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GALVANOMAGNETIC PROPERTIES OF LOW DENSITY FOILS FABRICATED FROM EXFOLIATED GRAPHITE

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Abstract—We investigated the influence of the over-oxidation process on the resistivity and structure of graphite intercalation compounds with sulphuric acid. Staging phenomena and amorphization were observed. The magnetoresistance and Hall effect at low temperature of low density carbon foils, prepared from exfoliated graphite with different structural defects were studied. The heat treatment temperature and time of oxidation appear to be the parameters which govern the degree of 3D or 2D ordering in the carbon foils. The weak localization phenomenon for 2D electronic systems is invoked to explain the negative magnetoresistance as well as the low temperature dependence of the resistivity of samples.

Keywords: A. inorganic compounds, B. chemical synthesis, D. electrical properties, D. transport properties

1. INTRODUCTION

The interest in the study of graphite intercalation compounds (GICs) and graphite-based materials arises from the quasi-two-dimensional structure and, hence, there is the possibility of the investigation of interesting physical phenomena. New possibilities for the understanding of the physical properties of GIC-based materials are opening by the fabrication of low density carbon foils. These foils have also a great future for different applications.

Weak localization is a general phenomenon which occurs in a disordered medium [1, 2]. The 2D weak localization in partially graphitic bulk carbons [3–5] and in carbon fibers [6] has been observed already. The influence of acceptor intercalation on the weak localization in carbon fibers means that, owing to intercalation, the concentration of holes increases and the absolute magnitude of the negative magnetoresistance decreases [7]. In the absence of spin-dependent scattering mechanisms, a negative magnetoresistance at low temperatures with a quadratic dependence on magnetic field B at low fields followed by a logarithmic dependence on B at higher fields and a logarithmic increase of the resistivity on temperature are the two main features of the weak localization effect for 2D systems [1, 2, 8]. It was interesting to investigate the features of weak localization in well characterized low density carbon foils with a different nature.

Here we report the results of a study on the temperature dependence of the conductivity, Hall effect and negative magnetoresistance of different types of carbon foils with different defects and structure.

2. EXPERIMENTAL

Highly oriented pyrolitic graphite annealed at $T > 3300$ K with an angle of disorientation near 1° along the c-axis was used. The first stage GIC of H_2SO_4 was synthesised by the liquid phase method in the presence of $K_2Cr_2O_7$. The process of intercalation was controlled *in situ* by X-ray diffraction and resistivity measurements. X-Ray analysis was carried out on a diffractometer Dron-2 with CuK_α irradiation, and a Ni filter. Two types of samples (A and B) were fabricated.

The process of sample fabrication is shown by the scheme in Fig. 1. Type A samples were prepared from the over-oxided first stage of H_2SO_4 GIC with different times of over-oxidation (Fig. 1.1). At first hydrolyzation of the samples was made (2). Then the material was dried at 110°C during 24 h (3). The exfoliation was carried out at $T = 900$°C (4). Samples for measurements were pressed from the exfoliated graphite. After fabricating the samples we did not carry out any heat treatment. The results of X-ray analyses (the crystalline disorientation angle α) and some parameters of the samples (the time of over-oxidation t, the angle of crystallite c-axis disorientation α, electron μ_e and hole μ_p mobility's and concentrations n, p) on which physical measurements

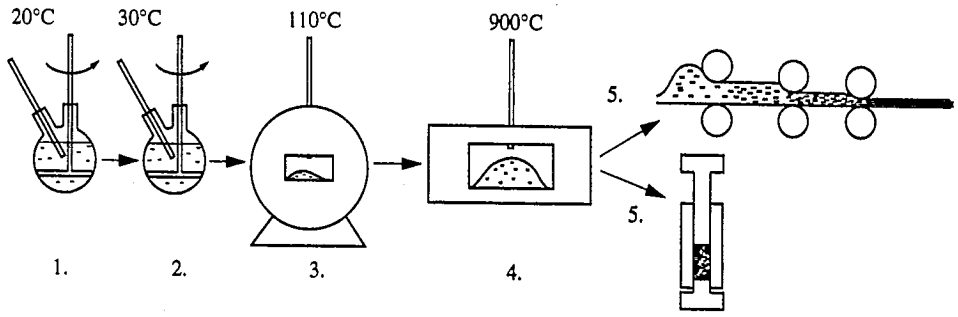

Fig. 1. Scheme of foil fabricating: (1) intercalation, (2) hydrolyzation, (3) drying, (4) exfoliation, (5) pressing or rolling.

were carried out are listed in Table 1. The value of α is almost independent of the oxidation time.

The second type of samples (B) was prepared by the same procedure, from first stage sulphuric acid GIC, without over-oxidation. The foil was fabricated by rolling of exfoliated graphite (5). We investigated B type samples without heat treatment and with HTT equal to 2100, 2450 and 2800°C in an inert atmosphere. The interlayer distance d_0 depends on the HTT. The density of foils and the value of d_0 are listed in Table 2.

3. RESULTS

At atmospheric pressure, the resistivity increases when the temperature decreases in both types of samples. For temperatures less than 1–2 K, the temperature dependence of resistivity saturates. A similar temperature dependence of the conductivity at super low temperatures was observed previously in carbon fibers [6, 7]. In Fig. 2, the temperature dependence of the resistivity is shown for type B samples N5 with different HTT.

For type A samples the Hall coefficient does not depend on temperature in the temperature range $0.35 < T < 50$ K, but the sign changes from negative to positive in low magnetic fields. As an example the magnetic field dependence of the Hall coefficient R_H is shown for sample N2 in Fig. 3. Making use of the two carrier band model and experimental magnetic field dependence of the Hall coefficient (points) we fitted the data to the theory (solid lines). Electron and hole mobilities μ_n, μ_p and concentrations n, p which we used as parameters were evaluated by this procedure and are listed in Table 1. The electron mobility is higher because the carrier scattering on crystallite boundaries plays the dominant role in foils and this scattering is more effective for holes. For samples B the same results were obtained only for samples without heat-treatment. For heat-treated samples the Hall coefficient has only a positive sign.

At low temperatures the negative magnetoresistance is observed for both types of samples, of which the absolute value depends on temperature. In Fig. 4, as an example, we plotted the dependence of the conductivity on magnetic field (points) of sample type B N5 at different temperatures. The amplitude of the negative magnetoresistance is comparable for the different samples and disappears when $T > 5$ K. The positive component of the magnetoresistance becomes more important for $B > 0.1$ T (Fig. 4).

4. DISCUSSION

The increase of the resistance when the temperature decreases and negative magnetoresistance with quadratic dependence on magnetic field in low fields and logarithmic dependence in high field may be described fully by the theory of quantum corrections to the conductivity for the 2D case [1, 2, 8, 9] which is valid for $kT \ll E_F$. The temperature dependence of the resistivity (Fig. 2) and the negative magnetoresistance (Fig. 4) give a possibility to determine some electron parameters of the samples, for example, the wave function phase relaxation time τ_ψ. The value of τ_ψ depends on electron–electron or electron–phonon relaxation. The relation between τ_ψ and characteristic

Table 1. Time of over-oxidation t, the angle of crystallite disorientation α, resistivity ρ, electron and hole mobilities μ_n, μ_p and concentrations n, p at $T = 4.2$ K for different samples A of foils

N	t (h)	α (deg)	ρ (4.2 K) (10^{-5} Ωm)	μ_n (m^2/V s)	μ_p (m^2/V s)	n (10^{21}(m^{-3}))	p (10^{23}(m^{-3}))
2	1	31.86	5.1	0.326	0.013	3.1	8.6
3	1.5	32.43	2.5	0.344	0.0014	0.84	176
5	4	32.79	1.8	0.235	0.0022	2.94	148
6	23	33.52	4.8	0.263	0.0014	0.37	91

Table 2. Interlayer distance d_0 and density d of foils B, fabricated from exfoliated graphite of H_2SO_4 first stage GIC

N	HTT	d_0 (Å) no heat tr.	d_0 (Å) 2100°C	d_0 (Å) 2450°C	d_0 (Å) 2800°C	d (g/cm^3)
1		3.363	3.371	3.367	3.363	0.70
4		3.365	3.364	3.361	3.361	1.15
5		3.364	3.365	3.361	3.357	1.30
6		3.367	3.365	3.362	3.360	0.85

values of the energy relaxation time or of the inelastic scattering relaxation time was calculated in Refs [2, 9]. The 2D behaviour of carriers in our sample may be ascribed to the turbostratic structure of crystallites which every sample has.

The temperature dependence of the conductivity of two dimensional disordered systems in zero magnetic field, due to the occurrence of both weak localization

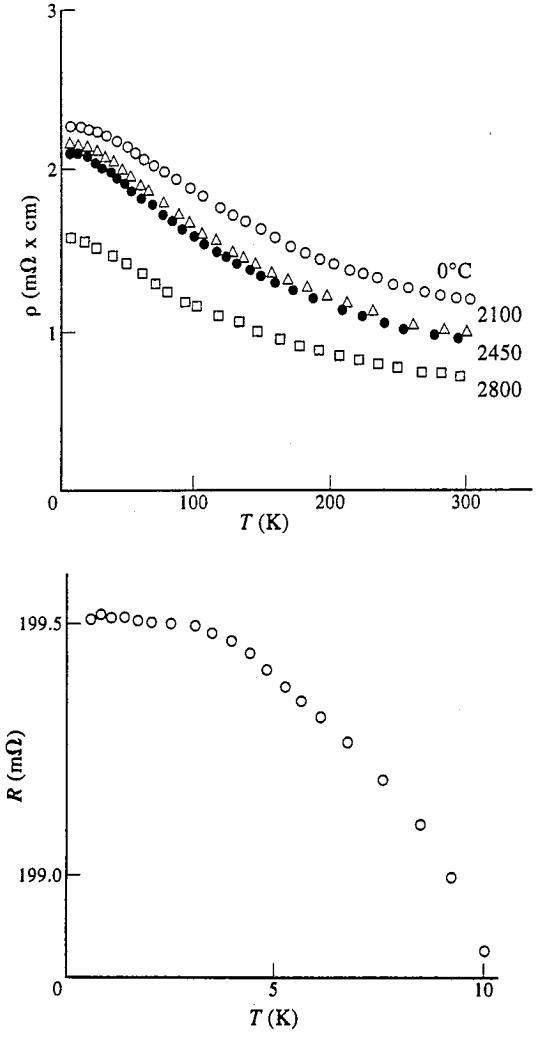

Fig. 2. Temperature dependence of the resistivity of the sample B N5 with different heat treatment temperature (a) and low temperature behavior of resistance (b) for the sample with HTT $T = 2800$°C.

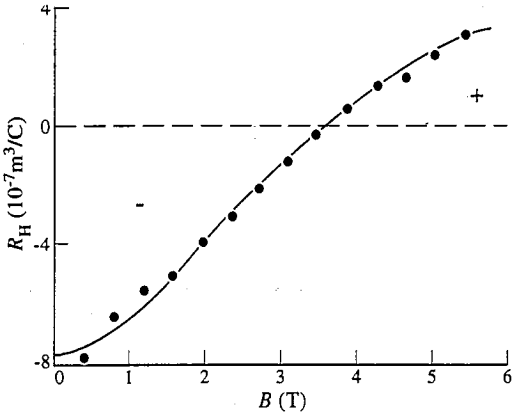

Fig. 3. Magnetic field dependence of the Hall coefficient at $T = 4.2$ K for sample A N2. Points are experimental data, solid lines are the theoretical calculations according to the two carrier model.

and electron–electron interaction effects is given by

$$\sigma(T_2) - \sigma(T_1) = [\beta + (1-\beta)p + \Lambda]\frac{e^2}{2\pi^2\hbar}\ln(T_2/T_1), \quad (1)$$

where Λ is a constant of the electron–electron interaction in a diffusion channel, p is the exponent in the temperature-dependence of the wave function phase relaxation time τ_ψ on T [2, 9]

$$\tau_\psi = aT^{-p}. \quad (2)$$

For electron–electron scattering in weakly disordered metals it was found that $p = d/2$ in contrast with the result $p = 2$ predicted in the clear limit whatever the dimensionality of the system. For electron–phonon scattering p ranges from 2 to 4 in the dirty limit at low temperatures. The coefficient β is determined by the scattering on superconducting fluctuations. The strength of the electron–electron interaction contribution is given by Λ, where Λ—which is a measure of the screening by other charge carries—has a value close to 1 in the weak screening limit.

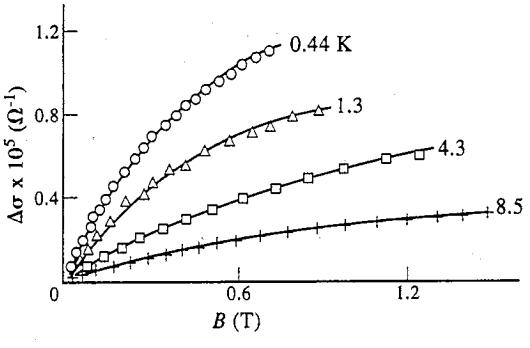

Fig. 4. Magnetoconductivity as a function of magnetic field for a sample B N5 with HTT $T = 2800$°C at different temperatures. Points are experimental data, solid lines are the theoretical calculations according to weak localization theory.

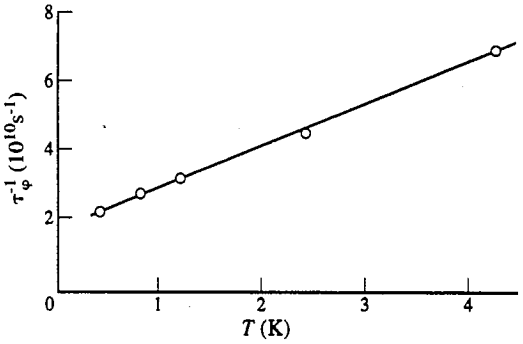

Fig. 5. Temperature dependence of the wave function phase relaxation time τ_ψ^{-1} for a sample B N6 without heat treatment.

The correction to the sheet conductivity σ in a magnetic field B has the form [2]

$$\sigma(B) - \sigma(0) = \frac{e^2}{2\pi^2\hbar}(1-\beta)f_2\left(\frac{4DeB\tau_\psi}{\hbar}\right). \quad (3)$$

Here the function f_2 describes the localization and D is the diffusion coefficient of the carriers. The function $f_2(x) \approx x^2/24$ for $x \ll 1$ and $f_2(x) \approx \ln(x)$ for $x \gg 1$. According to Ref. [2], the dependence (3) is valid if the magnetic length $l_h = (\hbar c/eH)^{1/2}$ is more than the mean free path 1. For investigating samples with low mobilities it is possible to use formula (3) in our magnetic fields. A magnetic field suppresses the weak localization. The magnetic field dependence of Λ is important only for $g\mu_B B/kT > 1$ (μ_B is the Bohr magneton) and in our case at low temperatures we may neglect this dependence. In principal it is possible to separate the weak localization and the electron–electron interaction as was done for 2D electrons at super low temperature in Ref. [10]. We may analyze experimental data without corrections which describe the electron–electron interaction [2]. Making use of the formula

$$D = \mu E_f/e = \pi\hbar^2/e^2m^*\rho, \quad (4)$$

we calculated the diffusion coefficient. Here ρ is the sheet resistivity of a sample, m^* is the effective mass.

Using τ_ψ as a parameter we may fit theoretical curves to experimental negative magnetoresistance. In Fig. 4 we plot the calculated dependence $\Delta\sigma = \sigma(B) - \sigma(0)$ using solid lines. From this fitting we evaluated the τ_ψ dependence on temperature for different samples. The dependence $\tau_\psi(T)$ does not obey the power law (2) with any reasonable p. If we suppose that $1/\tau_\psi = 1/\tau^* + 1/\tau$, where τ does not depend on the temperature, in this case the temperature dependence of τ^* may be described by eqn (2) with $p \approx 1$. In Fig. 5, as an example, the temperature dependence of $1/\tau_\psi$ is shown for sample B N6 (without heat-treatment). Moreover, in addition to the negative magnetoresistance due to a weak localization effect, the Lorentz-type quadratic positive magnetoresistance was taken into account in performing a detailed quantitative analysis of the data obtained in our samples. Lorentz magnetoresistance is important in magnetic fields where $B > 0.1$ T. Since the mosaic spread cannot be neglected in our samples, the observed magnetoresistance is not directly given by relation (3). We assumed that only the magnetic field component perpendicular to the graphite layer produces the negative magnetoresistance. The apparent magnetoresistance $\Delta\rho/\rho_0$ is given by

$$\Delta\rho/\rho = (1/\pi)\int_{-\pi/2}^{\pi/2} \times f(\theta)\{\Delta\rho(B^*\cos\theta, T)/\rho(0, T)\}\,d\theta, \quad (5)$$

where θ is the angle between the normal to a graphite layer and the magnetic field direction. The weight function $f(\theta)$ was taken in the gaussian form with the standard deviation.

5. CONCLUSION

It is shown that the time of the over-oxidation has almost no effect on the angle of disorientation of crystallites in foils. There are two types of carriers in the foils and the electron mobility is higher than the hole mobility in the samples without heat treatment. In heat-treated samples, the Hall coefficient is always positive. The quantum corrections to conductivity for the 2D case play the dominant role for the explanation of galvanomagnetic properties of low density carbon foils. The main features of low-temperature galvanomagnetic properties of foils as compared with turbostratic bulk carbon are: (i) a saturation of the temperature dependence of the resistivity for temperatures down to 0.3 K; (ii) the heat treatment changes the interlayer distance but negative magnetoresistance is observed in samples even with the HTT $T = 2800$°C; (iii) the temperature dependence of τ_ψ obeys a power law (2) with exponent $p \approx 1$ if we suppose a temperature-independent contribution in τ_ψ.

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