

Electrical Conductivity of Fine Crystalline Graphite under the Influence of Hydrostatic Pressure

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It was investigated the influence of hydrostatic pressure on the electrical conductivity of fine crystalline graphite in the temperature range of (77-293) K. It was revealed that the reduction of electrical resistivity in specimens of fine crystalline anisotropic graphite under the hydrostatic pressure action is due to increasing overlap between the valence and conduction bands that leads to an increase in the concentration of free charge carriers. The change of the overlap between the valence and conduction bands was estimated. It is shown that a decrease in the distance between the graphite layers under pressure is an irreversible process: when load is removed, the electrical resistance increases slightly, but does not acquire the initial value.

Keywords: Fine crystalline pyrolytic graphite, Mechanical load, Electrical conductivity, Fermi energy.

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1. INTRODUCTION

The production of conductive composite materials by using as a filler nanocarbon structures, such as various types of ultrafine graphite, carbon fibers, expanded graphite, fullerenes, carbon nanotubes, nanographite, is one of the priority directions of modern materials science. Composite materials with nanocarbon filler have a number of advantages compared with "traditional" composite materials due to low density, machinability (the ability to be formed and to manufacture products of any form), corrosion resistance, ecological cleanliness and low cost. A special problem when producing composite materials with nanocarbon filler is to maintain the stability of their electrophysical properties under the action of external, in particular, mechanical loads.

As known, the electrical resistance of the composites with nanocarbon filler is considered as the sum of the electrical resistances of the nanocarbon filler particles R_{sp} and contact electrical resistances between the filler particles R_k : $R = R_{sp} + R_k$ [1]. Obviously, the parameters R_{sp} and R_k will vary with the mechanical load that leads to a change in the total electrical resistance of the composite samples. The change in the sample electrical resistance in compression is the result of several competing processes. When the samples are compressed in a limited volume, there is the strain of the samples and their microdestruction that causes an increase in the electrical resistance of individual graphite particles R_{sp} . The electrical resistance of the composite significantly depends on the orientation of the graphite particles in the sample, since the graphite particles themselves are characterized by high anisotropy of the electrical resistance, for example, in monocrystalline graphite the value of the anisotropy of the electrical resistance ρ_d/ρ_a reaches the value of 10^3-10^5 [1]. Under the action of external mechanical load, the change in the contact resistance between the graphite filler particles is evident. Thus, the establishment of the regularities of changing the electrical conductivity of nanocarbon filler particles under pressure is a very topical task in view of the common use of such a filler in composite materials. The literature contains a number of articles [2-4], in which the mechanisms of ele-

ctrical conductivity of carbon nanotubes and other nano-scale carbon structures under the hydrostatic pressure action are investigated. However, the data on studying the dependences of electrical resistance of layered graphite nanostructures (nano- and expanded graphite) on external pressure are almost absent in the literature.

The aim of the work was to establish the regularities of changing the electrical conductivity of fine crystalline graphite under the action of hydrostatic pressure.

2. EXPERIMENTAL RESULTS OF STUDYING THE ELECTRICAL RESISTANCE OF FINE CRYSTALLINE GRAPHITE UNDER THE HYDROSTATIC PRESSURE ACTION

A bulk sample of fine crystalline pyrolytic graphite (FCPG) was chosen for the investigations, since the parameters of its structure (distance between the neighboring graphite layers $d_{002} = 0.340$ nm, crystallite size along the graphite planes $L_b = 30$ nm, parameter of the preferred orientation of crystallites $p = 10^3$) are close to the parameters of the nanographite structure.

We performed the studies of the electrical resistance (ρ_a) along the graphite planes in the samples of fine crystalline anisotropic graphite in the temperature range of (77-293)°K and under the hydrostatic pressure action up to 1.2 GPa.

In Fig. 1 we illustrate the temperature dependence of the electrical resistance $\rho_a(T)$ for FCPG.

As seen from the figure, in the temperature range of (77-293)°K a linear increase in the resistivity is observed with decreasing temperature: the value of ρ_a varies from $7.4 \cdot 10^{-6}$ Ohm·m at 293°K to $9.9 \cdot 10^{-6}$ Ohm·m at 77°K. Thus, FCPG is characterized by a negative temperature coefficient of resistance, the value of which is equal to $\sigma = 1.6 \cdot 10^{-3}$ K⁻¹.

In Fig. 2 we present the dependence of the electrical resistivity along the graphite planes on the pressure at room temperature for two FCPG samples: sample No 1 was slowly loaded to the pressure of 1.2 GPa (curve 1), and then was unloaded to zero pressure (curve 2). Sample No 2 was rapidly loaded and then unloaded to zero pressure (see curve 3).

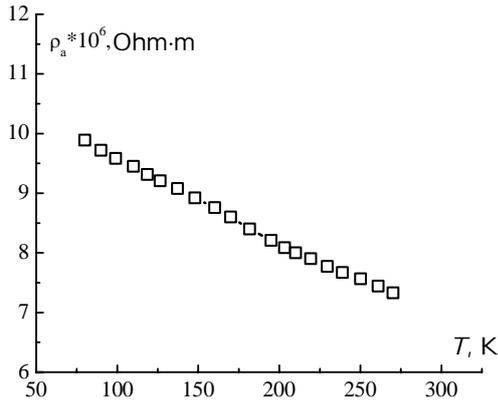


Fig. 1 – Dependence $\rho_a(T)$ for the samples of fine crystalline anisotropic graphite in the absence of the load

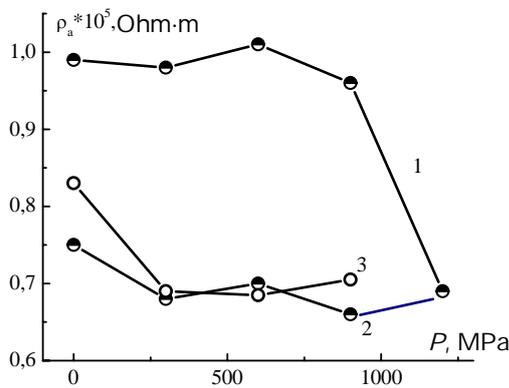


Fig. 2 – Dependence $\rho_a(p)$ for the samples of fine crystalline anisotropic graphite at room temperature: sample No 1, slow loading (1), unloading (2), sample No 2, unloading after fast loading (3)

As seen from the figure, when the sample is loaded to the pressure of 0.9 GPa, the resistivity along the graphite planes almost does not depend on pressure; a sharp decrease in ρ_a by approximately 30 % is observed with increasing pressure to 1.2 GPa. When the load is removed, a certain hysteresis is observed in the dependence $\rho_a(p)$: the value of ρ_a almost does not vary with decreasing pressure to 0.3 GPa; when the pressure is removed, the resistance slightly increases, but does not reach the initial value. Curves 2 and 3 practically coincide that indicates a good reproducibility of the results.

In Fig. 3 we present the temperature dependence of the resistivity ρ_a along the graphite planes for FCPG at constant pressure of 1.2 GPa (cooling and heating) and after removal of the load (heating).

As seen from the figure, when loading up to 1.2 GPa at room temperature, the resistivity in the FCPG sample decreases that coincides with the data shown in Fig. 2. With decreasing temperature in the loaded sample, the resistance decreases, as well as in the unloaded sample, almost linearly. However, the temperature coefficient of resistance in the temperature range from 300 K to 200 K is equal to $\sigma_{300-200} \sim 0.004 \text{ K}^{-1}$. And when the sample is cooled below 200 K, σ_{200-77} decreases in absolute value to 0.002 K^{-1} . Both values of the temperature coefficient of resistance for the loaded sample are larger than for the unloaded sample. Thus, the loaded FCPG sample is characterized by a more pronounced temperature dependence of the resistance. When the sample is heated under pressure, the effect of changing the temperature coefficient of

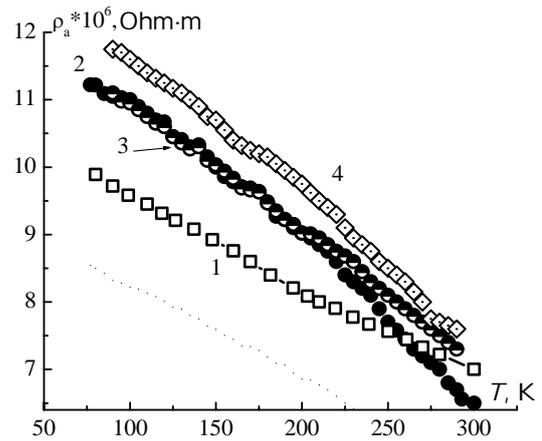


Fig. 3 – Dependence $\rho_a(T)$ for the samples of fine crystalline anisotropic graphite at constant pressure: without load (1), at constant pressure $p = 1.2 \text{ GPa}$, cooling (2), heating (3), after removal of the load (4)

electrical resistance at the temperature of 200 K is very weakly expressed. When the load is removed, the value of the resistance ρ_a slightly increases. With decreasing temperature for the unloaded FCPG sample, the effect of changing the temperature coefficient of resistance at the temperature of 200 K is also observed, although it is expressed not as bright as for the loaded sample.

3. ELECTRICAL CONDUCTIVITY MECHANISMS OF FINE CRYSTALLINE GRAPHITE UNDER THE HYDROSTATIC PRESSURE ACTION

As shown in a number of works [5-7], the preferential scattering of charge carriers at the grain boundaries determines the magnitude and behavior of the temperature dependence of the electrical resistance along the graphite planes for fine crystalline graphite materials. As known, graphite materials are characterized by very high Debye temperature (2300 °C) that causes a slight, compared with metals, scattering of current carriers on phonons in a wide temperature range [7]. The free path of charge carriers at phonon scattering L_{ph} for graphite materials is approximately equal to $\sim 10^{-7} \text{ m}$ at room temperature. The crystallite sizes for fine crystalline graphite materials are equal to $\sim 10^{-8} \text{ m}$, and therefore, the contribution of scattering at the grain boundaries will be the preferential one.

In the framework of the model of electrical conductivity of materials, which have two types of charge carriers, taking into account the preferential scattering of charge carriers at the grain boundaries, the expression for the material resistivity can be written as

$$\rho = \left(e^2 \left(\frac{n}{m_n^* v_n} + \frac{p}{m_p^* v_p} \right) \right)^{-1} / L_b, \quad (1)$$

where n, p are the concentrations of electrons and holes, respectively; $m_{n,p}^*$ and $v_{n,p}$ are the effective masses and velocities at the Fermi surface, respectively, of electrons and holes; L_b is the free path in scattering of charge carriers at the grain boundaries. Assuming that the effective free path of electrons and holes is the same, for fine crystalline graphite materials the ratio $L_b \ll L_{pur}, L_d, L_{ph}$ holds, where L_{pur} is the free path of charge carriers in

scattering by impurities, L_d – in scattering by defects. A drop in the electrical resistance with increasing temperature above the liquid nitrogen temperature is caused by an increase in the concentration of current carriers with increasing temperature, since their scattering at the grain boundaries is a temperature independent process.

As shown in a number of papers, application of hydrostatic pressure along the C -axis leads to a decrease in the distance between graphite layers [8-10]. The value of the relative compressibility along the C -axis for graphite is equal to $\beta = \Delta C / C \Delta p \sim 2 \cdot 10^{-11} \text{ Pa}^{-1}$, where ΔC is the re-sizing along the C -axis, C is the initial size along the C -axis, and Δp is the applied pressure [10]. Thus, application of pressure of $\sim 1.2 \text{ GPa}$ along the C -axis of the FCPG sample leads to a decrease in the distance between graphite layers by the value of $\sim 0.008 \text{ nm}$. That is, the interplanar distance decreases from $d_{002} = 0.340 \text{ nm}$ to the value $d_{002} = 0.332 \text{ nm}$, which is somewhat less than the value of the interplanar distance in highly oriented pyrolytic graphite (HOPG). Such a decrease in the interplanar distance in FCPG when applying hydrostatic pressure, obviously, leads to an increase in the overlap between the valence and conduction bands, which for FCPG is equal to $\Delta E \sim 0.002 \text{ eV}$.

As known, the electronic spectrum of graphite is described within the Slonczewski-Weiss-McClure model [11], according to which the dispersion law can be more simply written as

$$E_{\pm} = 2\gamma_2 \cos^2 \xi \pm \hbar^2 k^2 / 2m^*(\xi), \quad (2)$$

$$2m^*(\xi) = \frac{4}{3} \cdot (\hbar / a_0)^2 \cdot (\gamma_1 / \gamma_0^2) \cos \xi, \quad (3)$$

where $a_0 = 0.246 \text{ nm}$ is the elementary translation vector, γ_0 is the resonance integral for the π -orbitals of the neighboring atoms, γ_1 is the interaction energy of identically located atoms in the adjacent graphite layers, γ_2 is the interaction energy of the displaced carbon atoms in the adjacent graphite layers. From (2) and (3), given that the Fermi energy is determined as $E_F = (4/3)\gamma_2$, it is possible to derive the value of the extremal cross-section of the hole part of the Fermi surface

$$S_d = (4/3)^2 \cdot (\pi / a_0^2) \cdot (\gamma_1 \gamma_2 / \gamma_0^2). \quad (4)$$

The expression for a similar cross-section of the electronic surface differs only in the value of the coefficient at $\gamma_1 \gamma_2 / \gamma_0^2$. In order to determine the deformation of the electron spectrum of graphite with changing the interplanar distance, it is necessary to know the dependence on pressure of all the parameters included in equations (2) and (3). As follows from X-ray studies of the graphite compressibility to the value of 1.6 GPa , the change in the parameter a_0 for such pressures in comparison with the changes in the interplanar distances can be neglected. Therefore, it is assumed that parameter γ_0 in the range of pressures, for which the studies were carried out, is

pressure-independent. In [12], the Shubnikov-de Haas effect in HOPG was investigated in order to obtain the extremal cross-section area of the Fermi surface at various pressures. The values of γ_2 were calculated based on the conducted studies, and in the absence of the applied hydrostatic pressure $\gamma_{20} = 0.0196 \text{ eV}$, in the presence of the applied pressure of 0.8 GPa – $\gamma_{28} = 0.0225 \text{ eV}$. The values of the Fermi energy were also determined: at zero pressure $E_{F0} = 0.026 \text{ eV}$ and at the pressure of 0.8 GPa $E_{F8} = 0.030 \text{ eV}$. Thus, the results of the work directly indicate an increase in the overlap between the valence and conduction bands when applying pressure along the C -axis. Indeed, the overlap of the valence and conduction bands in graphite is determined as $\Delta E = 2\gamma_2$. When the applied pressure increases from 0 to 0.8 GPa , the overlap increases from 0.0392 eV to 0.0450 eV .

We will use the results of [12] to estimate the change in the overlap between the valence and conduction bands under the action of hydrostatic pressure in FCPG. We will assume in the first approximation that the change in the parameter γ_2 when applying pressure along the C -axis occurs linearly with respect to pressure. Let us evaluate the value of the relative change in the parameter γ_2 when applying pressure for HOPG: $\chi = \Delta\gamma_2 / \gamma_{20} \Delta p$, where $\Delta\gamma_2$ is the change in the overlap parameter when applying pressure, γ_{20} is the value of the parameter γ_2 at zero pressure, Δp is the applied pressure, and $\chi = 1.85 \cdot 10^{-10} \text{ eV}^{-1}$. We will use the obtained value of the coefficient χ to evaluate the change in the parameter γ_2 , the value of the overlap between the valence and conduction bands ΔE , as well as the value of the Fermi energy E_F for FCPG when applying pressure of 1.2 GPa . The carried out calculations give the following values, respectively: $\gamma_{212} = 1.22 \cdot 10^{-3} \text{ eV}$, $\Delta E_{12} = 2.44 \cdot 10^{-3} \text{ eV}$, and $E_{F12} = 1.63 \cdot 10^{-3} \text{ eV}$. Thus, the application of pressure of 1.2 GPa along the C -axis for samples of fine crystalline graphite leads to an increase in the overlap between the valence and conduction bands and, correspondingly, to a shift of the Fermi level by about 20 % compared with the unloaded sample. We will estimate whether this change in the Fermi energy correlates with the change in the value of the resistivity of FCPG sample under load. As seen from Fig. 2, the change in the resistivity of the FCPG sample under load to 1.2 GPa is equal to $\sim 30\%$ that coincides well with the shift of the Fermi level. However, we note that the change in the resistivity of the FCPG sample under load occurred not linearly relative to pressure, but leapingly when achieving applied pressure of $\sim 1 \text{ GPa}$.

Thus, a decrease in the resistivity in FCPG samples when applying hydrostatic pressure is associated with an increase in the overlap between the valence and conduction bands that leads to an increase in the concentration of free charge carriers. A decrease in the distance between the graphite layers under pressure and, correspondingly, an increase in the overlap of the valence and conduction bands is an irreversible process, i.e. when the load is removed, the electrical resistance somewhat increases, but does not acquire the initial value.

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