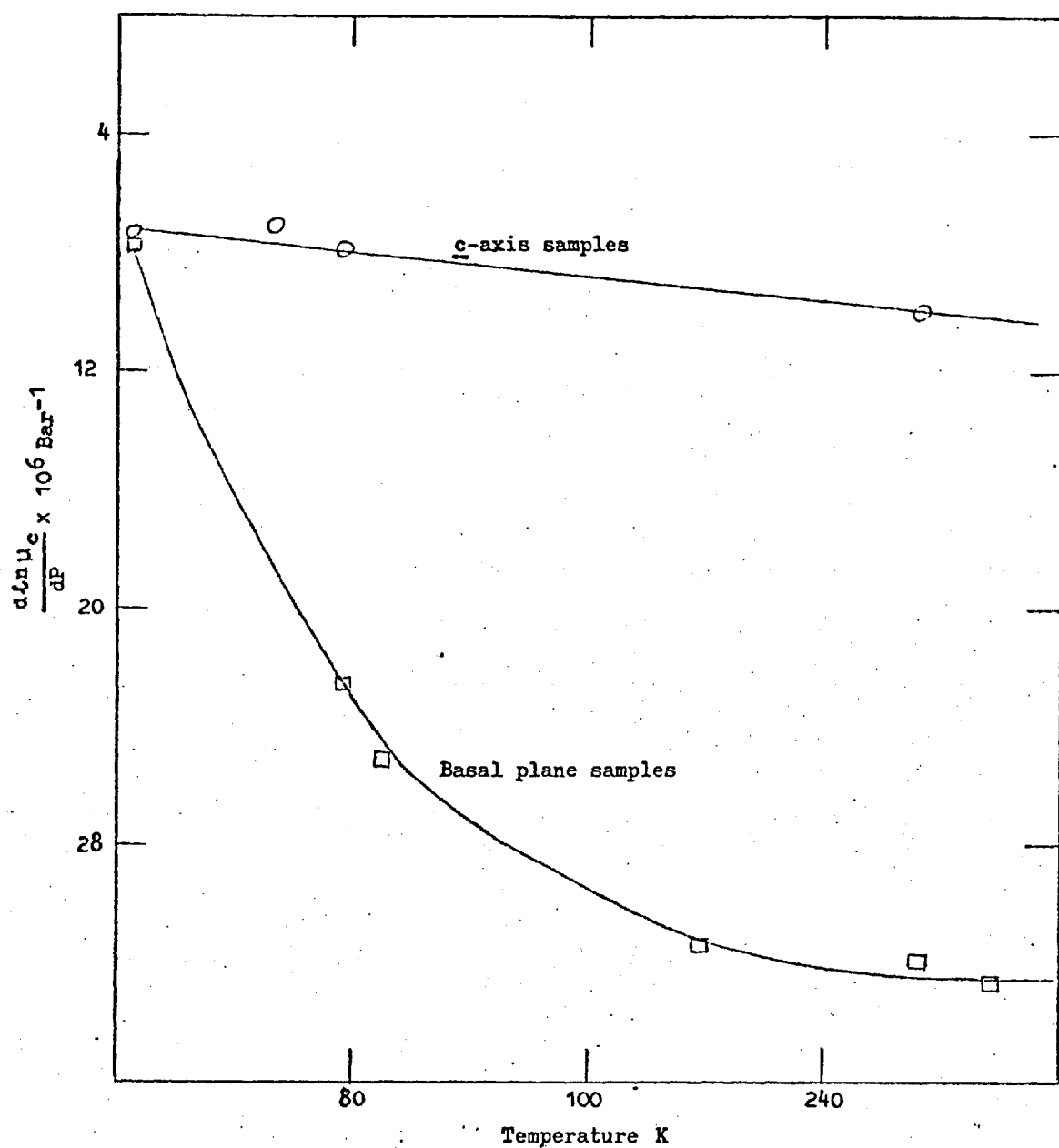
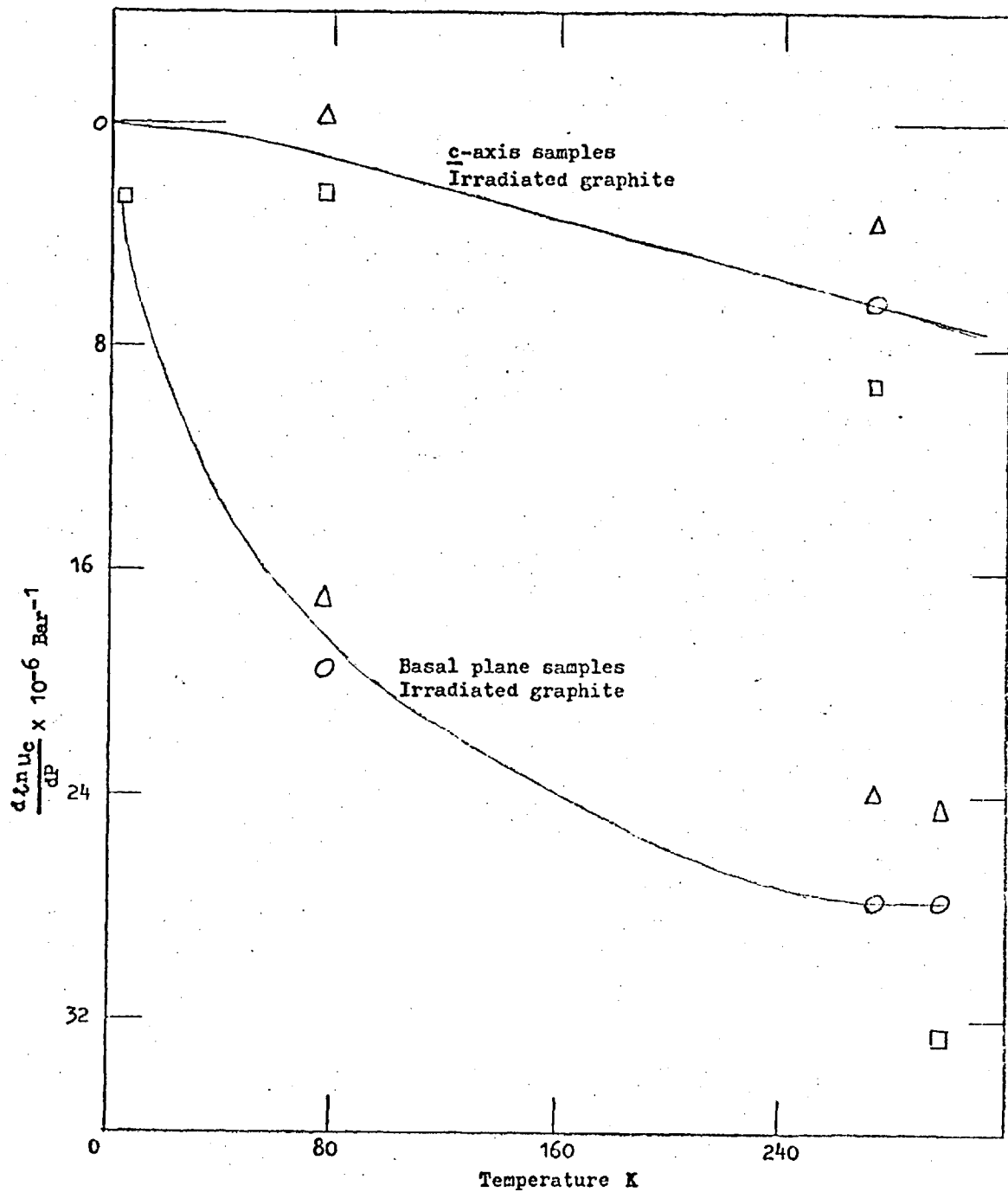


Fig.6.12

Pressure dependence of carrier mobility decreasing in both principle directions with decreasing temperature



□ HaT/3 , ○ HaT/4 , △ HaT/N

Fig.6.13

Pressure dependence of carrier mobility decreasing in irradiated graphite with decreasing temperature

CHAPTER VII

DISCUSSION AND CONCLUSIONS

7.1 INTRODUCTION

Transport processes in graphite are dominated by the gross anisotropy which exists between parameters measured with current in the basal plane and those measured with current along the c-axis. But the absolute value of the anisotropy is a matter of some debate. In single crystal graphite at 300 K a conduction anisotropy of ~ 100 was measured by PRIMAK and FUCHS (1954) and WAGONER (1960), while BHATTACHARYA (1959) and DUTTA (1953) favour a value closer to $10^4 - 10^5$. However, in pyrolytic graphite there is no doubt that at room temperature σ_{11}/σ_{33} lies in the range 4000 - 5000 rising to 88,000 at liquid helium temperatures.

Measurements described in Chapters V and VI provide completely new, and in some cases, unexpected information on the anisotropic transport properties of pyrolytic graphite. The low, anisotropic and temperature dependent pressure coefficient of resistance cannot be described solely in terms of previous theories of transport in graphite. In this chapter carrier-carrier scattering terms are introduced and together with a proper emphasis on ionized impurity scattering, is shown to account for the experimental observations.

7.2 TRANSPORT IN PYROLYTIC GRAPHITE

Basal plane and c-axis conduction in pyrolytic graphite, as a function of temperature, has been discussed at length by YOUNG (1968) and is summarized in Fig.7.1. It is now well established that c-axis properties cannot be dismissed through path tortuosity arguments in which c-axis conduction is shorted by basal plane conduction due to possible plane normal misalignment. Above 60 K the c-axis mean free path is constant and limited by longitudinal acoustic phonons to about $3 \text{ \AA}$. Below 45 K λ_c

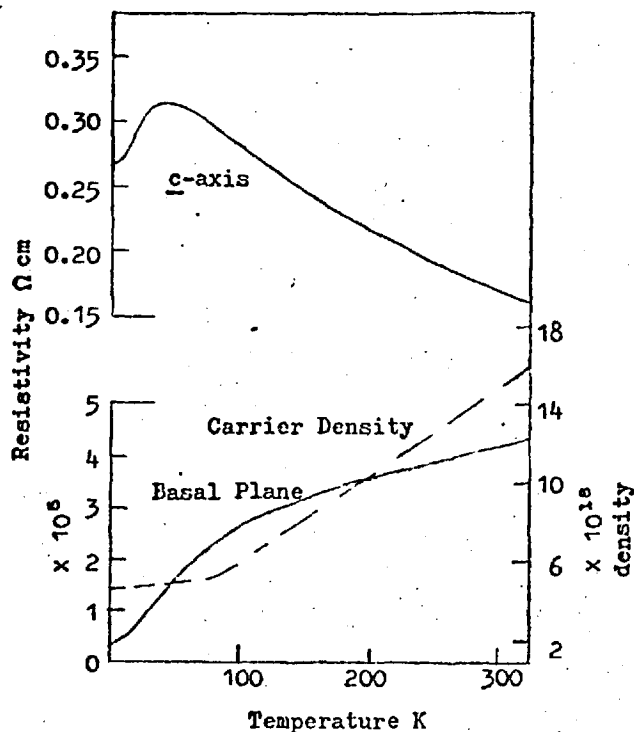


Fig. 7.1

Conduction properties of pyrolytic graphite as a function of temperature

risks with decreasing temperature and is limited ultimately ^{by} scattering at stacking faults.

Basal plane conduction has received more attention and is now quite well understood. McCLURE (1958) has shown that in single crystal graphite, a mean free path of 150,000 Å at 4.2K falls to 10,000 Å at 77K and 3000 Å at room temperature. Over the same temperature range, the carrier density $n_e + n_h$ rises from 5.7×10^{18} to $1.5 \times 10^{19} \text{ cm}^{-3}$ and, being

a scalar quantity, is assumed to be isotropic. The behaviour of the mobility ratio μ_e / μ_h is quite different in single crystal and pyrolytic graphite. In the former, μ_e / μ_h decreases linearly from 1.1 to 0.79 between room and liquid helium temperatures, whereas in synthetic graphite μ_e / μ_h initially decreases with decreasing temperature but reaches a minimum of about 80K increasing thereafter, (WOORE (1968)). The previous explanation (SPAIN et al (1967)), in terms of greater trigonal fluting of the hole surface, leading to an increased electron mobility compared to that of the hole, is now no longer tenable since electron and hole surfaces have been interchanged. However the suggestion by BENDER and YOUNG (1972b) that ionized impurities selectively scatter holes twice as effectively as electrons is sufficient to account for the mobility minimum when it is realized that ionized impurity scattering can reduce carrier mobility at temperatures as high as 100K. Early deviations of the mobility from a $T^{-1.2}$ temperature dependence, confirms that in poor pyrolytic graphite

scattering by ionized impurities with a $T^{+1.5}$ dependence dominates conduction below 100K.

Irradiation by fast neutrons introduces a small number of defects which both scatter charge carriers and act as electron traps, thus lowering the Fermi level. Basal plane resistivity typically increases four times on irradiation to 10^{18} nvt. The temperature dependence changing from the strong positive behaviour of Fig.7.1 to a weak negative dependence, decreasing by a factor of ~ 0.64 over 300K. On the other hand c-axis resistance changes with irradiation are small and irregular at low irradiation doses (COOPER et al (1971)), but when the acceptor yield exceeds the carrier concentration the resistance decreases and the temperature dependence, although reduced, remains weakly negative.

The results of Chapters V and VI, corrected for compressibility, are collected for convenience in Table 7.1. Errors quoted are root mean square deviations for an average of five runs, and HOWELL's (1969) results are included. It is apparent that an increase in conductivity resulting from the application of hydrostatic pressure generally lags behind the increase in density. The same is true for c-axis transport in two other situations:

- (1) An increase of temperature from 60 to 300K should result in an increase in conductivity which follows the decrease in density since the mean free path is fixed. But the conductivity is found to increase by only a factor of ~ 2.0 while the density increases by a factor of almost three.
- (2) Irradiation to neutron doses in excess of 10^{18} nvt can increase the concentration of charge carriers. SPAIN et al (1967) have measured a density increase of ~ 3.3 but the c-axis conductivity rises by only a factor of approximately two.

Clearly the theory of transport properties employed by SPAIN et al (1967) McCLURE and SMITH (1963) and SOULE (1958) is incomplete and is unable to account for the anomalies described above. However we may pursue this

model a little further in order to establish a base for the calculations of section 7.4.

TABLE 7.1

	Temperature K	$\frac{d \ln \sigma}{dP} \times 10^{-6} \text{ bar}^{-1}$	Fast Neutron Dose nvt
Basal Plane	297	2.9 ± 1.5	0
		2.9	1.2×10^{16}
		7.8	1.2×10^{17}
		11.0	1.0×10^{18}
	273	3.6 ± 1.5	0
		7.8	1.2×10^{17}
		11.6	1.0×10^{18}
	198	4.2 ± 1	0
	90	10.4 ± 1	0
	77	13.0 ± 1	0
		16.0	1.2×10^{17}
		18.4	1.0×10^{18}
	52	26.0 ± 1	1.2×10^{17}
	4.2	27.8 ± 6	0
		32.8 ± 1	1.2×10^{16}
<u>c</u> -axis	273	25.5 ± 1.5	0
		26.3	1.2×10^{16}
		29.2	1.2×10^{17}
		32.0	1.0×10^{18}
	77	27.6 ± 1	0
		33.0	1.2×10^{16}
		35.7	1.0×10^{18}
	52	28.3 ± 1	0
	4.2	28.2 ± 1	0
$d \ln n_e / dP$	$37.1 \pm 1.5 \times 10^{-6} \text{ bar}^{-1}$		
$d \ln n_h / dP$	$34.1 \pm 1.5 \times 10^{-6} \text{ bar}^{-1}$		

McCLURE (1958) has shown that the carrier mean free path in the basal plane at 298K is of the order of 300 Å in single crystal specimens and carrier velocities at the Fermi surface are respectively $v_e = 1.5 \times 10^8 \text{ cm sec}^{-1}$ and $v_h = 0.8 \times 10^8 \text{ cm sec}^{-1}$ with an average hole effective mass of $0.039 m_0$, and electron effective mass of $0.057 m_0$. Perpendicular to the basal planes average effective masses are larger because of the anisotropic band structure and cigar shaped Fermi surfaces. SPAIN, UBBELOHDE and YOUNG (1967) and SPAIN (1971) have characterised c-axis transport by an electron mass $m_e = 14.0 m_0$, a hole mass $m_h = 5.7 m_0$ and an average carrier velocity ~ 60 times less than that in the basal plane. The ratio of basal plane to c-axis conductivities as described by equation (3.25), will take the approximate form:

$$\frac{\sigma_a}{\sigma_c} \approx \frac{10 m_0 v \lambda_a}{0.05 m_0 \cdot 60 v \lambda_c} \approx \frac{3.3 \lambda_a}{\lambda_c} .$$

At 300K the conductivity ratio has been determined to be between 4000 and 5000. The basal plane mean free path is then some 1200 to 1500 times that in the c-axis. If scattering mechanisms such as carrier-carrier and ionized impurity scattering are to be effective in reducing both c-axis and basal plane conduction, then the mean free path resulting from such scattering events must itself be highly anisotropic.

7.3 ANISOTROPIC SCATTERING CROSS-SECTIONS

Below the degeneracy temperature of 220K carrier-carrier scattering in graphite will result in a mean free path which is determined inversely by the carrier density and total scattering cross-section, and is directly proportional to the Pauli exclusion factor $(E_f/kT)^2$. According to equation (3.51)

$$\lambda_{c-c} = \frac{1}{N Q_{c-c}} \left(\frac{E_f}{kT} \right)^2 . \quad \dots (7.1)$$

It was shown in section 3.5.7 that application of the Born approximation, the partial wave method or the simple classical plasma formula, will result in a total scattering cross-section which is largely determined by

the inverse of the square of the interaction energy of the colliding particles:

$$Q_{c-c} \propto \frac{1}{W^2} .$$

It is well known that the scattering of a carrier of mass m_1 by a carrier of mass m_2 , when the interaction between them depends on their relative coordinates, can be reduced to the scattering of a particle of reduced mass $(m_1 m_2 / m_1 + m_2)$ in the same potential field.

As discussed in section 3.5.8, electron-hole scattering will influence conductivity in graphite to zero order, the mean free path due to this scattering process will then take the form:

$$\lambda_{e-h} \propto \frac{\left(\frac{m_e^* m_h^*}{m_e^* + m_h^*} \right)^2 v_{rel}^4}{4N} \cdot \left(\frac{E_f}{k_B T} \right)^2 \dots (7.2)$$

where v_{rel} is the relative approach velocity.

The average effective mass for transport along the c-axis is ~200 times greater than the average mass describing basal plane properties, whereas the mean basal plane velocity is approximately sixty times greater than that describing propagation perpendicular to the planes. An anisotropy therefore exists between the scattering cross-section for electron-hole collisions in the basal plane and for the same collision occurring between particles propagating along the c-axis:

$$\left(\frac{Q_a}{Q_c} \right)_{e-h} = \left(\frac{m_e^{*c} m_h^{*c}}{m_e^{*c} + m_h^{*c}} \right)^2 \cdot (v_{e-h}^4)_{\underline{c}\text{-axis}} / \left(\frac{m_e^{*a} m_h^{*a}}{m_e^{*a} + m_h^{*a}} \right)^2 \cdot (v_{e-h}^4)_{\underline{a}\text{-axis}} \dots (7.3)$$

The carrier-carrier mean free path will have the inverse of this anisotropy.

Ionized impurity scattering is described by the same scattering process, except that in this case one of the scattering particles is fixed. The anisotropy in the total scattering cross-section will then be determined by the ratio of the average kinetic energy of a particle propagating along

a basal plane to that of a particle with velocity directed perpendicular to this plane:

$$\left(\frac{Q_a}{Q_c}\right)_{\text{c-ion impurity}} = \frac{\left(\frac{m_{av}^* v_{av}^4}{m_{av}^* v_{av}^4}\right)_{\text{c-axis}}}{\left(\frac{m_{av}^* v_{av}^4}{m_{av}^* v_{av}^4}\right)_{\text{basal plane}}} \quad \dots (7.4)$$

7.4 CALCULATED PRESSURE COEFFICIENTS

7.4.1 Pristine Pyrolytic Graphite - Basal Plane

Basal plane conduction in pyrolytic and single crystal graphite has been extensively studied and we may use experimentally derived parameters with some confidence as a basis for the calculation of pressure coefficients. Electron micrograph measurements of good pyrolytic graphite by SPAIN et al (1967) showed single crystal domains ranging from 2 to 5 μm in diameter, whereas estimates of the boundary scattering lengths from thermal conductivity measurements arrived at values between 2 and 3 μm . The pyrolytic graphite used in this work is of reasonable quality and basal plane crystallite dimensions are taken to be close to 3 μm .

By assuming an overall mean free path of 3 μm at liquid helium temperatures, we may estimate the mean free path at 77 and 298 K from the measured change in carrier density, carrier velocity and conductivity. Knowing the overall carrier mean free path at 4.2 and 298 K will enable us to estimate the basal plane pcc at 298 K from the measured value at 77 K.

A typical sample of the material used in this work, e.g. IFP 37, has a resistivity ration

$$\left(\frac{R_{77}}{R_{4.2}}\right)_{\text{basal plane}} = 4.9$$

WOORE (1969) has shown that the density increases by a factor of 1.1 in the temperature interval 4.2-77 K but the velocity at the Fermi surface is not substantially altered (McCLURE (1958)). Thus:

$$\frac{\sigma_{77}}{\sigma_{4.2}} = \frac{1.10 \lambda_{77}}{\lambda_{4.2}} = \frac{1}{4.9}$$

If $\lambda_{4.2\text{K}} = 3 \mu$ then $\lambda_{77} = 5566 \text{ \AA}$.

The pressure coefficient of conductivity is related to the various scattering mechanisms through equation (6.2), namely

$$\frac{d \ln \sigma}{dP} = \frac{d \ln n}{dP} + \frac{\lambda_1}{\lambda_1 + \lambda_2} \frac{d \ln \lambda_2}{dP} \quad \dots (7.5)$$

where λ_1 and λ_2 are pressure independent and pressure dependent mean free paths respectively. $d \ln n / dP$ has been determined in section 5.3.2 to take the average values of $35.6 \times 10^{-6} \text{ bar}^{-1}$. HOWELLS (1969) has listed six values for $d \ln \sigma / dP$ at 77 K in samples of the material IFP 37 with a mean value of $13.2 \times 10^{-6} \text{ bar}^{-1}$. Applying equation (7.5) to the above parameters

$$13.2 = 35.6 + \frac{\lambda_1}{\lambda_1 + \lambda_2} \frac{d \ln \lambda_2}{dP} \cdot 10^6 .$$

If electron-hole scattering accounts for λ_2 then from equation (7.1) $d \ln \lambda_2 / dP = - d \ln n / dP$ and $\lambda_1 = 1.69 \lambda_2$. Since

$$\frac{1}{\lambda_1} + \frac{1}{\lambda_2} = \frac{1}{5566}$$

then $\lambda_1 = 14954.6 \text{ \AA}$ and $\lambda_2 = 8859.4 \text{ \AA}$ in the basal plane at 77 K.

On raising the temperature to 298 K the density increases by a factor of 2.84 (WOORE (1969)). The carrier velocity increases, reducing the carrier-carrier scattering cross-section such that

$$\frac{(Q_{e-h})_{298}}{(Q_{e-h})_{77}} = \frac{(v_e + v_h)_{77}^4}{(v_e + v_h)_{298}^4} = \left(\frac{1.47}{2.30} \right)^4 = 0.167 .$$

At 77 K the Pauli Exclusion factor $(E_F / k_B T)^2$ equals 8.16 for a degeneracy temperature of 220 K corresponding to a Fermi level of 0.019 eV. On raising the temperature above 220 K this factor no longer applies. The increase in density, decrease in scattering cross-section, and removal of the Pauli exclusion factor means that a carrier-carrier mean free path of 8859.4 $\text{\AA}$ at 77 K described by equation (7.1), becomes at 298 K equal to 2289 $\text{\AA}$:

$$\lambda_2 = 2289 \text{ \AA} - \text{basal plane .}$$

(298 K)

The overall mean free path at 298K can be obtained from the value at 77K by substituting the values quoted above for the change in conductivity, carrier density and carrier velocity, into equation (6.1). Table 6.2 lists the measured conductivity ratio σ_{298}/σ_{77} for four preparations of pyrolytic graphite, with an average value of 0.663. Then:

$$\lambda_{\text{overall } 298\text{K}} = 0.365 \lambda_{\text{overall } 77\text{K}}$$

and

$$\lambda_{\text{overall } 77\text{K}} = 2034 \text{ \AA}.$$

The pressure independent mean free path is therefore 18,258 Å.

We are now in a position to estimate the basal plane pcc at 298K.

Applying equation (7.5)

$$\begin{aligned} \left(\frac{d \ln \sigma}{dP} \right)_{298}^{\text{basal plane}} &= \left\{ 35.6 - \frac{18258}{18258 + 2289} \cdot 35.6 \right\} \times 10^{-6} \\ &= 3.96 \times 10^{-6} \text{ bar}^{-1}. \end{aligned}$$

Which is in quite good agreement with the measured value of $2.9 \times 10^{-6} \text{ bar}^{-1}$.

If the temperature is reduced from 77 to 4.2K the density decreases slightly, by the factor of 1.1, carrier velocities at the Fermi surface are unchanged but the $(E_f/k_B T)^2$ factor increases by 336.2 and the carrier-carrier mean free path by a factor of 369.8. At 4.2K the carrier-carrier mean free path for basal plane transport is therefore $8859.4 \times 369.8 = 327.6 \mu\text{m}$. Carrier-carrier scattering is therefore completely ineffective when compared with a crystallite dimension of $3 \mu\text{m}$ and the pcc should accurately reflect the increase in density with pressure.

7.4.2 Pristine Pyrolytic Graphite - c-axis

Knowing the basal plane mean free path due to electron-hole scattering at room temperature, we may estimate from equation (7.3) the corresponding mean free path for carriers propagating along the c-axis. Total approach velocities in the basal plane are on average ~60 times total electron-hole approach velocities along the c-axis (SPAIN (1971)). Using

the values of basal plane and c-axis mean electron and hole masses quoted in section 7.2, and applying equation (7.3), the ratio of electron-hole scattering cross-sections in the c-axis and the basal plane becomes :

$$\left(\frac{Q_{\underline{c}\text{-axis}}}{Q_{\underline{a}\text{-axis}}} \right)_{\text{e-h}} = 423.5$$

A basal plane electron-hole mean free path of 2289 Å at 298 K therefore corresponds to a c-axis mean free path of 5.40 Å. The overall mean free path for c-axis conduction can be determined from the measured anisotropy in c-axis and basal plane conduction since the basal plane mean free path is known to equal 2034 Å at 298 K. For pyrolytic graphite of reasonable quality, a conductivity ratio $\sigma_{\underline{a}\text{-axis}} / \sigma_{\underline{c}\text{-axis}}$ of 4500 leads to an overall mean free path for c-axis transport of 1.55 Å. The pressure independent mean free path λ_1 at 298 K is therefore

$$\frac{1}{\lambda_1} = \frac{1}{1.55} - \frac{1}{5.40} \quad , \quad \lambda_1 = 2.17 \text{ Å at } 298 \text{ K.}$$

caxis

The pcc for carriers propagating perpendicular to the basal plane is then according to equation (7.5)

$$\left(\frac{d \ln \sigma}{dP} \right)_{\underline{c}\text{-axis}} = \left(35.6 - \frac{2.17}{2.17 + 5.40} \cdot 35.6 \right) \times 10^{-6} = 25.39 \times 10^{-6} \text{ bar}^{-1}$$

298 K

compared with the experimental value of $25.5 \pm 1.5 \times 10^{-6} \text{ bar}^{-1}$ at 273 K.

Reducing the temperature to 77 K introduces the Pauli exclusion factor, the decrease in density and velocity, and leads through application of equation (7.1) to a carrier-carrier mean free path

$$\begin{aligned} \lambda_{\text{e-h}} \text{ at } 77 \text{ K} &= \lambda_{\text{e-h}} \times 3.87 \\ &\quad \text{298 K} \\ &= 20.9 \text{ Å} . \end{aligned}$$

Between 298 and 77 K c-axis conductivity decreases by a factor of 1.82. As the density decreases by a factor of 2.84, and the velocity at the Fermi surface by 1.56 the overall mean free path λ_{77} at 77 K is given by the

equation

$$\frac{\sigma_{77}}{\sigma_{298}} = \frac{1}{1.82} = \frac{n_{298} \times \lambda_{77} \times 1.56}{2.84 \times \lambda_{298} \times n_{298}}$$

Then λ_{77} (c-axis) = 1.55 Å which is the same as the overall mean free path applying at 298K. The pressure independent mean free path λ_1 is then given by

$$\frac{1}{\lambda_1} = \frac{1}{1.55} - \frac{1}{20.9}, \quad \lambda_1 = 1.67 \text{ Å at } 77 \text{ K}.$$

The pcc for c-axis transport at 77K takes the form

$$\frac{d \ln \sigma}{dP} = \left(35.6 - \frac{1.67}{1.67 + 20.9} \cdot 35.6 \right) \times 10^{-6} = 32.96 \times 10^{-6} \text{ bar}^{-1}$$

compared with a measured value of $27.6 \pm 1 \times 10^{-6} \text{ bar}^{-1}$. As the temperature is reduced from 77 to 4.2K the carrier-carrier mean free path is increased by the factor 369.8 quoted in section 7.4.1 leading to a carrier-carrier mean free path of 7728.8 Å.

BENDER and YOUNG (1973) have recently estimated a stacking fault spacing of 1370 Å and, as this would be the dominant scattering mechanism at liquid helium temperatures, a pcc of

$$\frac{d \ln \sigma}{dP} = \left(35.6 - \frac{1370}{1370 + 7729} \times 35.6 \right) \times 10^{-6} = 30.24 \times 10^{-6} \text{ bar}^{-1}$$

would result, compared with a measured value of $\sim 28.2 \times 10^{-6} \text{ bar}^{-1}$.

On the other hand a stacking fault spacing of $\sim 30 \text{ Å}$ is usually quoted for pyrolytic graphite of poor quality. In this case carrier-carrier scattering is completely ineffective at 4.2K and the pcc should equal $d \ln n / dP$.

For material of reasonable quality the pcc at 4.2K will therefore lie between 30.2 and $35.6 \times 10^{-6} \text{ bar}^{-1}$.

7.5 ABSOLUTE CARRIER-CARRIER MEAN FREE PATH

Formulae based on the Born approximation will only approximately describe the total scattering cross-section when colliding carriers propagate along the c-axis and will provide a poor estimate when carriers are moving parallel to the basal planes. However, it is instructive to examine the application of the Conwell-Weiskopf formula to carrier-carrier scattering to determine whether this approach may be applied to the calculation of carrier mean free paths, in particular to the calculation of the mean free path due to scattering by ionized impurities resulting from irradiation with fast neutrons. The Conwell-Weiskopf approach, discussed in section 3.5.6, assumes that the potential due to a point charge approaches zero discontinuously at a distance equal to half the particle separation $2d$ and leads to a velocity dependent mean free path of the form:

$$\ell(v) = \frac{\xi^2 M^2 v^4}{\pi N e^4 \ln \left(1 + \frac{\xi^2 M^2 v^4 d^2}{e^4} \right)} \quad \dots (7.6)$$

McCLURE and SPRY (1967) have used the linearised Thomas-Fermi model to discuss the scattering potential due to ionized impurity scattering centres, and have employed the high frequency dielectric constant ϵ_∞ which in graphite is approximately equal to 4.0. In this approach no allowance was made for the influence of the band structure on the screening of point charges due to conduction carriers. BOARDMAN and GRAHAM (1971) considered basal plane conduction limited by charged impurities. On including details of the band structure into a calculation of the dielectric constant the screening of charged impurities by conduction carriers was reduced, the effective scattering cross-section increased, and the mean free path reduced by a factor of seven.

Even though the band structure and crystal structure of graphite exhibit extreme anisotropy, VISSCHER and FALIKOV (1971) have shown that the screening length in the c-axis direction is equal, to within 10%, to the

screening in the basal plane. The same dielectric constant can be used to describe transport in both directions.

On substituting in equation (7.6) the carrier densities, total c-axis electron-hole approach velocity and reduced mass used in section 7.2. An electron-hole mean free path at 298 K of 9.09 Å is calculated. The calculations of section 7.4.2 suggest that a carrier-carrier mean free-path of 5.04 Å is consistent with the observed pressure coefficient of resistance at 298 K. Estimates of the carrier-carrier mean free path for transport perpendicular to the basal plane, based on the Conwell-Weiskopf model are therefore in agreement with those based on experiment to within a factor of two.

In the basal plane a total electron-hole approach velocity of $2300 \times 10^5 \text{ cm sec}^{-1}$ applies at 298 K with a reduced mass of $23.2 \times 10^{-3} m_0$. Substituting these values in equation 7.6 leads to a basal plane carrier-carrier mean free path of 62.9 Å compared with the experimental value of 2289 Å. Thus, as predicted in section 3.5.8, formulae based on the Born approximation cannot be used to estimate carrier-carrier scattering cross-sections for carriers propagating parallel to the basal planes.

7.6 IRRADIATED PYROLYTIC GRAPHITE

Introduction of electron traps through neutron irradiation reduces the pressure independent mean free path λ_1 and the p c c expressed through equation 7.5, tends to $d \ln n / dP$ as λ_1 approaches zero. This behaviour is found experimentally in both c-axis and basal plane conduction cf. Table 7.1. Estimates of carrier-ionized impurity mean free paths based on the Born approximation are subject to the same restraints as those applying to carrier-carrier scattering. In particular, the CONWELL-WEISKOPF formula is expected to account for carrier-ionized impurity scattering along the c-axis by over-estimating the mean free path by a factor of ~ 1.7 . In the basal plane the Cornwell-Weiskopf formula is not applicable.

7.6.1 c-axis Transport

At 298 K the average electron and hole velocity perpendicular to the basal planes is $\sim 19.2 \times 10^5 \text{ cm sec}^{-1}$, and the average effective mass about $9.9 m_0$. It is these values rather than the reduced mass and total approach velocity which we substitute in equation (7.6), to calculate the mean free path due to ionized impurity scattering.

In section 5.3.1 we found that irradiation with fast neutrons resulted in an acceptor yield of 23.7 nvt. An irradiation dose of say 10^{18} nvt therefore results in a value for half the acceptor separation $\underline{d}$ given by

$$d = \frac{1}{2} \cdot \frac{1}{(23.7 \times 10^{18})^{\frac{1}{3}}}$$

With these parameters, equation (7.6) gives a mean free path due to carrier-ionized impurity scattering of $6.36 \text{ \AA}$ and this is probably over-estimated by a factor of 1.7 leading to an ionized impurity controlled mean free path of $3.74 \text{ \AA}$.

The pre-irradiation pressure independent mean free path of 298 K for c-axis transport was shown in section 7.4.2 to be $2.17 \text{ \AA}$. After irradiation λ_1 is therefore given by

$$\frac{1}{\lambda_1} = \frac{1}{3.74} + \frac{1}{2.17}$$

and a pressure independent mean free path of $1.37 \text{ \AA}$ results.

We are now in a position to estimate the c-axis pcc at 298 K in material irradiated to 10^{18} nvt . Application of equation (7.5) with $\lambda_1 = 1.37 \text{ \AA}$ and λ_2 equal to the pre-irradiation figure of $5.40 \text{ \AA}$ results in a value for $d \ln \sigma / dP$ equal to $28.39 \times 10^{-6} \text{ bar}^{-1}$. This figure is, as expected, larger than the $25.39 \times 10^{-6} \text{ bar}^{-1}$ calculated for pristine graphite and is within 12% of that found experimentally.

Reducing the temperature increases the total scattering cross-section due to ionized impurities and classically the mobility follows a $T^{1.5}$ temperature dependence. In the present case the ratio of the ionized impurity

mean free path at 77K to that at 298K is given by the expression

$$\left(\frac{\lambda_{77}}{\lambda_{298}} \right)_{\text{ionized impurity}} = \frac{\left(\frac{V_{e,h}}{298} \right)^4}{\left(\frac{V_{e,h}}{77} \right)^4}$$

where $V_{e,h}$ is the average electron, hole velocity in the c-axis. A mean free path of 3.74 Å at 298K therefore corresponds to a value of 0.62 Å at 77K. A pre-irradiation pressure independent mean free path of 1.67 Å and a carrier-carrier mean free path of 20.9 Å leads through equation (7.5) to a pressure coefficient of resistance at 77K of $34.27 \times 10^{-6} \text{ bar}^{-1}$ which is in good agreement with the measured value of $35.7 \times 10^{-6} \text{ bar}^{-1}$.

At liquid helium temperatures the carrier-ionized impurity mean free path is approximately the same as at 77K. The carrier-carrier mean free path has increased as outlined in section 7.4.1 by a factor of 369.7 and the p c c should equal that of $d \ln n / dP$ namely $35.57 \times 10^{-6} \text{ bar}^{-1}$.

7.7 COMPARISON OF THEORY WITH EXPERIMENT

Perhaps the most enigmatic feature of the measurements on pressure coefficient of resistance in pyrolytic graphite is the unexpected gross anisotropy between the pressure dependence of conduction - in and perpendicular to the basal plane. The introduction of carrier-carrier scattering terms with anisotropic scattering cross-sections has permitted a calculation of this anisotropy. The carrier-carrier scattering cross-section was effectively fixed at 77K for basal plane transport by assuming the experimental value for $d \ln \sigma / dP$. Values of the p c c at any temperature and in both principle directions were then calculated through application of equations (7.1) and (7.5). Theoretical results together with the experimental findings of Table 7.1 are plotted in Fig.7.2. Curves are alphabetically labelled in pairs, the prime denoting a theoretical result. 'a' refers to c-axis conduction in pyrolytic graphite irradiated with fast neutrons to

10^{18} nvt. 'c' refers to basal plane transport in the same material; in this case there is no theoretical result. Labels 'b' and 'd' refer to unirradiated pyrolytic graphite with current perpendicular and parallel to the basal plane respectively.

Theoretical values for the anisotropy factor

$$A_x = \left(\frac{d \ln \sigma}{dP} \right)_{\underline{c}\text{-axis}} / \left(\frac{d \ln \sigma}{dP} \right)_{\underline{a}\text{-axis}}$$

are listed with the experimental values for several fixed temperature points in Table 7.2. 'Ax' decreases monotonically and theoretical predictions tend towards the experimental results as the temperature is reduced to 4.2K. Below 200K theory agrees with experiment to within 19%.

TABLE 7.2

Temperature K	$\left(\frac{d \ln \sigma}{dP} \right)_{\underline{c}\text{-axis}} / \left(\frac{d \ln \sigma}{dP} \right)_{\text{basal plane}}$	
	<u>Theory</u>	<u>Experiment</u>
297	6.4	9.7
273	5.6	6.9
198	3.9	4.1
90	2.6	2.3
77	2.5	2.1
52	2.0	1.8
42	0.9	1.0

On referring to Fig.7.2 it can be seen that basal plane conduction in pristine graphite is well described by a model incorporating carrier-carrier scattering- at temperatures above $\sim 50\text{K}$. However, it should be borne in mind that the experimental determination of $d \ln \sigma / dP$ at lower temperatures carries a rather large uncertainty of $\pm 6 \times 10^{-6} \text{ bar}^{-1}$. The disagreement at low temperatures may not be as large as it appears.

Perpendicular to the basal planes there is very good agreement between theory and experiment at and around room temperature. As the

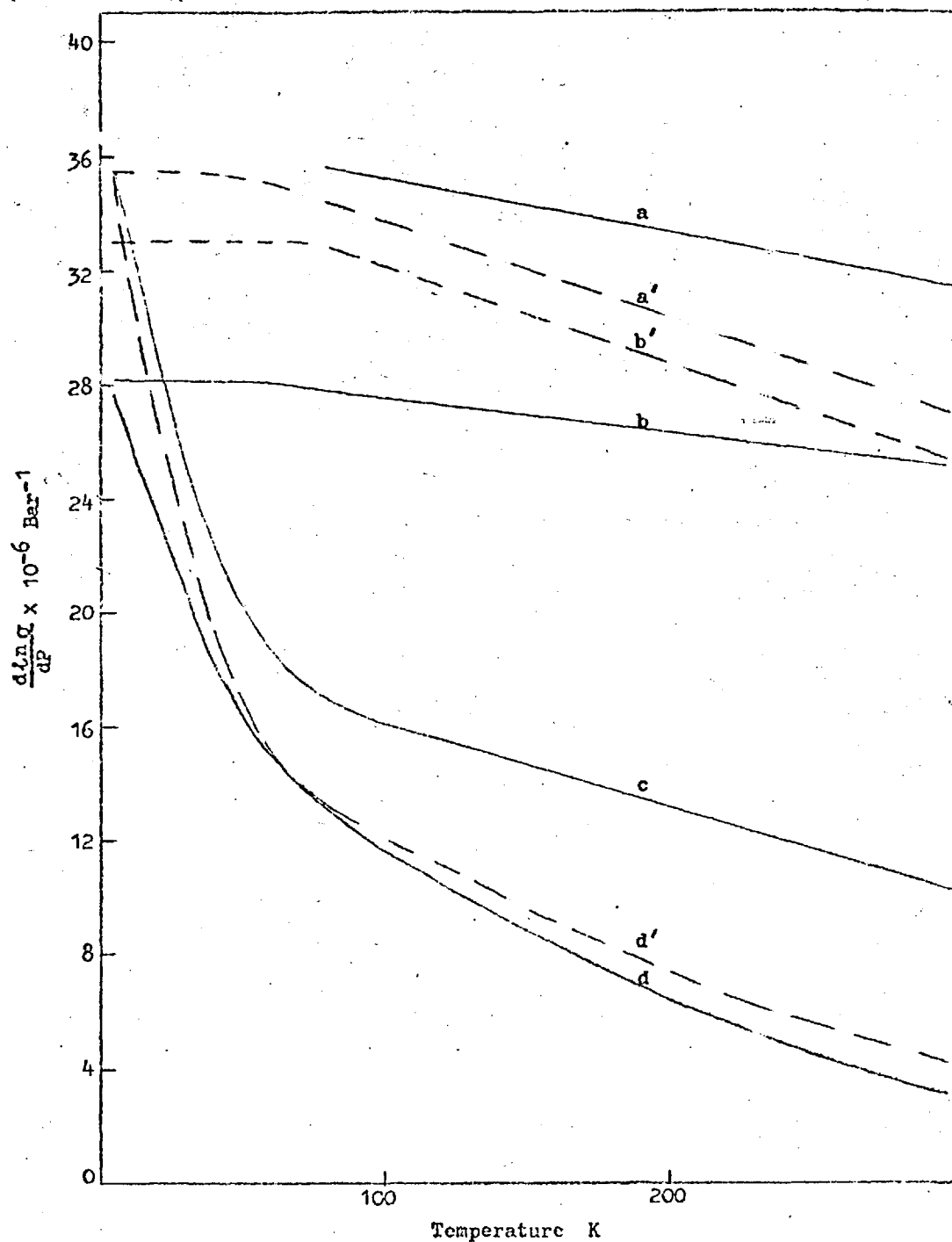


Fig.7.2
Temperature dependence of the conductivity pressure coefficient in pyrolytic graphite. Full lines denote experimental and dashed lines theoretical results

temperature is reduced, experiment and theory separate until at 4.2K the experimental result differs by 20% from the theoretical value. The failure of the pcc to reach a value equal to $d \ln n / dP$ at 4.2K suggests that the mean free path due to stacking fault scattering is in fact greater than the 30 Å quoted for poor material. The upper limit of 1370 Å determined by BENDER and YOUNG (1972c) predicts a pcc which is within 7% of the measured value.

7.8 CONCLUSIONS

This investigation provides the first comprehensive study of the influence of applied pressure on c-axis and basal plane conduction in pristine and neutron irradiated graphite. An important feature is the simultaneous determination of the change in carrier density with pressure. At the start of the research (1966) there was no information available on the change in quantum oscillations with pressure. ANDERSON et al (1967) subsequently showed that in single crystal graphite both the electron and hole surfaces expand in pyrolytic material, only the change in the electron period could be determined. Similarly ITSKEVICH and FISCHER (1967) were unable to identify the hole oscillation, but showed that in synthetic graphite the electron surface expands on application of pressure. The present study therefore provides the first determination of the effect of pressure on the hole oscillation in synthetic material. A value for $(d \ln n_h / dP)_{p.g.}$ of $34.1 \times 10^{-6} \text{ bar}^{-1}$ is less than the $42.9 \times 10^{-6} \text{ bar}^{-1}$ determined for single crystal graphite by Anderson et al. However, there is excellent agreement between the measured pressure dependence of the electron density in this work and both that of Itskevich and Fischer and Anderson et al. A novel isobaric freezing technique enabled pressures of 400 bar to be applied to graphite samples at 4.2K and by-passed the problem of transmitting pressure through solid helium.

For the first time quantum oscillations were observed in graphite irradiated with fast neutrons. The short period characterising the surface centred at point K of the Brillouin zone, was found to increase, and the long period characterising the two outer surfaces, was found to decrease. However, irradiation is known to depress the Fermi level (SPAIN et al (1967)) and results in a contracting electron surface and an expanding hole surface. Electrons are therefore located at the centre of the Brillouin zone edge with holes around points H, H'. This conclusion is in complete agreement with the most recent estimates of carrier location by SCHROEDER et al (1968); KECHIN (1970) and WOOLLAM (1971). The present study and the work of COOPER et al (1971) forms an important part of the growing evidence for negative γ_2 .

The measurement of c-axis conduction as a function of pressure was made possible by the development of a suitable sample geometry and lead arrangement. The pressure coefficients of c-axis and basal plane resistance determined at room temperature is in complete agreement with previous work by SPAIN (1964) to higher pressures. All measurements below room temperature are new and there are no results available for comparison. However, HOWELL (1969) repeated and extended these measurements to include the fixed temperature points 198 and 90K and found exactly the same behaviour. The gross anisotropy in the pressure dependence of conduction of c-axis and basal plane transport, decreases with decreasing temperature and is removed entirely by 4.2K.

Irradiation with fast neutrons has a marked influence on basal plane transport, increasing the pressure coefficient of resistance at 273K from near zero to $11.6 \times 10^{-6} \text{ bar}^{-1}$. c-axis transport is affected to a lesser extent. At lower temperatures the pressure coefficient of resistance of both basal plane and c-axis transport is increased by irradiation until at liquid helium temperatures the increase in conductivity on application

of pressure equals that of the carrier density. HOWELL, YEOMAN and YOUNG (1970) have shown that the pressure characteristics of poor quality pyrolytic graphite is similar to that of good quality material irradiated with fast neutrons.

The inclusion of carrier-carrier scattering as an important scattering mechanism has resolved difficulties in interpretation caused by the anisotropy existing between the pressure dependence of c-axis and basal plane conduction. The suggestion by McCLURE (1964) that particle-particle interactions should be important in graphite with properties parallel to the basal planes being more affected than those in the perpendicular direction has been entirely vindicated. Zero order hole-hole scattering and the first order influence of carrier-carrier scattering on the velocity distribution function have not been specifically included in the analysis. But, fixing the scattering cross-section at 77 K by assuming a value for the pressure coefficient of resistance effectively includes all processes contributing to the carrier-carrier mean free path. An electron-hole scattering cross section with an anisotropy $\{(Q_{e-h})_{\underline{c}\text{-axis}} / (Q_{(e-h)}^{\text{basal plane}})\}$ of 423.5 describes a scattering event which affects both c-axis and basal plane transport.

Parallel to the basal planes, carrier-carrier scattering is the dominant scattering processes at room temperature in good pyrolytic graphite. Irradiation reduces the fixed mean free path, and the increase in carrier density due to the application of pressure is then only partially balanced by the decrease in mobility resulting from the increased carrier-carrier scattering. Poor quality pyrolytic graphite with a fixed mean free path of $\ll 3 \mu\text{m}$ exhibits the same behaviour as irradiated good quality graphite. As the temperature is reduced, the mean free path due to carrier-carrier scattering increases at a rate described by the exclusion principle factor $(E_F/k_B T)^2$. In the basal plane there is good agreement between the

calculated pressure dependence of conduction and that measured experimentally except at 4.2K where the experimental error is large at $\pm 6 \times 10^{-6} \text{ bar}^{-1}$. Perpendicular to the basal planes the agreement is good down to $\sim 200\text{K}$ and thereafter becomes progressively poorer, suggesting that the fixed mean free path due to stacking fault scattering is larger than that generally quoted.

The Debye-Conwell model has been shown to be a good description of electron-hole scattering between carriers moving perpendicular to the basal planes, but to be completely inapplicable to basal plane transport. This result was anticipated in section 3.5.8 and in the case of basal plane transport can be traced to a breakdown of the Born approximation.

APPENDIX AI

LOCATION OF EXTREMAL AREA OF CROSS-SECTION OF

MAJORITY HOLE SURFACE INCLUDING γ_4, γ_5

When γ_4 and γ_5 are included, the expression for the cross-sectional area of the majority hole surface takes the form:

$$A_H = \frac{(E_f^2 - E_f(\Delta + \gamma_1 \Gamma_m + \frac{1}{2} \gamma_5 \Gamma_m^2 + \frac{1}{2} \gamma_2 \Gamma_m^2) + \frac{1}{2} \gamma_2 \Gamma_m^2 (\Delta + \gamma_1 \Gamma_m + \frac{1}{2} \gamma_5 \Gamma_m^2))}{(\gamma_0 - \gamma_4 \Gamma_m)^2}$$

To obtain the extremal area of cross-section we differentiate wrt Γ and equate to zero, which results in a quartic in Γ .

$$2 \gamma_4 \gamma_2 \gamma_5 \Gamma^4 + \left(\frac{3}{2} \gamma_4 \gamma_1 \gamma_2 + \frac{1}{4} \gamma_2 \gamma_5 \right) \Gamma^3 + \left(\frac{3}{2} \gamma_1 \gamma_2 \gamma_0 + \gamma_2 \gamma_4 \gamma_1 \right) \Gamma^2 - \Gamma (\gamma_2 \gamma_0 \Delta - \gamma_0 \gamma_2 E_f - \gamma_0 \gamma_5 E_f - \gamma_4 E_f \gamma_1) - (2 \gamma_4 E_f^2 - 2 \gamma_4 E_f \Delta - \gamma_0 \gamma_1 E_f) = 0 .$$

If the band parameter values of section 3.2.3 are substituted into this equation, it can be shown that the coefficient of Γ^2 is respectively 15 and 150 times that of Γ^3 and Γ^4 . As $\Gamma_m \sim 1$ higher order terms in Γ may be neglected in comparison with terms of order ≤ 2 . On reduction to a quadratic the equation may be solved for Γ_m :

$$\Gamma_m =$$

$$E_f \frac{(\gamma_0 \gamma_2 + \gamma_0 \gamma_5 + \gamma_4 \gamma_1) - \gamma_0 \gamma_2 \Delta \pm \left\{ (E_f(\gamma_0 \gamma_2 + \gamma_0 \gamma_5 + \gamma_4 \gamma_1) - \gamma_0 \gamma_2 \Delta)^2 - 4 \left(\frac{3}{2} \gamma_1 \gamma_0 \gamma_2 - \gamma_4 \gamma_2 \gamma_1 \right) (2 \gamma_4 E_f^2 - \gamma_0 \gamma_1 E_f - 2 \gamma_4 E_f \Delta) \right\}^{\frac{1}{2}}}{(3 \gamma_1 \gamma_2 \gamma_0 - 2 \gamma_4 \gamma_2 \gamma_1)}$$

APPENDIX AII

VOLUME ENCLOSED BY MAJORITY ELECTRON

SURFACE INCLUDING γ_4, γ_5

The volume enclosed by the majority electron surface is obtained by evaluating the integral:

$$V_e = \frac{8}{3} \frac{\pi}{a_0^2} \int_{\Gamma=2}^{\Gamma=\sqrt{\frac{2E_f}{\gamma^2}}} \frac{\frac{1}{4} \gamma_2 \gamma_5 \Gamma^4 - \frac{1}{2} \gamma_1 \gamma_2 \Gamma^3 + \Gamma^2 \left(\frac{1}{2} \gamma_2 \Delta - \frac{1}{2} E_f \gamma_2 - \frac{1}{2} E_f \gamma_5 \right) + \Gamma E_f \gamma_1 + E_f (E_f - \Delta)}{(\gamma_0 + \gamma_4 \Gamma)^2} dk_z$$

To facilitate solution we expand the denominator as a power series in γ_4

$$(\gamma_0 + \gamma_4 \Gamma)^{-2} = \gamma_0^{-2} - \frac{2 \gamma_4 \Gamma}{\gamma_0^3} + \frac{6 \gamma_4^2 \Gamma^2}{2! \gamma_0^4} \dots$$

As $\gamma_4 = 0.18$ and $\gamma_0 = 2.88$ higher order terms progress monotonically to zero. We thus neglect terms with γ_4 of order greater than unity. Then:

$$V_e = \frac{8}{3} \frac{\pi}{a_0^2} \gamma_0^{-2} \int_{\Gamma=2}^{\Gamma=\sqrt{\frac{2E_f}{\gamma^2}}} \frac{1}{4} \gamma_2 \gamma_5 \Gamma^4 - \frac{1}{2} \gamma_1 \gamma_2 \Gamma^3 + \Gamma^2 \left(\frac{1}{2} \gamma_2 \Delta - \frac{1}{2} E_f \gamma_2 - \frac{1}{2} E_f \gamma_5 \right) + \Gamma E_f \gamma_1 + E_f (E_f - \Delta) dk_z$$

$$- \frac{16}{3} \frac{\pi}{a_0^2} \frac{\gamma_4}{\gamma_0^3} \int_{\Gamma=2}^{\Gamma=\sqrt{\frac{2E_f}{\gamma^2}}} \frac{1}{4} \gamma_2 \gamma_5 \Gamma^5 - \frac{1}{2} \gamma_1 \gamma_2 \Gamma^4 + \Gamma^3 \left(\frac{1}{2} \gamma_2 \Delta - \frac{1}{2} E_f \gamma_2 - \frac{1}{2} E_f \gamma_5 \right) + \Gamma^2 E_f \gamma_1 + \Gamma E_f (E_f - \Delta) dk_z$$

We require the integrals $\int \Gamma^n dk_z$, $n = 1, 2, \dots, 5$ and recall that $\Gamma = 2 \cos \frac{k_z c_0}{2}$. Let

$$\frac{k_z c_0}{2} = x,$$

then

$$dk_z = \frac{2}{c_0} dx$$

and

$$\int \Gamma^n dk_z = \left(\frac{2}{c_0} \right)^n \int \cos^n x dx.$$

Such integrals may be obtained from tables, e.g. 'Mathematical Data' by H.B. Dwight, MacMillan Publishing Co., N.Y. 1961.

$$\int \Gamma^5 dk_z = \frac{32}{c_0} \int \cos^5 x dx = \frac{32}{c_0} \left[\frac{5}{8} \sin x + \frac{\sin 3x}{48} + \frac{\sin 5x}{80} \right]$$

$$\int \Gamma^4 dk_z = \frac{16}{c_0} \int \cos^4 x dx = \frac{16}{c_0} \left[\frac{3x}{8} + \frac{\sin 2x}{4} + \frac{\sin 4x}{32} \right]$$

$$\int \Gamma^3 dk_z = \frac{8}{c_0} \int \cos^3 x dx = \frac{8}{c_0} \left[\sin x - \frac{\sin 3x}{3} \right]$$

$$\int \Gamma^2 dk_z = \frac{4}{c_0} \int \cos^2 x dx = \frac{4}{c_0} \left[\frac{x}{2} - \frac{\sin 4x}{4} \right]$$

$$\int \Gamma dk_z = \frac{2}{c_0} \int \cos x dx = \frac{2}{c_0} \sin x$$

The limits of integration are from $x=0$ to $x = \cos^{-1} \frac{1}{2} \sqrt{\frac{2E_f}{\gamma_2}}$.

In the evaluation of $\int \Gamma^5 dk_z$ the terms $\frac{5 \sin 3x}{48}$ and $\frac{\sin 5x}{80}$ are small compared with the first term, similarly for $\int \Gamma^4 dk_z$, $\frac{\sin 4x}{32}$ is small compared with the first two terms. On omitting these terms the volume expression reduces to

$$V_e = \frac{16}{3} \frac{\pi}{a_0^2 \gamma_0^3 c_0} \left\{ 4 \gamma_2 \gamma_5 \left(\gamma_0 \int \cos^4 x dx - 4 \gamma_4 \int \cos^3 x dx - 4 \gamma_1 \gamma_2 \left(\gamma_0 \int \cos^2 x dx + 4 \gamma_4 \int \cos^4 x dx \right) \right) + \right. \\ + \left(\frac{1}{2} \gamma_2 \Delta - \frac{1}{2} E_f \gamma_2 - \frac{1}{2} E_f \gamma_5 \right) \left(4 \gamma_0 \int \cos^2 x dx - 16 \gamma_4 \int \cos^3 x dx \right) + 2 E_f \gamma_1 \left(\gamma_0 \int \cos x dx - 4 \gamma_4 \int \cos^2 x dx \right) + \\ \left. + E_f (E_f - \Delta) \left(\int \gamma_0 dx - 4 \gamma_4 \int \cos x dx \right) \right\} \Bigg|_{x=0}^{x = \cos^{-1} \frac{1}{2} \sqrt{2E_f/\gamma_2}}$$

Substituting the limits yields the final expression:

$$V_e = \frac{16}{3} \frac{\pi}{a_0^2 \gamma_0^3 c_0} \left[\left(\frac{2 \gamma_2 E_f - E_f^2}{\gamma_2^2} \right)^{\frac{1}{2}} \left(\gamma_0 \gamma_4 \gamma_5 - 4 \gamma_1 \gamma_2 \gamma_4 + \frac{1}{2} \gamma_0 \gamma_2 \Delta - \frac{1}{2} \gamma_0 E_f \gamma_2 - \frac{1}{2} \gamma_0 E_f \gamma_5 - 2 E_f \gamma_1 \gamma_4 \right) + \right. \\ + \left(\frac{2 \gamma_2 - E_f}{2 \gamma_2} \right)^{\frac{1}{2}} \left(2 E_f \gamma_1 \gamma_0 - \frac{8}{3} \left(-\gamma_4 \gamma_2 E_f + \gamma_4 \gamma_2 \Delta - \gamma_4 E_f \gamma_5 \right) \left(\frac{2 \gamma_2 - E_f}{2 \gamma_2} \right) \right. \\ + 8 \gamma_4 \gamma_2 \Delta - 8 \gamma_4 E_f \gamma_2 - 8 \gamma_4 E_f \gamma_5 - 4 \frac{\gamma_1 \gamma_2 \gamma_0}{3} \left(\frac{2 \gamma_2 - E_f}{2 \gamma_2} \right) - 4 \gamma_1 \gamma_2 \gamma_0 - 4 \gamma_4 E_f (E_f - \Delta) - 10 \gamma_4^2 \gamma_5 \Big) \\ \left. + \cos^{-1} \sqrt{\frac{E_f}{2 \gamma_2}} \left(\frac{3}{2} \gamma_4 \gamma_5 \gamma_0 - 6 \gamma_1 \gamma_2 \gamma_4 + \gamma_0 \gamma_2 \Delta - \gamma_0 E_f \gamma_2 - \gamma_0 E_f \gamma_5 - 4 E_f \gamma_1 \gamma_4 \right) + E_f (E_f - \Delta) \gamma_0 \right]$$

APPENDIX AIII
ANALYSIS OF OSCILLATORY DATA

WOORE (1969) has described in detail the programs 'DVMOUT', 'FRIER' and 'GENFRR' which were used together with the small program 'POLYFIT' to analyse oscillations in the magnetoresistance of graphite as a function of applied magnetic field.

The experimental data, as collected, consisted of the voltage drop across the sample and a simultaneous reading of the current supplied to the superconducting magnet, cf. Fig.5.1. Magnet current readings were converted to magnetic field with the proportionality factor described in section 4.4.5. Data in this form was plotted and punched onto cards as oscillations in voltage superimposed on a strongly rising, almost parabolic midline. An approximate midline to the oscillations was drawn graphically by joining antinodes and taking midpoint values as a function of increasing magnetic field. Voltage readings at the midpoints were punched, together with the corresponding magnetic field, onto a card deck containing the oscillatory data, and used as the input for program DVMOUT.

DVMOUT fitted the notional midline, using the method of least squares, to a cubic expression and generated values of the voltage midline for each value of the magnetic field. To remove the experimental midline, DVMOUT subtracted the generated midline from the actual experimental amplitudes and at this stage converted sample voltage into resistance, and magnetic field into reciprocal field ($1/H$). A card deck produced with this information provided the starting material for program FRIER. However, a slight midline still remains, cf. Fig.5.2. DVMOUT outputs were therefore plotted and a graphical midline determined and fitted by 'POLYFIT' to a sixth order polynomial, the coefficients of which were included as input to FRIER.

One of the practical problems in the fitting process was the statistical weighting of data. A weighting factor proportional to the inverse of both the amplitude envelope and the magnetic field was punched on each card as an integral number, 1-999. Data in this form was fed to the program FRIER which employed the subroutine VAO 4 A to minimise a function defined as the sum of the squares of the residuals $\sum R_i^2$, where R_i is the difference between experimental and computational values of the oscillatory magnetoresistance fitted to the Landau expression of equation (5.1). VAO 4 A changed each independent variable in turn. Some external control over which parameters were fitted was possible since P_i , ΔT_i , n_i , $U_i H$ could be locked at preset values or released for iteration. n_i remained close to the theoretical value of $(-\frac{1}{2})$ and was kept at that value, while $U_i H$ was determined by the known electron and hole effective masses, $m_e^* = 0.057 m_0$, $m_h^* = 0.039 m_0$. The amplitude and phase terms W_i and ψ_i were always free to iterate, but the coefficients of the sixth order polynomial could be individually locked at fixed values.

The subroutine VAO 4 A operated by first calling a subsidiary programme CALCFX to supply the function $\sum R_i^2$ and then began to alter one of the parameters which had been released for iteration together with W_i and ψ_i . After each alteration CALCFX supplied the value of $\sum R_i^2$, and the curvature of $\sum R_i^2$ in parameter space indicated to VAO 4 A the direction in which the parameters should be changed in order to reach a minimum in $\sum R_i^2$. Using the new parameter values, another of the released variables was changed until a minimum was reached in that particular parameter space. The program continued to iterate either until the time allowed was exceeded, or until successive iterations caused $\sum R_i^2$ to remain stable such that the built-in convergence criterion was satisfied. However, this happened only under very restrictive conditions. Normally iteration was continued until the change in $\sum R_i^2$ was proceeding extremely slowly towards the ultimate minimum

corresponding to changes of less than 0.5% in the period values, and changes of up to 1% in the Dingle temperatures.

A second criterion for terminating the fitting procedure was the requirement that all structural features of the experimental curves were seen to be reproduced by the parameter values produced by FRIER. For this purpose a fourth program GENFRR reproduced the Landau function $\Sigma G_i(r)$ of equation (5.1), and a plot of this function was compared with the curves produced by DVMOUT. The iterative process was terminated only when the computer fit to the experimental data was of the standard reached by those illustrated in Fig.5.5. Normally at least two, and occasionally three, harmonics were required to reproduce the oscillatory structure.

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