

CHAPTER 6

THE ELECTRONIC PROPERTIES OF IRRADIATED GRAPHITE

The electronic properties of graphite are very sensitive to irradiation and can be described in terms of energy band structure. A number of band models have been employed, of which the best known is the simple two-band model. This model will first be described, followed by a discussion of the unirradiated electronic properties, and finally an examination of the effects of irradiation on those properties.

6.1 Two-band Model

Electrical conduction in graphite can be described in terms of two slightly overlapping energy bands, with an energy level distribution as shown in Fig 6.1. For a perfect crystal the Fermi surface is near the overlap level. (The Fermi surface may be thought of as the level at which the states are exactly half occupied under the prevailing conditions.) Graphite is thus essentially a semiconductor with a zero energy gap, with equal numbers of electrons and holes contributing to conduction. The effect of irradiation is to introduce defects which reduce the mobility of the carriers by scattering the electrons and which trap some of the electrons, lowering the level of the Fermi surface. It is conventional to assume a parabolic energy-wave number relationship for each of the two bands near the overlap point:

$$E_e(k) = \frac{2}{2m_e} (k_x^2 + k_y^2) = \frac{2K^2}{2m_e} \text{ for electrons} \quad (6.1)$$

$$E_h(k) = E_0 - \frac{2}{2m_h} (k_x^2 + k_y^2) = E_0 - \frac{2K^2}{2m_h} \text{ for holes}$$

E_0 is the overlap ($E_0 > 0$) or separation ($E_0 < 0$) of the energy bands, m_e and m_h are the effective masses of electrons and holes, and K is the wave number measured from the edge of the Brillouin zone, which is hexagonal with top and bottom faces at $k_z = \pm\pi/d$, where d is the separation of the planes. (For a more comprehensive review of calculations on the Brillouin zone and energy bands see Kelly, 1981.)

Using the model represented by equation (6.1), Johnston (see Reynolds and Goggin, 1960) derived expressions for the electrical resistivity, Hall coefficient and magneto-resistivity of graphite:

Electrical resistivity

$$\rho_0 = \frac{V_x}{J_x} = \frac{1}{e(\mu_h n_h + \mu_e n_e)} \quad (6.2)$$

Hall coefficient

$$R = \frac{V_y}{B_z J_x} = \frac{1}{e} \frac{(\mu_h^2 n_h - \mu_e^2 n_e)}{(\mu_h n_h + \mu_e n_e)^2} \frac{1}{\cos^2 \alpha} \quad (6.3)$$

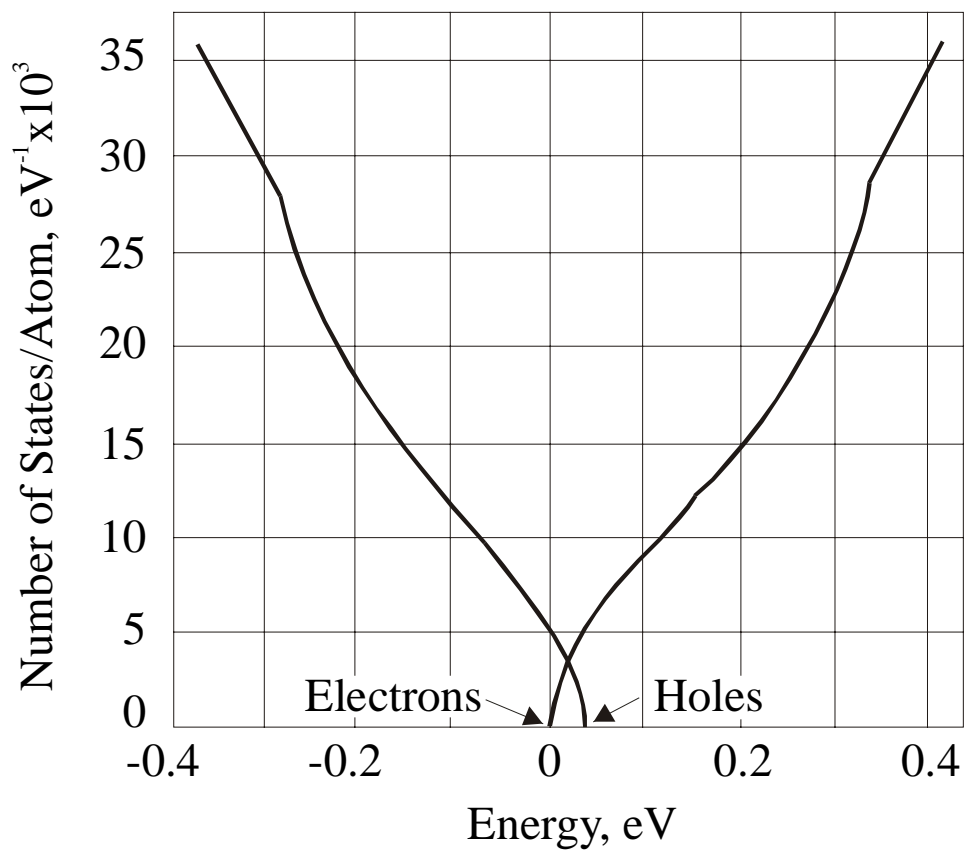


Figure 6.1 Density of electron energy states

Magneto-resistivity

$$\frac{\Delta\rho}{\rho} = \frac{B_z^2 \cos^2 \alpha}{\mu_h n_h + \mu_e n_e} \left| \mu_h^3 n_h + \mu_e^3 n_e - \frac{(\mu_h^2 n_h - \mu_e^2 n_e)^2}{\mu_h n_h + \mu_e n_e} \right| \quad (6.4)$$

n_h and μ_h are the concentration (cm^{-3}) and basal plane mobility ($\text{cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$) of the holes in the lower band, and n_e and μ_e are the same quantities for electrons in the upper band. The magnetic field B_z is in gauss divided by 10^{-8} and e is 1.6×10^{-19} C. The formulae are valid for the case in which the axis of the cylindrical energy surfaces is in the y - z plane at an angle α to the z (hexagonal) axis. Equations (6.3) and (6.4) are only valid for weak fields ($(\mu_h B_z)^2$ and $(\mu_e B_z)^2 \ll 1$). In high fields, especially at low temperatures, these properties oscillate with the field. B_x and B_y are both zero.

The carrier concentrations are given by

$$n_h = \frac{8\pi k T m_h}{2d} \ln \left[1 + \exp \left| \frac{E_0 - E_f}{k T} \right| \right] \quad (6.5)$$

$$n_e = \frac{8\pi k T m_e}{2d} \ln \left[1 + \exp \left| \frac{E_f}{k T} \right| \right]$$

where E_f is the Fermi energy measured from the bottom of the conduction band and k is Boltzmann's constant. It is also possible to write the carrier mobilities as

$$\mu_h = \frac{e \tau_h}{m_h} \quad \mu_e = \frac{e \tau_e}{m_e} \quad (6.6)$$

where τ_h, τ_e are the relaxation times for scattering.

6.2 Unirradiated Properties

Soule (1958), Shoenberg (1952) and Berlincourt and Steele (1955) performed experiments to determine how the above properties and the diamagnetic susceptibility vary with the magnetic field. This enabled McClure (1958) to calculate the band structure of graphite, giving values for the concentration and mobility of the carriers. Table VI.1 gives typical values at several temperatures, taken from McClure (with n in cm^{-3} and μ in $\text{cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$).

TABLE 6.1. PROPERTIES OF CURRENT CARRIERS IN GRAPHITE

	4.2 K	77 K	298 K
n_h	2.8×10^{18}	2.1×10^{18}	7.0×10^{18}
n_e	2.9×10^{18}	2.2×10^{18}	7.0×10^{18}
μ_h	104.0×10^4	7.3×10^4	1.0×10^4
μ_e	83.9×10^4	6.3×10^4	1.1×10^4

It can be seen that the carrier concentrations generally increase with temperature, whilst the mobilities decrease. The mobility decrease is dominant, and hence the resistivity of good graphite crystals increases with temperature.

The first measurements of the electrical resistivity of very perfect or highly oriented polycrystalline graphites parallel to the basal planes, ρ_a , appear to have been by Washburn (1915) and Ryschkewitsch (1923) who used Ceylon graphite. It was observed by Washburn and Krishnan and Ganguli (1939) that the resistivity perpendicular to the basal planes, ρ_c , was 200-10000 times greater than ρ_a . At an angle θ to the axis the resistivity is given by

$$\rho(\theta) = \rho_a \sin^2 \theta + \rho_c \cos^2 \theta \quad (6.7)$$

More modern studies on good graphite crystals began with Kinchin (1953) and Dutta (1953), followed by Primak (1956) and Soule (1958). Figs 6.2 and 6.3 show the results of Soule's measurements parallel to the basal planes and Primak's measurements perpendicular to the planes. It can be seen that the behaviour of ρ_c and ρ_a are different, the increase in ρ_c levelling off above ~ 100 K.

Klein (1966) has published numerous studies on highly oriented pyrolytic graphite of varying perfection. Fig 6.4 shows the variation of resistivity parallel (solid curves) and perpendicular (broken curves) to the deposition planes with heat treatment temperature. Extensive studies have also been published by Spain *et al* (1967). It has been found that the most perfect samples exhibit very similar behaviour to the best natural crystals. There is, however, a problem with the measurements of ρ_c in the more perfect samples which remains unresolved. The problem is that pyrolytic graphites give $\rho_c/\rho_a \sim 10^5$, whereas natural single crystals give $\rho_c/\rho_a \sim 10^2$, although some samples of natural graphite also give a high ratio (Spain, 1971). The view can be taken that it is either the natural graphites or else the highly oriented pyrolytic graphites which have the intrinsic resistivity.

If the natural graphites have the intrinsic resistivity, then an explanation needs to be found for the high resistivity of the pyrolytic graphites in the c direction. One proposal is that there are thin sheets of disordered material in the basal planes with a high resistance, although this has been rejected by Young (1968). Another proposed explanation is that localisation of the charge carriers is produced by defects in the pyrolytic graphite. Ono (1976) showed that a ρ_c/ρ_a value of $\sim 10^4$ at room temperature could be obtained with this explanation if the dislocation density was $\sim 10^{11} \text{ cm}^{-2}$, but this is about a hundred times greater than the value commonly observed in highly oriented pyrolytic graphite. This explanation also fails to correctly predict the temperature dependence.

If the highly oriented pyrolytic graphites have the intrinsic resistivity, then the low resistivity of natural graphites needs explaining. A possible explanation is the presence of screw dislocations with Burgers vector parallel to the hexagonal axis, causing a short circuit. However, this explanation requires dislocation densities of $\sim 10^{15} \text{ cm}^{-2}$, compared to observed densities of $\sim 10^6 \text{ cm}^{-2}$.

Imperfect orientations would mix the c and a directions, but it can be shown that this cannot account for the observed values of ρ_c in either highly oriented pyrolytic graphite or natural graphite.

It can be seen from equations (6.3) and (6.4) that the Hall coefficient depends essentially on the difference between the contributions of the positive and negative carriers to the conduction, whilst the magneto-resistivity depends mainly on the mobility of the carriers. (Magneto-resistivity is the change in electrical resistivity which occurs when a magnetic field is

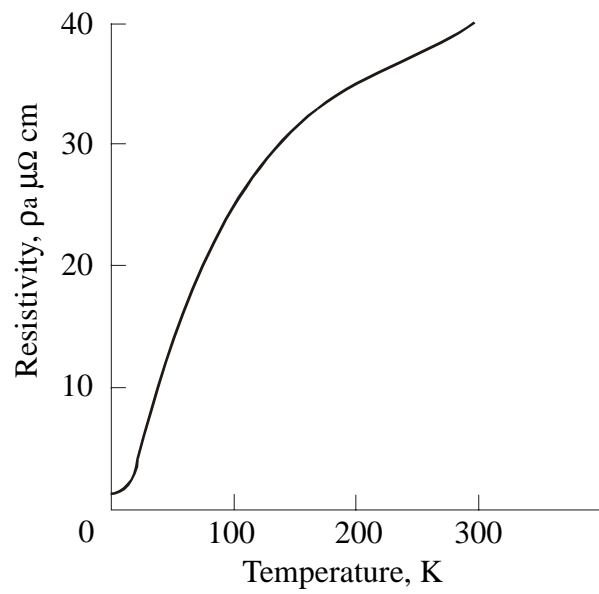


Figure 6.2 Electrical resistance of graphite crystals parallel to Basal planes

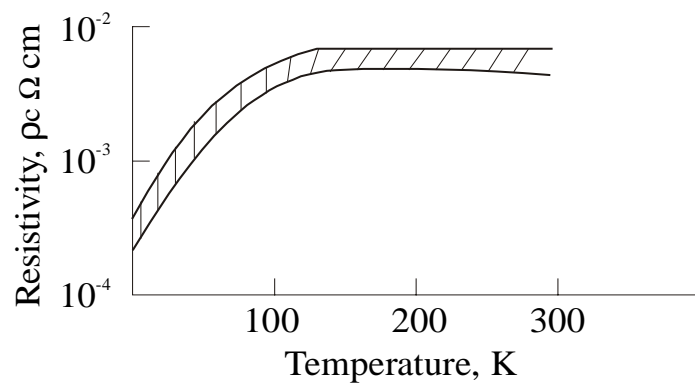


Figure 6.3 Electrical resistance of graphite crystals parallel to hexagonal axis

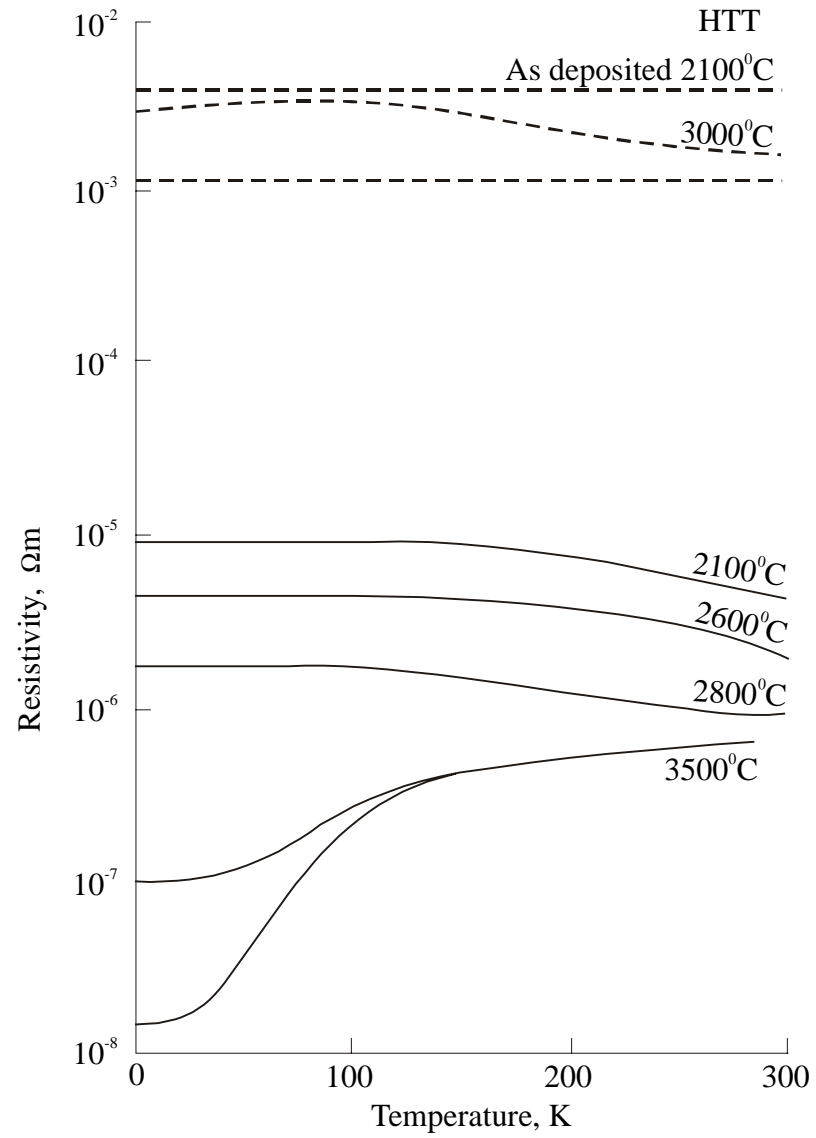


Figure 6.4 Variation of electrical resistivity of highly oriented pyrolytic carbons with heat treatment temperature

applied.) Tables VI.2 and VI.3 show typical values of Hall coefficient and magneto-resistance for different graphites.

TABLE 6.2. HALL COEFFICIENTS OF GRAPHITES

Material	Heat treatment temperature (°C)	Hall coefficient (R) at 300 K (cm ³ /C)
Petroleum-coke graphite (CSF)	2800	-0.06
Petroleum-coke graphite (AGX)	2600	-0.051
Petroleum-coke graphite (ECA)	3000	-0.049
Natural-graphite compact (pitch bonded)	3000	-0.038

TABLE 6.3. MAGNETO-RESISTANCE IN GRAPHITES AT 2140 GAUSS

Material	Heat treatment Temperature (°C)	Magneto-resistance ratio			
		300 K	195 K	77 K	4.2 K
Petroleum-coke graphite	2600	0.0016	0.0020	0.0039	
Petroleum-coke graphite (AGOT)	2800	0.0046			
Petroleum-coke graphite (C-15)	3000	0.013			
Single crystal		0.093		2.24	259

It can be seen that the magneto-resistance for polycrystalline graphites is much less than for single crystals. This is due to several factors:

- (i) Scattering of charge carriers at imperfections reduces the mean free path, reducing $\Delta\rho$.
- (ii) Imperfections also trap the charge carriers, reducing $\Delta\rho$.
- (iii) The presence of crystalline imperfections and boundaries increases ρ .

The first reported measurements of the Hall coefficient and magneto-resistance on graphite crystals were by Kinchin (1953). The measurements were made in a magnetic field of up to 9000 G parallel to the hexagonal axis. The Hall coefficient was measured at temperatures from 4.2 K to 473 K and was found to vary significantly with both temperature and field for temperatures below 77 K (increasing for lower temperatures, and first increasing then decreasing for higher fields). The magneto-resistance was measured as a function of field at 4.2 K and 290 K. At the higher temperature the variation with field was found to be proportional to $B^{1.74}$, and less rapid at the lower temperature for both single crystals and polycrystalline specimens. This clearly contradicts the theoretical variation of B^2 in equation (6.4). In the single crystals, the actual magnitude was found to be remarkably large, values of $\Delta\rho/\rho$ of 526 were reached at a specimen temperature of 4.2 K in a field of less than 10000 G, with a room temperature value as large as 0.43. A much more detailed study was performed by Soule (1958) on specially purified natural crystals cut to dumb-bell shapes at temperatures of 4.2, 77 and 298 K in fields ranging from 25 to 25000 G. The results are shown in Figs 6.5-6.7. The form of the temperature and field dependencies was different to that found by Kinchin, but was in good agreement with Berlincourt and Steele (1955). Both properties showed oscillations at 4.2 K: these are called Shubnikov-De Haas effects and are due to the quantisation of carrier orbitals in applied magnetic fields. Soule estimated carrier densities of $2\text{-}3 \times 10^{18} \text{ cm}^{-3}$ for both holes and electrons, and found μ_e/μ_h varied monotonically from 1.1 at room temperature to 0.77 at 4.2 K.

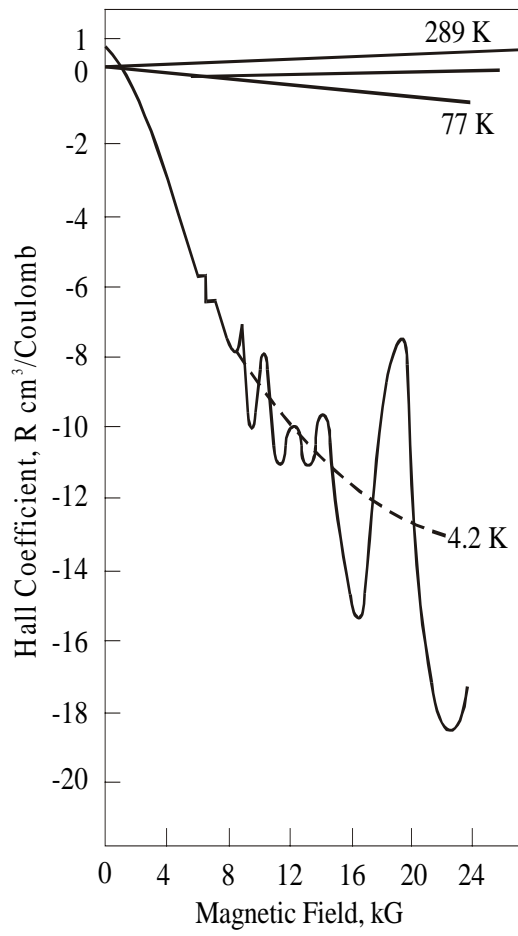


Figure 6.5 Hall effect of graphite crystal EP-14 high field parallel to hexagonal axis

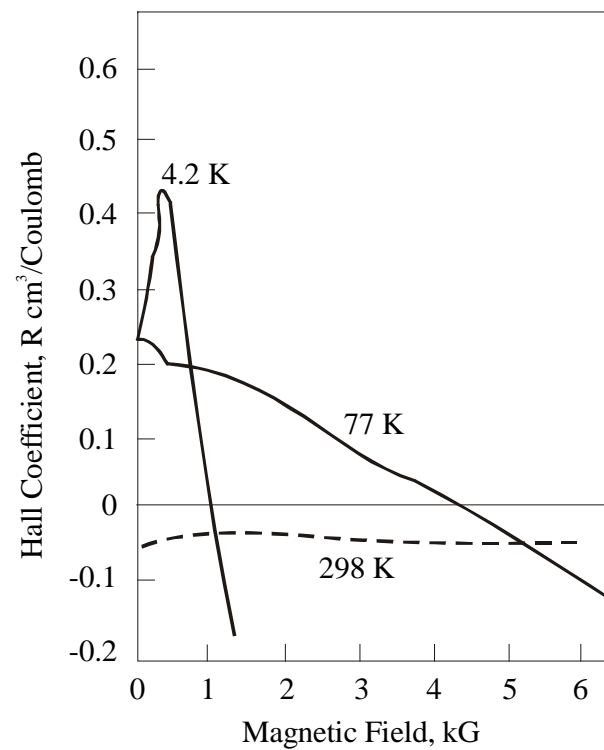


Figure 6.6 Hall effect of graphite crystal EP-14 low field parallel to hexagonal axis

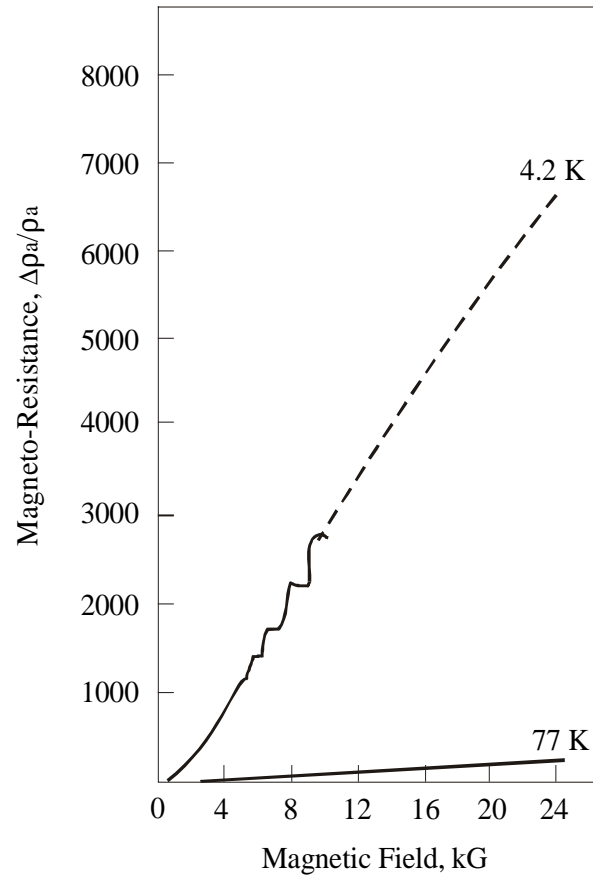


Figure 6.7 Magneto-resistance of graphite crystal EP-14 field parallel to hexagonal axis

Soule then used the magneto-resistance measurements at low fields to derive mobilities ranging from $\sim 10^4 \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ at room temperature to over $10^6 \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ at 4.2 K. These were the first reliable determinations of these quantities in the graphite crystal.

Measurements of the Hall coefficient of Kish graphite and highly oriented pyrolytic graphite have been published by Kawamura *et al* (1976, 1977) and Dillon *et al* (1978), respectively. At 298 K the Hall coefficient is similar in both single crystal and highly oriented pyrolytic graphite and shows very little dependence on the magnetic field. At 77 K the single crystal value is higher for fields below 3000 G but is similar to the pyrolytic graphite value for higher fields. The field dependence of both types of graphite is similar at 4.2 K, but the pyrolytic value is much lower.

The effect on the Hall coefficient and magneto-resistance of varying the heat treatment temperature of highly oriented pyrocarbons is shown in Figs 6.8 and 6.9 for measurements at ambient temperature. It is notable that the magneto-resistance is negative in the less perfect materials, which indicates that the number of charge carriers is increased or that the scattering is reduced by the magnetic field.

There are numerous measurements of the Hall coefficient and magneto-resistance of polycrystalline graphite. An important point to note is the negative magneto-resistance at low heat treatment temperatures. For heat treatment temperatures below 2600 °C the magneto-resistance increases with temperature, whereas above 2800 °C it decreases as the temperature increases. A thorough review of magneto-resistance behaviour is given by Delhaes (1971).

The thermo-electric power of graphite is expected to give an indication of the effective sign and concentration of current carriers. There are a number of published measurements on natural crystals and Kish graphites, which are shown in Fig 6.10. The measurements by Takezawa *et al* (1972) were on Kish graphite parallel to the basal planes and showed complicated behaviour at low temperatures. There is a sharp negative dip at 35 K and a broad positive peak at 120 K. There is a change in sign from negative to positive at 65 K and from positive to negative at 235 K. Fig 6.10 also shows results obtained by Tamarin *et al* (1969), which exhibit a similar behaviour.

Measurements of thermo-electric power on highly oriented pyrolytic graphite have been reported by Spain *et al* (1967), De Combarieu *et al* (1973), Rasor (1955) and Klein (1964). The effects of heat treatment temperature, as measured by Klein (1962) parallel to the basal planes, are shown in Fig 6.11. Fig 6.12 shows measurements by Klein perpendicular to the basal planes. The effect of a magnetic field on the thermo-electric power was investigated by Sugihara *et al* (1972) who measured the power in the basal planes in a magnetic field parallel to the hexagonal axis of Kish graphite: they found that the depth of the minimum at 35 K increased rapidly with the magnetic field, reaching $-200 \mu\text{V} \cdot \text{K}^{-1}$ at a field of 6.8 kOe.

Graphite has a very high diamagnetic susceptibility in the hexagonal axis direction. Detailed measurements on a graphite crystal were reported by Ganguli and Krishnan (1941) and Poquet *et al* (1960). Ganguli and Krishnan showed that the temperature dependence was characteristic of the susceptibility of a free electron gas. The difference in susceptibility perpendicular and parallel to the basal planes is about $30 \times 10^{-6} \text{ emu} \cdot \text{g}^{-1}$ at liquid helium temperatures, decreasing at higher temperatures. The susceptibility parallel to the basal planes is independent of temperature and is about $-0.5 \times 10^{-6} \text{ emu} \cdot \text{g}^{-1}$. The difference between the susceptibilities measured parallel (χ_1) and perpendicular (χ_2) to the basal planes was given by Poquet *et al* as

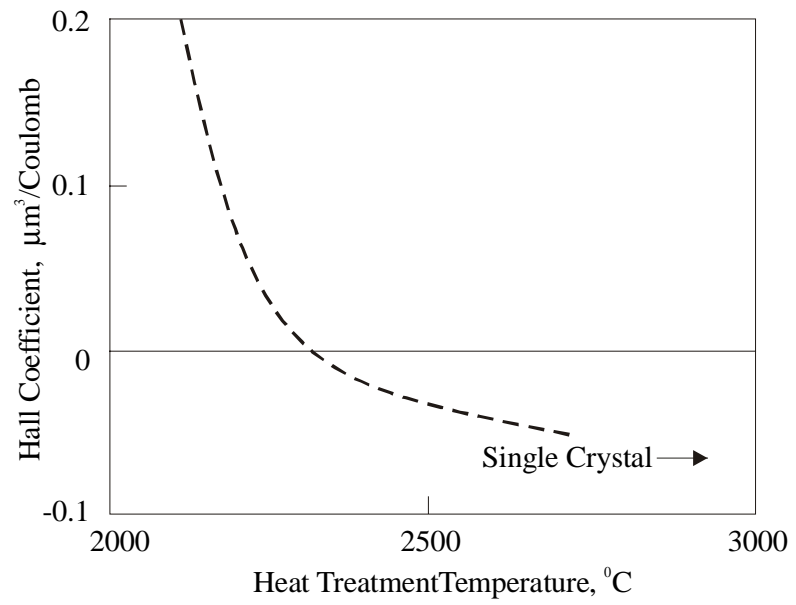


Figure 6.8 Hall coefficient at room temperature in pyrolytic carbons after heat treatment to various temperatures

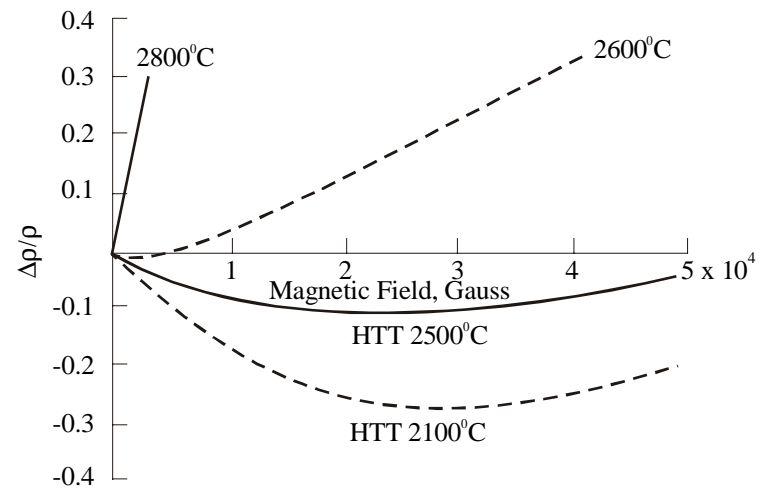


Figure 6.9 Field dependence of magneto-resistance in pyrolytic carbon after heat treatment to various temperatures

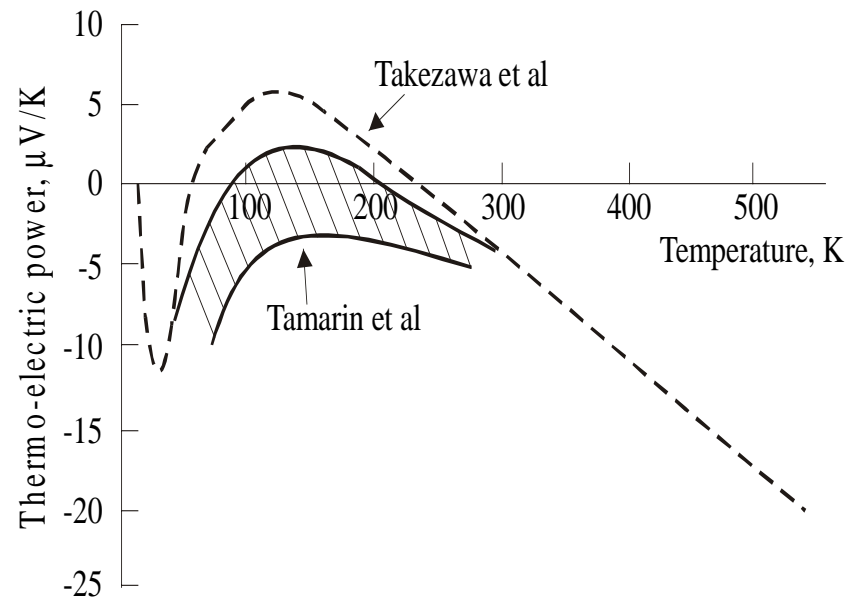


Figure 6.10 Thermo-electric power measurements on very perfect graphites

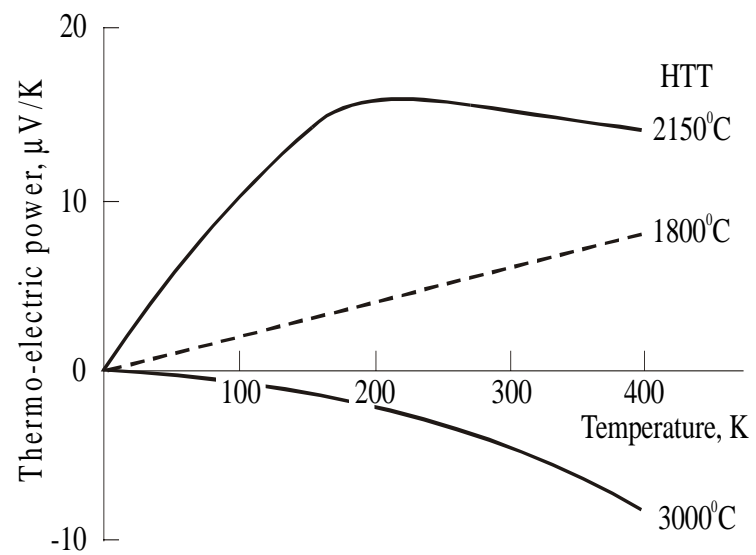


Figure 6.11 Thermo-electric power measurements on highly oriented pyrolytic graphite, parallel to basal planes

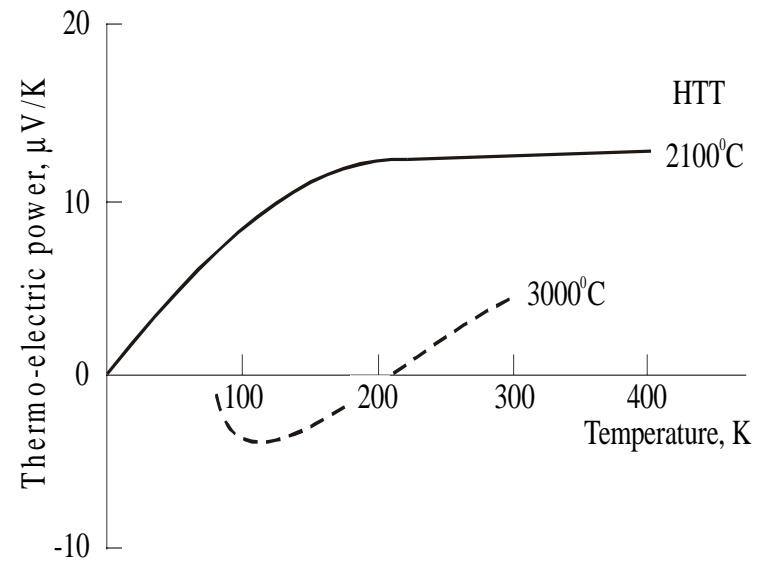


Figure 6.12 Thermo-electric power measurements on highly oriented pyrolytic graphite, perpendicular to basal planes

$$\chi_1 - \chi_2 = \left\{ 1.3 + 28.5 \left(1 - \exp \left| -\frac{330}{T} \right| \right) \right\} \times 10^{-6} \quad \text{emu.g}^{-1} \quad (6.8)$$

with average susceptibility

$$\bar{\chi} = \frac{\chi_1 + \chi_2}{3} = -7.2 \times 10^{-6} \quad \text{emu.g}^{-1} \quad (6.9)$$

Several attempts were made to calculate the high magnitude of the susceptibility (Hove, 1955; McClure, 1956; and Haering and Wallace, 1957). Eventually McClure (1960) showed that it was possible to explain the high susceptibility using the band parameters obtained from his analysis of the oscillatory Hall constant and magnetic susceptibility. The high susceptibility arises from band to band transitions, brought about by the changes in the band energies near the zone boundaries. McClure calculated the dependence of the susceptibility on temperature and the Fermi surface level.

There have been numerous measurements of susceptibility on polycrystalline graphites and soft carbons heat treated to various temperatures, particularly by the French (Mazza *et al*, 1962; Mazza, 1964; Pacault and Gasparoux, 1967) and by Fishbach (1971). The French found that the temperature dependence of the average susceptibility of soft carbons could be represented by

$$\bar{\chi} = \frac{1}{3} K_0 \left[1 - \exp \left| -\frac{T_0}{T} \right| \right] \quad (6.10)$$

K_0 and T_0 are functions of the heat treatment temperature. Table VI.4 shows values obtained by Pacault *et al* (1960), who found that $T_0 = 3.8 \times 10^4/L_a$, to within 10%. The susceptibility changes with the degree of graphitisation, reaching a maximum of around $22 \times 10^{-6} \text{ emu.g}^{-1}$ and then decreasing to a constant value of around $20 \times 10^{-6} \text{ emu.g}^{-1}$ as the graphitisation temperature increases. Some room temperature measurements on pyrocarbon have shown total susceptibilities of up to 1.5 times the single crystal value, with a value of $35 \times 10^{-6} \text{ emu.g}^{-1}$ for turbostratic pyrocarbon with $L_a \sim 250 \times 10^{-8} \text{ cm}$ (Fishbach, 1971) and rhombohedral graphite (Gasparoux, 1965). The results indicate that the susceptibility is dependent on both the crystallite size and the stacking order.

TABLE 6.4. EFFECT OF HEAT TREATMENT TEMPERATURE ON SUSCEPTIBILITY PARAMETERS DIAMAGNETIC

Heat treatment temperature (°C)	K_0 ($\times 10^{-6} \text{ g}^{-1}$)	T_0 (K)
Single crystal	-28.5	338
2650	-24.9	330
2000	-23.3	365
1900	-17.3	450
1800	-13.6	510
1700	-9.6	570

1600	-6.2	750
1500	-2.2	1550

Graphite also has a paramagnetic susceptibility, which has been investigated by measurements of electron spin resonance. Castle (1953, 1954) observed a spin resonance line with a g -value of 2.008 and a line width of 200 Oe in highly purified Ceylon graphite powder. A spin concentration of 10^{-4} to 10^{-5} per atom was found, which was attributed to the charge carriers. Wagoner (1960) thoroughly studied the spin resonance of a graphite crystal using 3 cm microwaves and found g -values at room temperature of 2.0495 with the magnetic field parallel to the hexagonal axis and 2.0026 with the field perpendicular to the hexagonal axis. The dependence on orientation is given by

$$g = 2.0026 + 0.047 \cos^2 \theta \quad (6.11)$$

where θ is the angle between the field and the hexagonal axis. Line widths were only a few G. This anisotropy increases with decreasing temperature, with a value of 2.127 at 77 K for the field parallel to the hexagonal axis, with the perpendicular value unchanged. Wagoner showed that the temperature dependence and line shape were in agreement with the paramagnetic susceptibility being due to the charge carriers.

6.3 Irradiated Properties

The effect of irradiation on the electronic properties of graphite is similar at all irradiation temperatures, although higher doses are required to produce the same effect at higher temperatures. It introduces:

- (i) Scattering centres, reducing the charge carrier mobility.
- (ii) Traps for electrons.
- (iii) Additional electron spin resonance.

The earliest studies are summarised by Hove (1956). Polycrystalline nuclear graphites, such as KC and CSF, were irradiated with fast neutrons. The electrical resistivity increases by a factor of around three, then decreases slowly, later increasing slowly, with the fractional change being independent of the direction and the initial rate of increase of resistivity depending inversely on the irradiation temperature. The Hall coefficient rises from a small negative value to a positive peak which then decreases. The magneto-resistance falls rapidly to zero. The diamagnetic susceptibility falls and the spin resonance intensity increases. The thermo-electric power changes in a complex way. These measurements were compared with a theory containing two unknowns, the relaxation time τ and the degeneracy energy ΔE , based on the Wallace model of the energy band structure of graphite (Wallace, 1947a, 1947b). This theory gives:

Resistivity

$$\frac{\rho}{\rho_0} = \left| \frac{\tau_0}{\tau} \right| \frac{\{\ln 2 \cosh(\Delta E_0 / 2kT)\}}{\{\ln 2 \cosh(\Delta E / 2kT)\}} \quad (6.12)$$

Hall coefficient

$$R = \frac{9\pi}{16} \frac{a^2 d}{ek^2 T^2} \frac{\tanh(\Delta E / 2kT)}{\{\ln 2 \cosh(\Delta E / 2kT)\}^2} \quad (6.13)$$

Diamagnetism

$$\chi = C_2(T) \operatorname{sech}^2(\Delta E / 2kT) \quad (6.14)$$

Magneto-resistance

$$A = C_1(T) \frac{\tau^2 \operatorname{sech}^2(\Delta E / 2kT)}{\{\ln 2 \cosh(\Delta E / 2kT)\}} \quad (6.15)$$

Thermo-electric power

$$Q = \pm \frac{2k}{e} \left[\frac{\sum_{i=0}^{\infty} \frac{(-1)^i}{(i+1)^2} \phi \left| \frac{[i+1]|\Delta E|}{2kT} \right| - \left(\frac{\Delta E}{2kT} \right)^2 \tanh \left(\frac{|\Delta E|}{2kT} + \frac{|\Delta E|}{2kT} \right)}{\{\ln 2 \cosh(\Delta E / 2kT)\}} \right] \quad (6.16)$$

where

$$\phi(x) = 1 - \exp(-x) \left| 1 + x + \frac{x^2}{2} \right|$$

C_1 and C_2 are temperature-dependent parameters. Use of these equations as a ratio of initial to final properties allows the unknowns to be evaluated. It was also assumed that the electrons are trapped at a constant rate, dN_e/dt .

The relationship for the Hall coefficient was fitted to the data using equation (6.13). The results then completely determined the variation of diamagnetism. The relaxation time could then be obtained from equation (6.12) and the magneto-resistance determined. The same analysis was also performed on the observed annealing curves. It was found that the thermo-electric power was not quite consistent with the others, requiring a value of dN_e/dt 40% larger.

Whilst this analysis is satisfactory in many ways, it says nothing about which defects contribute to τ and dN_e/dt . Simple theories of scattering suggest that for scattering by interstitials and vacancies, τ is proportional to the density of states, and for scattering by boundaries and dislocations, τ is constant.

Austerman and Hove (1955) irradiated polycrystalline reactor graphite at 4 K with 1.25 MeV electrons and measured the change in electrical resistivity produced by the irradiation and changes which occurred during subsequent annealing. The annealing results are shown in

Fig 6.13. No annealing takes place below 80 K, but there is a sudden increase in the resistivity, peaking at 140 K, followed by a decrease. The decrease can be explained by reintegration of the interstitial atoms with the vacant lattice sites, and the increase by either an increase in the number of scattering centres or the release of electrons from electron traps.

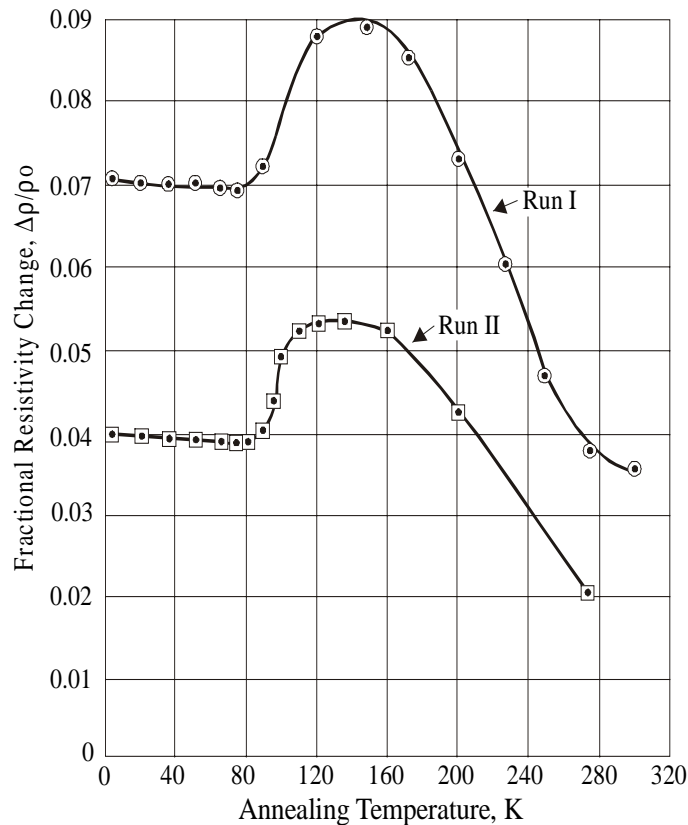


Figure 6.13 Effect of annealing on electrical resistivity of graphite irradiated at 4K

Polycrystalline graphite was irradiated at liquid nitrogen temperatures by 4 MeV electrons by Reynolds and Goggin (1960), followed by pulse annealing. They measured the changes in the electrical resistivity, the Hall coefficient and the magneto-resistivity and found that all three properties had the inverse annealing peak reported by Austerman and Hove. The results are summarised in Fig 6.14. The results were analysed using equations (6.2) - (6.4) to give the number of trapped electrons and the carrier mobilities. During irradiation the number of electron traps increases and the mobility of the carriers decreases. Similar changes are produced during the initial stages of annealing. It is believed (Simmons, 1965) that the effects are caused by a

dispersal of close vacancy-interstitial pairs under the influence of a short-range force in the vicinity of the vacancies. When an interstitial atom is far enough from a vacancy it can capture an electron, becoming a scattering centre and reducing the mobility of the electrons.

Changes in electrical resistivity under irradiation by protons and neutrons have a similar annealing behaviour to that for electron irradiations (Austerman, 1958; Hove, 1959). A similar annealing peak to that found by Austerman and Hove (1955) was reported by Klabunde *et al* (1961) on pyrolytic graphite irradiated with neutrons at liquid helium temperatures.

Studies on more perfect and highly oriented graphite were reported by Primak and Fuchs (1954, 1956). They irradiated flakes of natural graphite at 35-60 °C. A considerable increase in the electrical resistivity was observed both parallel and perpendicular to the basal planes. Parallel to the planes the change was around a factor of 10, which was about five times larger than for a polycrystal irradiated under the same conditions. If the irradiation damage is assumed to be identical in both samples, then the greater change in the natural graphite is due to the smaller value of the initial resistivity. Highly oriented pyrolytic graphites were irradiated with neutrons by Blackman *et al* (1961a), who showed that the resistance changes increased with the perfection. However, they also found that the resistivity parallel to the hexagonal axis decreased, contradicting the results of Primak and Fuchs (1954, 1956).

Primak and Fuchs also studied the effect of irradiation on the temperature coefficient of resistivity. In natural graphite the coefficient is positive, due to the variation of electron scattering with temperature. Radiation defects are a temperature-independent scattering, and hence reduce the temperature coefficient. Artificial graphites, however, have a negative coefficient, due to the variation of the number of electrons in the conduction band with temperature. Irradiation produces electron traps and increases the number of current carriers, and since this is independent of the temperature reduces the temperature coefficient. Comparing relative changes in electrical resistivity, ρ/ρ_0 , with relative changes in thermal resistivity, κ_0/κ , shows that they are roughly equal for low doses, but as the dose is increased ρ/ρ_0 saturates at ~ 3 , whereas κ_0/κ continues to increase, reaching values of 100. This shows that the saturation in resistivity is not due to a saturation of radiation defects. Fig 6.15 compares the effect of annealing on electrical and thermal resistivity changes on a sample which has received a very large dose. It can be seen that the annealing of the thermal resistivity is almost complete before the electrical resistivity begins to anneal.

Fig 6.16 shows the effect of irradiation on the Hall coefficient of polycrystalline graphite, determined by Kinchin (1954). The curves can be interpreted as being caused by the irradiation producing electron traps. The trapping of electrons results in an excess of positive charge carriers, causing the sign of the Hall coefficient to change from negative to positive, as indicated by equation (6.3). As the irradiation increases, the number of positive current carriers increases, and the Hall coefficient tends towards becoming inversely proportional to the number of current carriers. Blackman *et al* (1961a) studied the effect of irradiation on the Hall coefficient of

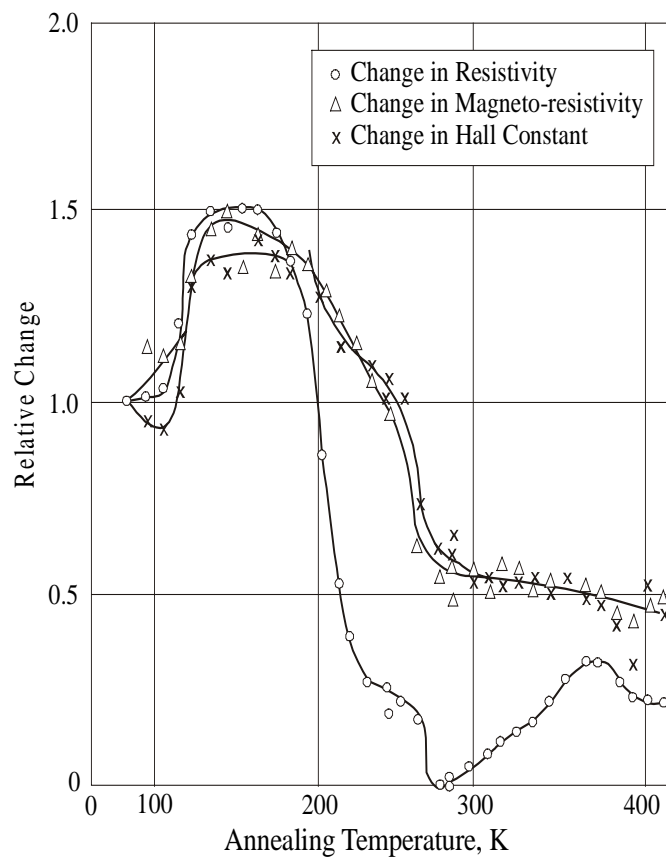


Figure 6.14 Effect of annealing on electrical properties of graphite irradiated at 77 K

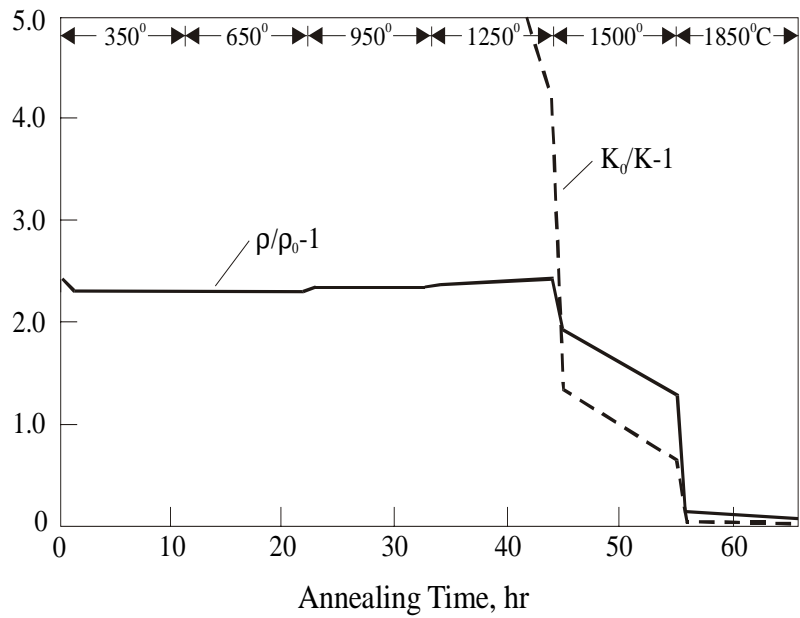


Figure 6.15 Effect of annealing on the resistivity of irradiated graphite

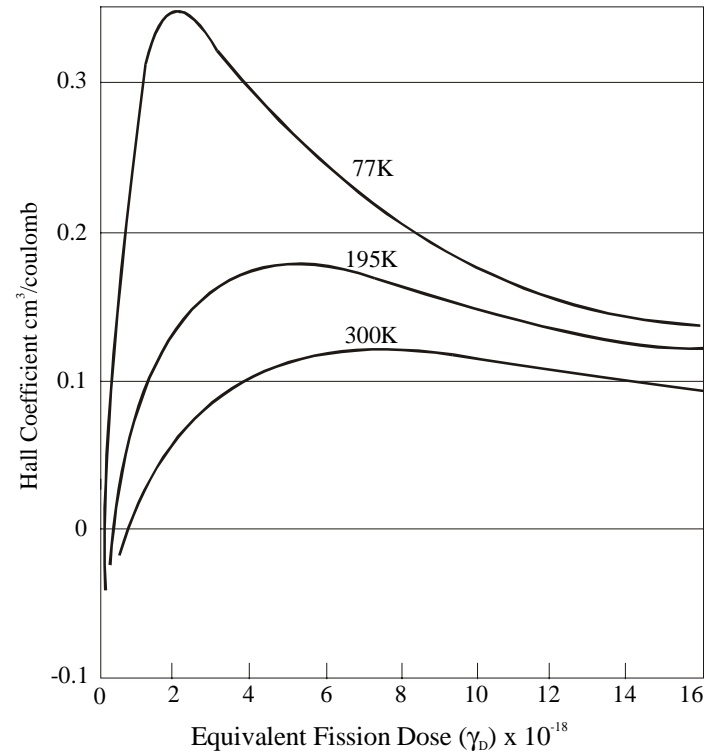


Figure 6.16 Effect of irradiation at 30°C on the Hall coefficient of polycrystalline graphite

pyrolytic graphites and found that the effect was very similar to polycrystalline graphite, although the changes were larger.

Kinchin (1954) also examined the effect of irradiation on magneto-resistivity; the results are shown in Fig 6.17. The reduction in magneto-resistance with increasing irradiation can be interpreted, using equation (6.4), as being due to a reduction in the carrier mobilities by scattering from radiation defects.

The effect of annealing on the Hall coefficient and magneto-resistivity was studied by Eatherly and by Hook (see Hove, 1956) using pulse annealing. Similar anomalies to those reported for the annealing effect on electrical resistivity were found.

The effect of irradiation on the thermo-electric power parallel to the basal planes for pyrolytic graphite was investigated by Blackman *et al* (1961b) and is to change the sign from negative to positive, although the negative dip in Fig 6.10 is still present. Blackman *et al* (1961a) also studied the effect of irradiation perpendicular to the basal planes and found that the initially slightly positive power ($\sim 4.0 \mu\text{V.K}^{-1}$) was considerably increased to $39 \mu\text{V.K}^{-1}$ after a small irradiation with neutrons. Annealing had little effect below temperatures of 2000°C , above which recovery occurred.

As mentioned earlier, graphite has a high diamagnetic susceptibility. This is considerably reduced by irradiation. Measurements obtained by Hove and McClelland (1957) are shown in Fig 6.18. Hove and McClelland interpreted the reduction in susceptibility as being due to a lowering of the energy of the Fermi surface due to electron trapping. McClelland (1952) described the effect of annealing on the diamagnetic susceptibility - the behaviour is generally the same as for electrical properties.

The effect of irradiation on electron spin resonance was investigated by Hennig and Smaller (1955) for polycrystalline graphite and by Müller (1961) and Wagoner (1961) for natural graphite crystals. Müller's work showed that the electron spin resonance in both unirradiated and irradiated graphite was due to the current carriers. Müller examined the effect of irradiation on the g -value and found that irradiation reduced the g -value, asymptotically approaching 2 at high doses. (Recall the values quoted earlier for unirradiated graphite of 2.0495 and 2.0026 for the magnetic field perpendicular and parallel to the basal planes, respectively.) This can be explained by irradiation induced electron traps lowering the Fermi level into the valence band.

It can be concluded that, whilst the understanding of the electronic properties of graphite is satisfactory with regard to the relationships between the different properties, there is difficulty identifying the defects responsible for particular effects.

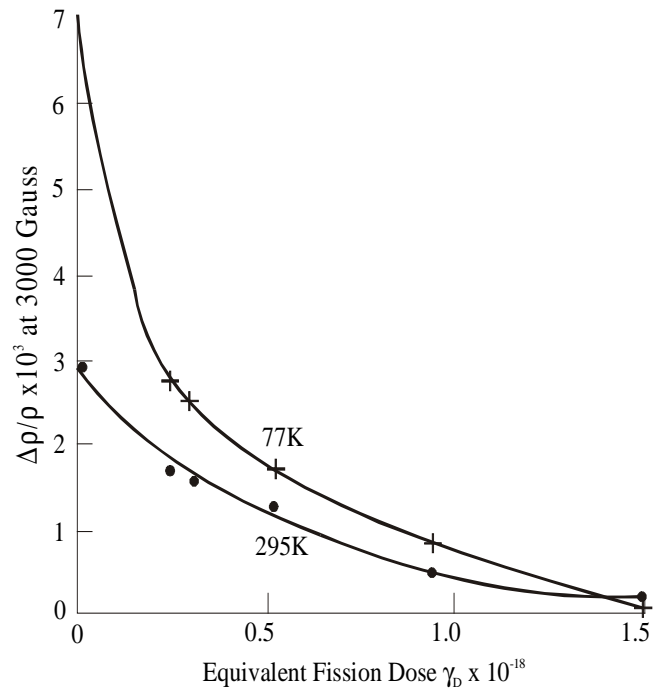


Figure 6.17 Effect of irradiation at 30°C on the magneto-resistivity of polycrystalline graphite

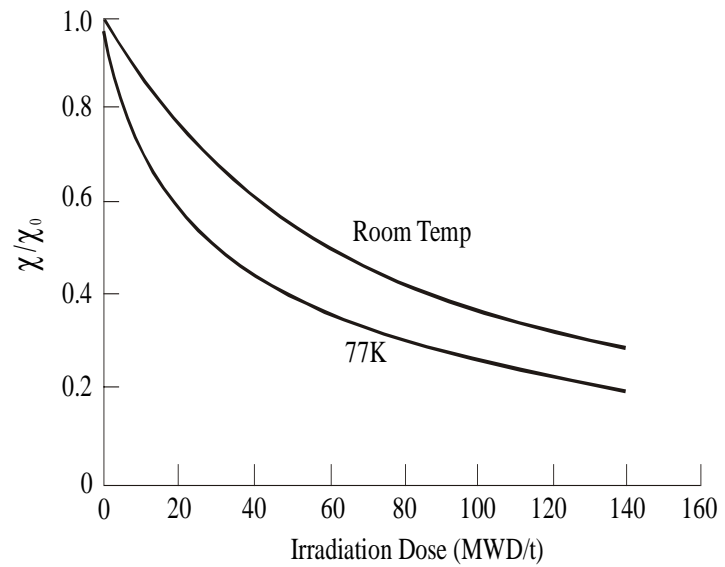


Figure 6.18 Effect of irradiation at 30°C on the diamagnetic susceptibility of AGOT-KC graphite

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