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Electrical transport properties of natural and synthetic graphite

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Resistivity and magnetoresistance measurements were performed on a series of natural graphite crystals and highly oriented pyrolytic graphite (HOPG) samples as a function of temperature from 4.2 K to 293 K using a contactless r.f. technique. Resistance ratios of the natural graphite between 4.2 K and 293 K ranged from about 30 to 49. Carrier mobility of natural graphite was observed to obey at $T^{-3/2}$ behaviour up to about 35 K. An anomalously high power dependence of μ versus T was observed below 35 K. A new model describing the dispersion of mobility of electrons and holes is presented which gives exact agreement with magnetoresistance results in the low field regime.

1. Introduction

Although there is a considerable body of work on the galvanometric properties of graphite, fundamental questions remain unresolved concerning the carrier concentration and mobility behaviour of carriers as a function of temperature. This is perature resistivity and magnetoresistance data available on good natural graphite crystals. At higher temperatures, where the ratio of basal plane conductivity to $\vec{c}$–axis conductivity is thought to be not greater than 10^4, standard bridge measurements are entirely satisfactory. However, at temperatures approaching 4.2 K, measurement problems may arise because of the increased anisotropy which is due to the uneven injection of current into the quasi two-dimensional planes of graphite and the inability of the current to then distribute itself evenly over reasonable bridge dimensions when the anisotropy is sufficiently large. This problem has been encountered in other highly anisotropic systems and has been overcome using a contactless eddy current technique [1–3]. Resistivity and magnetoresistance measurements have been performed (over temperatures ranging from 4.2 K to 293 K) in the low field regime on eight purified natural graphite samples and four HOPG samples. The use of the r.f. induction technique ensures correct galvanometric measurements over the full temperature range. The natural graphite crystals, having the dimensions of $5 \times 5 \times 0.025\ mm^3$, are among the best studied, as characterized by the measured resistance ratio between 4.2 K and 293 K of about 30 to about 50. The study of a number of crystals of such a high quality provides statistically useful data.

An experimental model of mobility dispersion is proposed which fits the magnetoresistance data as a function of temperature precisely in the low field regime. According to this model the electrons and the holes are each divided into two distinct groups, such that each group contributes one-half of the total conductivity. The ratios of the mobilities of each group are the same for electrons and holes at each temperature.

The mobility behaviour of the carriers as a function of temperature is discussed.

2. Experimental procedure

Specially purified samples of natural graphite were cut to $5 \times 5\ mm^2$ using an air-abrasive technique and cleaved to a thickness of about 0.025 cm. Resistivity and magnetoresistance measurements were performed on eight of these samples between 4.2 K and 293 K.

In order to overcome the difficulties encountered in using the conventional 4-point bridge method for measuring electrical transport properties on highly anisotropic materials, an r.f. induction technique was used for making electrical transport measurements. This technique measures conduc-

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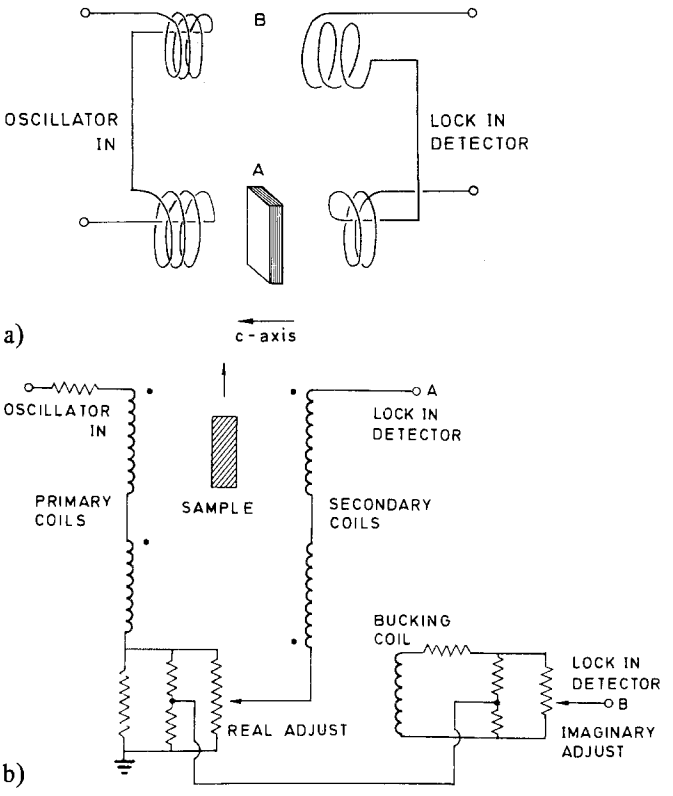

Figure 1 (a) Air–coil induction for resistivity versus temperature measurements. (b) Schematic of r.f. induction probe electronics.

tivity only along the basal plane and is therefore insensitive to the degree of anisotropy. The r.f. eddy current technique also does not require contacts. The nature of the graphite studied restricts the sample geometries to small thin plates, for which this technique is well suited. The technique used is a modification of a 100 kHz technique which employed a ferrite core at room temperature [1]. The frequency has now been changed to 1 kHz to overcome scatter due to a small skin depth at high frequencies, and problems with hysteresis loss, edge defects and variation of sample placement. Also, the ferrite core has been eliminated in order to permit low temperature measurements.

The electrical conductivity of a sample is determined by measuring the change in mutual inductance between a pair of coaxial coils upon introduction of the sample between the coils. A second identical pair of balance coils in series opposition are positioned parallel to the first as shown in Fig. 1. After nulling, insertion of the sample results in a net signal due only to the change in mutual inductance of the first pair of coils. A phase-sensitive detector is used to select the phase of the signal corresponding to the conductivity of the sample. According to the semi-empirical theory [1], the voltage change of the phase due to the resistive component of a sample in the non-skin limited range is given to first order by

$$\Delta V = \frac{kes^2}{\rho}$$

where e = thickness, s^2 = surface area, ρ = resistivity and k = a constant determined empirically. Numerous calibration data show this equation to be correct within the parameter ranges of interest and provide a value for k. The effect of varying the excitation frequency was studied to insure that transport data were obtained only in the non-skin depth limited regime.

An electromagnet with programmable sweep control was used to obtain magnetic fields up to 20 kG. Examination of the field between the pole pieces showed that the magnetic field was extremely homogenous over the volume of the sample. A calibrated Hall probe was used to measure the field. By sweeping on both sides of zero, it was possible to determine the zero very accurately and to measure fields to within a gauss.

Low temperature measurements were performed from 1.6 K to room temperature using standard cryogenic techniques. Fixed points were obtained using liquid nitrogen and helium baths. Tempera-

TABLE IA Resistivity, resistance ratios, $\langle H\rangle^*$, $t^\dagger$, $q^\ddagger$ mobility and carrier density, $n^\S$, of natural graphite at selected temperatures

Sample	ρ(293 K) ($\mu\Omega$ cm)	$\frac{\rho(293\,K)}{\rho(77\,K)}$	$\frac{\rho(293\,K)}{\rho(4.2\,K)}$	$\langle H\rangle$(293 K) (× 10^3 G)	$\langle H\rangle$(77 K) (× 10^3 G)	$\langle H\rangle$(4.2 K) (G)	t(293 K)	t(77 K)	t(4.2 K)
1	37.63	1.953	49.4	8.55	1.184	24.24	0.776	0.760	0.707
2	46.32	1.715	29.3	9.018	1.244	43.34	0.770	0.754	0.716
3	41.59	1.923	35.3	7.95	1.313	36.50	0.777	0.773	0.729
4	43.03	1.909	45.5	8.709	1.293	27.63	0.760	0.762	0.737
5	38.24	1.785	30.2	9.560	1.349	38.73	0.742	0.761	0.743
6	37.86	2.074	48.6	8.912	1.326	28.41	0.783	0.759	0.740
7	85.71¶	1.908	31.2	8.70	1.395	35.84	0.779	0.761	0.733
8	39.32	1.976	36.3	8.715	1.335	36.72	0.768	0.766	0.744

TABLE IB

Sample	$\bar{\mu}$(293 K) (× 10^4)	$\bar{\mu}$(77 K) (× 10^4)	$\bar{\mu}$(4.2 K) (× 10^6)	μ_1(293 K) (× 10^3)	μ_1(77 K) (× 10^4)	μ_1(4.2 K) (× 10^6)	μ_2(293 K) (× 10^4)	μ_2(77 K) (× 10^5)	μ_2(4.2 K) (× 10^6)
1	1.10	7.58	3.16	8.15	5.27	1.93	1.68	1.35	8.84
2	1.02	7.10	1.82	7.39	4.83	1.13	1.66	1.34	4.72
3	1.18	7.09	2.25	8.84	5.19	1.43	1.79	1.12	5.24
4	1.03	6.98	3.04	7.16	4.88	1.97	1.84	1.22	6.64
5	0.89	6.67	2.21	5.86	4.65	1.46	1.87	1.18	4.58
6	1.07	6.75	2.98	8.30	4.67	1.95	1.52	1.22	6.35
7	1.09	6.45	2.32	8.21	4.50	1.49	1.61	1.14	5.22
8	1.05	6.84	2.72	7.54	4.86	1.54	1.75	1.16	4.81

All multiplication factor units in this table are in $cm^2\ V^{-1}\ sec^{-1}$.

TABLE IC

Sample	q(293 K)	q(77 K)	q(4.2 K)	n(293 K) (× 10^{19} cm^{-3})	n(77 K) (× 10^{18} cm^{-3})	n(4.2 K) (× 10^{18} cm^{-3})
1	0.486	0.389	0.218	1.51	4.28	2.59
2	0.444	0.361	0.239	1.32	3.26	2.17
3	0.494	0.464	0.273	1.27	4.08	2.36
4	0.389	0.399	0.297	1.41	3.97	2.17
5	0.314	0.394	0.318	1.83	4.37	2.23
6	0.547	0.384	0.307	1.54	5.07	2.68
7	0.510	0.394	0.285	–	–	–
8	0.432	0.420	0.321	1.51	4.59	2.47

*$\langle H\rangle = H|\sigma_H/\sigma_0 = 1/2$

†$t = \sigma_H/\sigma_0|H = \langle H\rangle/2$

‡$q = \mu_1/\mu_2$

§$n = 1/\rho e\bar{\mu}$

¶ Anomalously high resistivity value is due to macroscopic cracks.

tures below 4.2 K and 77 K were obtained either by allowing the probe to warm slowly from 4.2 K, or by passing a steady flow of cold He gas through the sample space. A heater was used to elevate the probe temperature above the ambient value of 77 K.

3. Results and discussion

The room temperature basal-plane resistivity and the resistance ratios, $\rho(293\,K)/\rho(77\,K)$ and $\rho(293\,K)/\rho(4.2\,K)$, of natural graphite are shown on Table IA. The ratio between room temperature and 4.2 K varies from about 30 to about 50. Kinchin [4] has measured the resistivity along the basal plane of a Travancore natural graphite crystal and observed a resistance ratio of 12 between room temperature and 4.2 K Soule [5] observed maximum resistance ratios of 16.7 and 37.0 for purified natural graphite single crystals. These values also controst with HOPG, in which resistance ratios range typically from about 5 to about 20, and "recrystallized graphite", in which values of 4.38 and 13.3 are typical

TABLE IIA Resistivity, resistance ratios, $\langle H\rangle^*$, $t^\dagger$, $q^\ddagger$, mobility and carrier density, $n^\S$, of HOPG at selected temperatures

Sample	ρ(293 K) ($\mu\Omega$ cm)	$\frac{\rho(293\,K)}{\rho(77\,K)}$	$\frac{\rho(293\,K)}{\rho(4.2\,K)}$	$\langle H\rangle$(293 K) (kG)	$\langle H\rangle$(77 K) (kG)	$\langle H\rangle$(4.2 K) (G)	t(293 K)	t(77 K)	t(4.2 K)
1	44.20	1.048	2.53	12.590	2.379	626.5	0.718	0.762	0.732
2	38.65	1.747	15.29	8.954	1.796	96.17	0.768	0.760	0.718
3	40.79	1.772	13.63	8.610	1.585	78.56	0.781	0.765	0.727
4	43.95	1.434	3.27	10.500	2.355	639.2	0.797	0.769	0.736

TABLE IIB

Sample	$\bar{\mu}$(293 K) ($\times 10^3$)	$\bar{\mu}$(77 K) ($\times 10^4$)	$\bar{\mu}$(4.2 K) ($\times 10^5$)	μ_1(293 K) ($\times 10^3$)	μ_1(77 K) ($\times 10^4$)	μ_1(4.2 K) ($\times 10^5$)	μ_2(293 K) ($\times 10^4$)	μ_2(77 K) ($\times 10^4$)	μ_2(4.2 K) ($\times 10^5$)
1	6.30	3.80	1.32	3.92	2.66	0.849	1.61	6.65	3.01
2	9.34	4.99	8.25	6.03	3.46	5.13	2.07	8.95	21.10
3	11.00	5.75	10.38	8.44	4.07	6.58	1.60	9.77	24.60
4	9.45	3.91	1.31	8.40	2.81	0.848	1.11	6.42	2.89

All multiplication factor units in this table are in $cm^2\ V^{-1}\ sec^{-1}$.

TABLE IIC

Sample	q(293 K)	q(77 K)	q(4.2 K)	n(293 K) (cm^{-3})	n(77 K) (cm^{-3})	n(4.2 K) (cm^{-3})
1	0.243	0.400	0.282	2.24	3.90	2.71
2	0.292	0.387	0.243	1.73	5.66	3.00
3	0.528	0.417	0.267	1.39	4.72	2.01
4	0.778	0.438	0.294	1.50	5.22	3.55

*$\langle H\rangle = H|\sigma_H/\sigma_o = 1/2$

†$t = \sigma_H/\sigma_o|H = \langle H\rangle/2$

‡$q = \mu_1/\mu_2$

§$n = 1/\rho e\bar{\mu}$

[6]. The resistivity ratios of natural graphite, between room temperature and 77 K, shown in Table IA, range from 1.9 to 2.0. This compares to a range from about 0.8 to 1.7 for recrystalized graphite [6] and a value of about 1.8 for good HOPG [7] as shown in Table IIA.

The room temperature resistivity values range from 37.6 to about 46 $\mu\Omega$ cm, with corrections made for ideal graphite density. Sample number 7 is anomalously high because of large scale cracks and defects. A value of 41 $\mu\Omega$ cm was obtained by Soule [5] for a natural graphite sample. High quality samples of synthetic graphite also have room temperature values of resistivity ranging from 38 to 42 $\mu\Omega$ cm. Dillon *et al.* [8], using a d.c. technique with solder or silver epoxy contacts, obtained an absolute resistivity of 39.5 ± 0.5 $\mu\Omega$ cm at 298 K using the bridge method which agreed closely with 39.7 ± 0.5 $\mu\Omega$ cm using the Van der Pauw method.

A large degree of variation is not expected for high quality graphite samples, in spite of variations of crystallite size and number of defects because at this temperature, resistivity is dominated by thermal phonons. Room temperature resistivity and resistance ratios of HOPG are shown in Table IIA for comparison.

The resistivity as a function of temperature for sample number 6 was measured from 4.2 K to 300 K and is shown in Fig. 2. These results are in good agreement with Soule's measurements above 40 K [5]. The greater detail at lower temperatures shows the approach to a residual resistivity at around 10 K due to defect scattering. Spain *et al.* [6] have also presented data of resistivity normalized to room temperature for a large number of hot-pressed samples. The best of these approach rather closely the behaviour of the natural graphite curves although there is little data presented around 4.2 K. Kinchin observed, for a natural graphite sample, a variation of resistance ratio, $\rho(273\,K)/\rho(T)$, with temperature of 12 at 4.2 K.

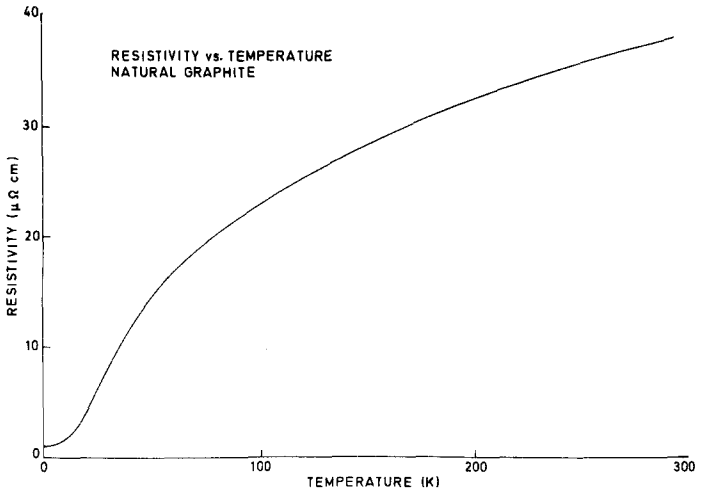

Figure 2 Resistivity versus temperature of natural graphite sample number 6.

This result and similar results for a series of polycrystalline samples were interpreted using the following formula for the mean free path

$$\frac{1}{l} = \frac{1}{l_b} + \frac{1}{l_{th}} \qquad (1)$$

where l = total carrier scattering mean free path (m.f.p.), l_b = boundary scattering m.f.p. $\approx$ diameter of the crystallites perpendicular to the c-axis and l_{th} = thermal m.f.p. and

$$\rho = 3.91 \times 10^{30} \frac{mv}{nl(1+a)} \mu\Omega \qquad (2)$$

where $a = \mu_h/\mu_e$ in which μ_h = hole mobility, μ_e = electron mobility, ρ = resistivity, and m, v, n and l are the electron effective mass, velocity, carrier density and mean free path respectively, all in CGS units. X-ray measurements were used to determine crystallite size and thus obtain a measure of l_b. As a result, Equation 1 was verified for several polycrystalline samples. Using the $n(1+a)$ values obtained from Hall measurements, values of mv as a function of temperature were determined from Equation 2. The low temperature value obtained was 2.3×10^{21} g cm sec^{-1} and at room temperature, the mean free path due to thermal scattering was 2350 Å.

Magnetoresistance data were obtained using intermediate fields ($\lesssim$ 20 kG) on all samples studied over a range of temperatures from 4.2 K to room temperature. It is useful to determine the drift mobility as a function of temperature, but in order to do this, a relationship must be found between the drift mobility and the magnetoresistance coefficient. A reasonable model is required to achieve this and, at the same time, a meaningful definition of average drift mobility should be derived. One problem is that the magnetoresistance coefficient, μ_M, is defined in the parabolic regime by $\Delta\rho/\rho = \mu_M^2 H^2$ and the magnetoresistance behaviour of graphite, even at fairly low fields, is not parabolic. Kinchin [4] observed for natural graphite a $H^{1.74}$ dependence of $\Delta\rho/\rho$ on fields up to 6 kG, with $\Delta\rho/\rho = 0.43$ at 5750 G. At 4.2 K, the field dependence was not as strong since, for example, $\Delta\rho/\rho\,(600\,\text{G}) = 24.6$ and $\Delta\rho/\rho\,(5750\,\text{G}) = 341$. Measurements performed on polycrystalline graphite between 77 K and 290 K showed a $\Delta\rho/\rho \alpha H^{1.74}$ dependence.

Soule has studied the Hall effect and magnetoresistance of purified natural graphite single crystals at 298 K, 77 K and 4.2 K. The structure of the Hall coefficient at low fields led Soule to propose minority carriers, which, although accounting for only a small fraction of the conductivity, could cause a large effect on the Hall constant, R, at very low fields. To have the desired effect, these holes (or electrons) must be very mobile. Soule's Hall results also show that μ_e/μ_h does not differ from 1 by more than about 20% for temperatures from 4.2 K to 298 K.

Above 77 K, the field dependence of the magnetoresistance was found to be $\Delta\rho/\rho_o = BH^{(1.78 \pm 0.03)}$. At 4.2 K, the field dependence was modified by saturation. In the moderate-field region, the majority carriers were thought to predominate in determining $\Delta\rho/\rho$ versus H^n behaviour.

Soule defined the mobility as follows

$$\Delta\rho/\rho_o H^2 = \mu^2 \qquad (3)$$

where $\mu^2 = \mu_e \mu_h$. Using this definition for average mobility and using values of $\Delta\rho/\rho_o$ at 3 kG, a

temperature dependence of $T^{-1.24}$ was obtained from 278 K to 312 K and a $T^{-1.2}$ behaviour was observed from room temperature to 77 K. This dependence was attributed to lattice scattering. At lower temperatures, the change of slope was attributed to an increased importance of impurity scattering.

Klein [9] has used Soule's definition of mobility to fit the following empirical formula

$$\frac{1}{\bar{\mu}} = \left(\frac{m^*v}{e \times 10^7}\right)\left(\frac{1}{L_p} + \frac{1}{L_b}\right) \quad (4)$$

where $m^*v = 2.4 \pm 0.8 \times 10^{-21}$ g cm sec^{-1} and L_p and L_b are the thermal and boundary mean free paths, respectively. Mobility was found to obey a $T^{-1.6}$ temperature behaviour above room temperature. Klein introduced a simple two band model in which the two bands are parabolic and overlap. On the assumption that the magnetoresistance coefficient equals the drift mobility, a good fit for the carrier density of the two band model is as follows

$$n = \left(\frac{16\pi m^*}{h^2 C_o}\right) kT \ln\left[1 + \exp\left(\frac{E_o}{2kT}\right)\right] \quad (5)$$

where $E_o = 0.01$ eV and $m^* = 0.0125\, m_o$.

Spain *et al.* [6], using the Soule definition of average mobility have observed a temperature dependence for pyrolytic graphite approaching $T^{-1.2}$. The mobility relation given by Equation 4 was also confirmed. The power dependence of $\Delta\rho/\rho_o$ with field was found to vary from $H^{1.7}$ to $H^{2.2}$ above 50 K. At 4.2 K, the change in the exponent from 2 at low fields to 1.2 at the highest field studied was attributed to saturation effects. More recently, Spain and Dillon [10] have examined the possibility of using Kohler's rule or other scaling relationships to determine the mobility. Kohler's rule is given by the following

$$\Delta\rho/\rho_o = F(\bar{\mu}H) \quad (6)$$

That is, a value for mobility, $\bar{\mu}$, can be found such that $\Delta\rho/\rho_o$ versus H falls on a universal curve and all of the dependence on temperature and purity is contained in $\bar{\mu} = \sqrt{(\mu_e \mu_h)}$. For a simple two band model

$$\frac{\Delta\rho}{\rho_o} = \frac{\mu^2 H^2 (1 + b^2) NPb/(N + bP)^2}{1 + [(N-P)/(N + bP)]^2 b^2 \mu^2 H^2} \quad (7)$$

wnere N and P are the electron and hole densities, respectively, of two slightly overlapping parabolic bands and $b = \mu_h/\mu_e$ is the ratio of hole mobility to electron mobility. Kohler's rule does not apply unless $N = P$ and Equation 7 reduces to $\Delta\rho/\rho_o = (\bar{\mu}H)^2$. A relaxed form of Kohler's rule applies if $(1 + b^2)NP/(N + bP)^2$ and $(N-P)^2 b/(N + bP)^2$ do not vary with temperature. In this case curves of $\Delta\rho/\rho_o$ versus H are scaled to an abscissa of $\bar{\mu}H$ rather than H and must be obtained self-consistently. For studies in the temperature range from 4.2 K to 293 K and for fairly low fields ($\mu H \leqslant 2$), the scaling of magnetoconductivity is equivalent to the scaling of the magnetoresistivity.

If

$$\bar{\mu}^2 \equiv \frac{(1 + b)^2 NPb}{(N + bP)^2} \mu^2$$

where $\mu = \mu_e$, then

$$\frac{\Delta\rho}{\rho} = \frac{\bar{\mu}^2 H^2}{1 + \alpha\mu^2 H^2} \quad (8)$$

and

$$\alpha = \frac{(N-P)^2 b}{NP(1 + b)^2} \quad (9)$$

Then, the quantity α encompasses all band structure effects, which for the high quality graphite studied here, will be only temperature dependent. In particular, α is related to the difference in the number of holes and electrons.

If the experimental data fits Equation 8, then the magnetoconductivity curves σ_H/σ_o versus H can be analysed in the following manner. From Equation 8, since $\Delta\rho/\rho_o = \sigma_o/\sigma_H - 1$, it follows that

$$\frac{\sigma_H}{\sigma_o} = \frac{1 + \alpha\bar{\mu}^2 H^2}{1 + (1 + \alpha)\bar{\mu}^2 H^2} \quad (10)$$

The values of α and $\bar{\mu}$ can be obtained from two experimental values of $\sigma_H/\sigma_o(H)$. Defining $\sigma_{\langle H\rangle} \equiv \frac{1}{2}\sigma_o$, then

$$\bar{\mu}^2 = \frac{1}{(1 - \alpha)\langle H\rangle^2} \quad (11)$$

The quantity $\langle H\rangle$ can be determined graphically from the σ_H/σ_o versus H curves. If the quantity $t \equiv \sigma_H/\sigma_o|H = \langle H\rangle/2$ is defined, then α can be determined since

$$\alpha = \frac{4 - 5t}{3(1 - t)} \quad (12)$$

The quantity t is determined operationally and so the two experimentally determined quantities, $\langle H\rangle$ and t, yield values of α and $\bar{\mu}$ that fit Equation 10. Experimentally determined values of $\langle H\rangle$ and t

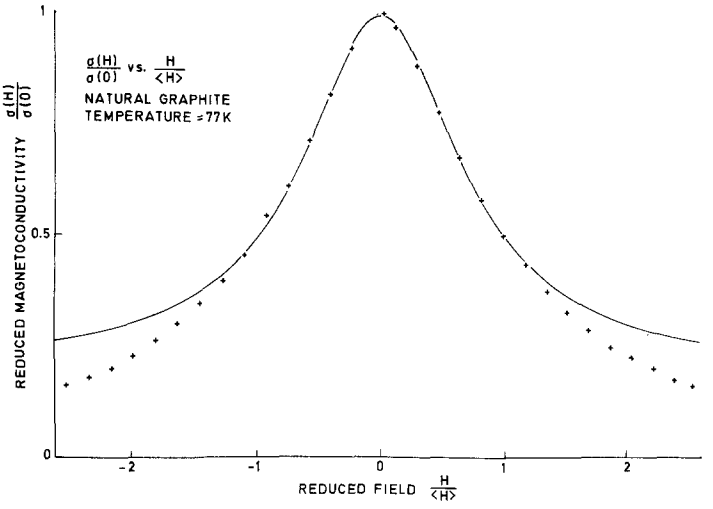

Figure 3 Experimental values of σ_H/σ_o versus $H/\langle H\rangle$ for sample number 8 with an attempted theoretical fit based on the simple two band model with no dispersion of electrons or holes.

for selected temperatures are presented in Table I.

The experimental values of reduced conductivity, σ_H/σ_o, have been plotted versus reduced field, $H/\langle H\rangle$, for sample number 8 at 77 K (the most suitable temperature for study) and is shown in Fig. 3. The scaled "theoretical" curve bases on the simple two band model described by Equation 10 gives very good agreement for fields up to $H/\langle H\rangle = 1$ but deviates from the experimental curve for $H/\langle H\rangle > 1$ and is 33% too high at $H/\langle H\rangle = 2$, as shown in Fig. 3. Spain concludes that the magnetoconductivity curves cannot be scaled, even in relaxed form, but recommends defining mobility as follows

$$\mu^* = 1/\langle H\rangle \tag{13}$$

where either $\sigma_{\langle H\rangle} = \frac{1}{2}\sigma_o$ or

$$(\Delta\rho/\rho_o)(\langle H\rangle) = 1 \tag{14}$$

This definition varies slightly from that given in Equation 11, but μ has only qualitative significance and either of these definitions based on scaling are improvements over Soule's definition [5].

A difficulty with the dispersionless two band approach is that since α differs from zero, according to Equation 9, $N \neq P$. However, N should be very close to P for $H \lessapprox \langle H\rangle$ within the temperature range studied. Dillon *et al.* have suggested that there is a dispersion of carrier mobilities and that either the dispersion of carrier mobilities along the zone edge or trigonal warping of constant energy surfaces may be responsible for this [8].

Another problem is that the value for the number of carriers obtained from galvanometric data lies below theoretical values, indicating that the $\bar{\mu}$ obtained from conductivity measurements may be too high. The two-band model may be inadequate and there may be corrections due to the variation of carrier effective mass and relaxation time along the vertical edge of the Brillouin zone. Also corrections may be required due to the non-degeneracy of carriers at non-zero temperatures.

Dillon *et al.* suggest a simple model that influences the value of $N + P$. An equal density of electrons and holes are assumed with each carrier type subdivided equally into two groups with mobilities differing by a factor of two.

An energy band relationship has been developed by Slonczewski and Weiss [11] which requires experiments to determine overlap parameters. Although uncertainties in band parameters exist, there is general agreement of free carrier density at low temperature. In addition to a model having an ellipsoidal Fermi surface and carriers with mobilities differing by a factor of two, Dillon *et al.* have considered a somewhat simplified Slonczewski and Weiss model using both a τ = constant and γ = constant scattering mechanism to account for mobility dispersion. These models do provide an explanation for the magnetoresistance behaviour in the low field region but do not yield a reasonable average carrier density. In fact, it appears that no reasonable variation of τ yields the correct result. Dillon *et al.* have suggested a model in which about half the electrons and holes have very short relaxation times compared to the remainder. Pietronero *et al.* have calculated the electrical conductivity of a charged layer of graphite within a tight binding framework for a single layer of graphite [12].

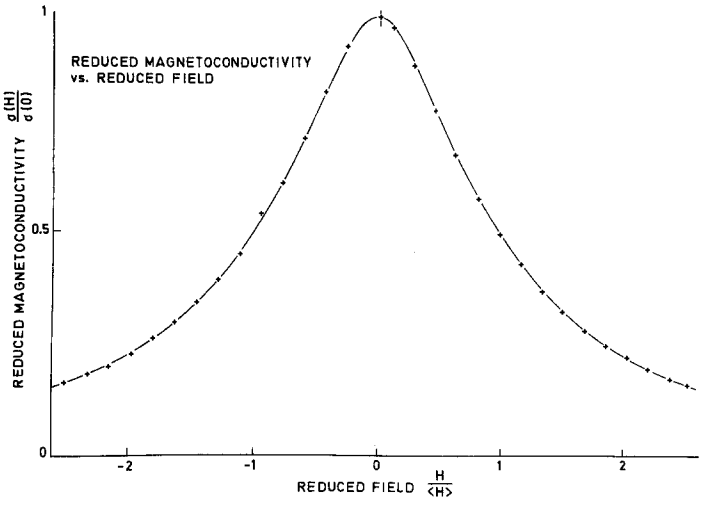

Figure 4 Experimental values of σ_H/σ_o versus $H/\langle H\rangle$ for sample number 8 with a theoretical fit based on a model having dispersion of electrons and holes.

An empirical model of electron and hole dispersion is presented in this work which provides a good theoretical fit for the experimental magnetoresistance data observed in the low field regime. A simple model is used in which the electrons and holes are each divided into two groups having different mobilities. The total magnetoconductivity is then given by

$$\sigma(H) = \frac{2\sigma_1}{1+\mu_1^2H^2} + \frac{2\sigma_2}{1+\mu_2^2H^2} \tag{15}$$

and the normalized magnetoconductivity is given by

$$\frac{\sigma_H}{\sigma_o} = \frac{1+(\mu_2^2 - \{\sigma_2/\sigma_1 + \sigma_2\}\{\mu_2^2 - \mu_1^2\})H^2}{1+(\mu_1^2+\mu_2^2)H^2+\mu_1^2\mu_2^2H^4} \tag{16}$$

Defining $H \equiv \langle H\rangle$ when $\sigma_H/\sigma_o = 1/2$, the value for $\langle H\rangle^2$ is given by

$$\langle H\rangle^2 = \frac{(1-2p)(\mu_2^2-\mu_1^2)}{2\mu_1^2\mu_2^2} + \frac{[(1-2p)^2(\mu_2^2-\mu_1^2)+4\mu_1^2\mu_2^2]^{1/2}}{2\mu_1^2\mu_2^2} \tag{17}$$

where $p \equiv \sigma_2/\sigma_1 + \sigma_2$ and p is a measure of the relative conductivity of the two kinds of carriers. The average mobility is as follows

$$\bar{\mu} = \frac{\sum_i \sigma_i}{\sum_i n_i} = \frac{\mu_1\mu_2}{(1-p)\mu_2 + p\mu_1} \tag{18}$$

If $q \equiv \mu_1/\mu_2$, then

$$\frac{\sigma_H}{\sigma_o}(x) = \frac{(1-p)}{1+x^2G(p,q)} + \frac{p}{1+x^2\dfrac{G(p,q)}{q^2}} \tag{19}$$

where $x \equiv H/\langle H\rangle$ and

$$G(p,q) = \mu_1^2\langle H\rangle^2 = q^2\mu_2^2\langle H\rangle^2 = \frac{(1-2p)(1-q^2)}{2} + \frac{[(1-2p)^2(1-q^2)^2+4q^2]^{1/2}}{2} \tag{20}$$

A good fit of this function for sample number 8 at 77 K is obtained with $p = 1/2$ and $q = 0.42$ and is shown in Fig. 4. A good fit was obtained for the sample at 4.2 K with parameters $p \approx 1/2, q = 0.31$. Since the fits are not very sensitive to p, if it is assumed, in general, that $p = 1/2$, then the value for q is given very simply in terms of t, the same experimental parameter discussed above in regard to the simple two-band model

$$(4t-2)q^2 + (17t-16)q + (4t-2) = 0 \tag{21}$$

and $\bar{\mu}$ reduces to the following

$$\bar{\mu} = \frac{2\sqrt{q}}{1+q}\frac{10^8}{\langle H\rangle} \tag{22}$$

in units of $cm^2\,V^{-1}\,sec^{-1}$.

Also

$$\mu_1 = \frac{\sqrt{q}}{\langle H\rangle} \tag{23}$$

$$\mu_2 = \frac{1}{\sqrt{q}\langle H\rangle} \tag{24}$$

so

$$\mu_1\mu_2 = \frac{1}{\langle H\rangle^2} \tag{25}$$

If it is assumed that $p = 1/2$ at all temperatures, then it is possible, using Equation 21, to calculate q from the values of t obtained graphically and discussed above.

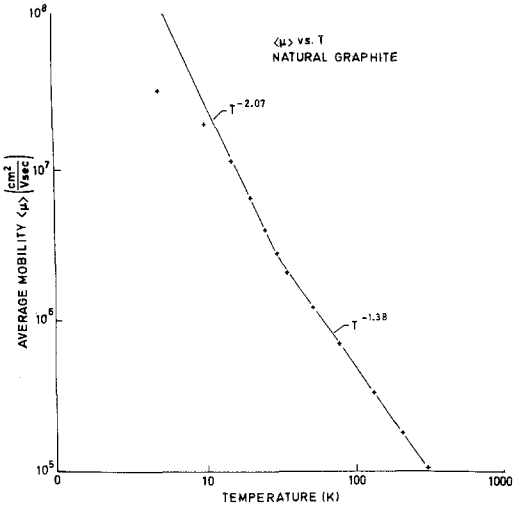

Figure 5 Log ⟨μ⟩ versus log T of natural graphite samples.

Experimentally determined values of ⟨*H*⟩ and *t*, as well as calculated values of *q*, $\bar{\mu}$, μ_1 and μ_2 are given for all natural graphite samples at selected temperatures in Table IA to C. The same quantities, determined for HOPG samples, are given in Table IIA to C. Using values of *t* determined in this way, it was found that μ_1 and μ_2 have the following behaviour as a function of temperature between 77 K and 293 K.

$$\mu_1 = \frac{A_1}{T^{n_1}}; \mu_2 = \frac{A_2}{T^{n_2}} \qquad (26)$$

where

$$A_1 = 2.04 \times 10^7 \text{ cm}^2 \text{ V}^{-1}\text{sec}^{-1}$$
$$A_2 = 7.2 \times 10^7 \text{ cm}^2 \text{ V}^{-1}\text{sec}^{-1}$$
$$n_1 = 1.39$$
$$n_2 = 1.47$$

These values of exponents are ≅ 1.5 and show that the mobilities of the carrier groups have roughly semi-conducting behaviour at temperatures as low as 77 K. The values of *average* mobility for all samples, $\langle\bar{\mu}\rangle = 2\mu_1\mu_2/\mu_1 + \mu_2$, were calculated and shown in Fig. 5. A low temperature change in slope and the anomalously high mobility exponent below this change has been observed elsewhere [13] and has not yet been explaind satisfactorily.

Since $n = 1/\rho e\mu$, the calculated values for average mobility and the experimental resistivity values were used to calculate carrier density as a function of temperature. The values of total carrier density, calculated in this manner, are provided at selected temperatures for natural graphite and HOPG in Tables I and II respectively. The total average carrier density at 4.2 K is 2.33×10^{18} cm^{-3}. The best empirical fit is as follows

$$N = \frac{N_o}{(\theta/T)} \ln(1 + e^{\theta/T}) \qquad (27)$$

where $\theta = \theta_o/(1 + T/\theta_1)$, $N_o = 2.33 \times 10^{18}$ cm^{-3}, $\theta_o = 46.5$ K and $\theta_1 = 860$ K, so the degeneracy temperature is roughly 47 K. The value of 2.33×10^{18} cm^{-3} is in good agreement with the values 2.30×10^{18} cm^{-3} and 2.41×10^{18} cm^{-3} obtained by Dillon *et al.* and is roughly half the total carrier density predicted by theory [8].

These results suggest that graphite is best characterized by comparing resistivity ratios between 4.2 K and room temperature and determining the mobility at these temperatures. The mobility, especially, gives an indication of the degree of defect or boundary scattering in pristine graphite.

4. Conclusion

Some of the highest resistance ratios, $\rho(293\text{ K})/\rho(4.2\text{ K})$, have been observed for natural graphite in this work. One value equalled 49 and all fell between 30 and 50. These high values were due both to the good quality of the purified natural graphite and to the r.f. induction technique which ensured that problems of poor current distribution due to high anisotropy were not present. A new model of mobility dispersion of electrons and holes was presented to explain low field galvanometric results. The variation of the mobility with temperature of each carrier was found to vary roughly as $T^{-3/2}$. The exponent of average carrier mobility was found to be anomalously high below 35 K.

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