Features of electric conductivity of quasi-two-dimensional graphites with impurity carriers

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(Submitted 30 June 1983)
Zh. Eksp. Teor. Fiz. **86**, 995–997 (March 1984)

The two-dimensional conductivity σ_s of noninteracting graphite layers doped with boron is investigated. For a degenerate system of impurity carriers, σ_s is practically independent of their density at $3\times10^{11}\leqslant n_s\leqslant 2.4\times10^{13}$ cm^{-2} and is equal to $(1.4\pm0.2)\times10^{-4}\,\Omega^{-1}$. An estimate of σ_s within the framework of the band model of two-dimensional graphite agrees well with experiment.

Quasi-two-dimensional graphites (QTDG) occupy a special place among the artificial graphites. They preserve on the average the two-dimensional lattice of the graphite layers, the layers are parallel and equidistant within the crystallite, but there is no azimuthal ordering in the direction perpendicular to the layers. The distance between layers $d_c = 0.342$–0.344 nm is noticeably larger than for single-crystal graphite, for which $d_c = 0.335$ nm. Consequently the QTDG is a good approximation of the hypothetical two-dimensional graphite (TDG) which comprises bundles of noninteracting monolayers.

According to Refs. 1 and 2, TDG is a two-dimensional zero-gap semiconductor with linear dispersion and density of states in the vicinity of the point of tangency of the filled and empty bands:

$$E=\pm\frac{\sqrt{3}}{2}a\gamma_0 k, \quad N_s(E)=\frac{8|E|}{3\pi\gamma_0^2a^2}, \tag{1}$$

where E is the electron energy; k is the wave number; a is the two-dimensional lattice parameter (0.246 nm); γ_0 is the two-dimensional band parameter[3] (3 eV): $N_s(E)$ is the density of states per unit energy and area with account taken of the double degeneracy in band and spin. Relations (1) are valid at $E\approx0.01$–0.8 eV.

The peculiarities of the band structure distinguish the QTDG from the other two-dimensional systems that are being intensively investigated at present.[4] We report here an investigation of the electric conductivity of QTDG as a function of the density of the hole carriers produced by boron or by intrinsic structure defects. When the carbon atoms are replaced by boron, the lattice parameters are almost unchanged and the band structure is not distorted.

As a realistic approximation of TDG we chose highly textured pyrocarbon. The samples were produced by depositing the products of pyrolysis of hydrocarbons with boron admixture on a flat substrate at 2100 °C. The samples selected had $d_c = 0.342$–0.344 nm and a density $\gamma = 2.19$–2.20 g/cm^3, which is a maximum for this value of d_c. This made it possible to determine from the volume conductivity σ_a along the layers the two-dimensional conductivity $\sigma_s = \sigma_a d_c$. On the basis of a texture analysis of the samples, the value of σ_s was increased by $\sim10\%$ to compensate for the influence of the texture factor. The two-dimensional carrier density was determined from the Hall coefficient R_H in the single-band approximation for degenerate systems: $n_s = |eR_H|^{-1}d_c$. The measurement error did not exceed 3% for σ_a and 10% for R_H.

In the samples investigated, n_s ranged from 3×10^{11} to 2.4×10^{13} cm^{-2}. For all samples, σ_s and R_H were independent of temperature at $T = 4.2$–77 K. When T was raised to 300 K, σ_s of samples with $n_s\leqslant6\times10^{11}$ cm^{-2} increased, and R_H decreased because of the lifting of the degeneracy.

As seen from the figure, when n_s is changed by almost two orders, σ_s at 77 K changes only within $\pm15\%$ at an average value $1.4\times10^{-4}\,\Omega^{-1}$. Thus, the increase of the impurity carrier density is almost completely offset by the decrease of their mobility.

Let us estimate σ_s of TDG in the Boltzmann-transport-equation approximation. For a degenerate system of carriers, as can be seen from (1), $n_s = k_F^2/\pi$ and

$$\sigma_s=2(e^2/h)k_Fl=2(e^2/h)(\pi n_s)^{1/2}l, \tag{2}$$

where k_F is the value of k at the Fermi level, l is the electron mean free path, and h is Planck's constant. We obtain the value of l assuming scattering by ionized impurities. Since in the case of doping by boron there is one electron for each impurity center, the screening effects can be neglected. According to Ref. 5, the differential cross section for scattering by an unscreened point charge e located in the plane of a two-dimensional system is

$$\sigma(\theta)=\frac{G\,\mathrm{th}(\pi G)}{2k\sin^2(\theta/2)}, \quad G=\frac{2\pi e^2}{\varepsilon hv}, \tag{3}$$

where θ is the scattering angle, ε is the dielectric constant, and v is the electron velocity. In this case k and v do not depend on θ and the transport scattering cross section is

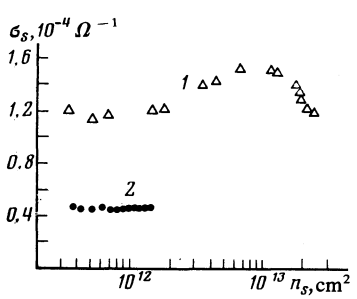

FIG. 1. Dependence of two-dimensional conductivity σ_s on the carrier impurity density n_s for QTDG: 1—with boron impurity; 2—with intrinsic structure defects. The measurements were made at $T = 77$ K.

 0038-5646/84/030580-02$04.00

$\sigma_c = 2\pi G \tanh(\pi G)$. Since $1/l = n_i \sigma_c$, while $n_i = n_s$ when the carriers are degenerate, we obtain, taking the equality $n_s = k_F^2/\pi$ into account,

$$1/l = 2(\pi n_s)^{1/2} G \operatorname{th}(\pi G). \quad (4)$$

It follows from (1) that v in TDG does not depend on E or n_s, and is equal to 9.7×10^7 cm/sec. Then G is a constant, $l \sim 1/\sqrt{n_s}$, and σ_s does not depend on n_s, in good agreement with experiment. Substituting for graphite the value[6] $\varepsilon = 5.4$ in (3) and (4), we get $l \approx 0.8\sqrt{n_s}$ and $\sigma_s \approx 10^{-4}\,\Omega^{-1}$. The estimate (2) of σ_s is naturally approximate, inasmuch as at $\sigma_s \approx 1.4 \cdot 10^{-4}\,\Omega^{-1}$ we have $kl \approx 2$, i.e., k is not a good quantum number. Furthermore, l was estimated without allowance for the influence of the impurities in the neighboring layers. If, however, we assume that l is equal to the distance between the impurities in the layer, the value of σ_s obtained from (2) coincides with the experimental data.

In the second set of experiments we investigated pyrocarbons in which the role of acceptors was played by the natural structure defects. Consequently the prepared samples had a sufficiently high content of intralayer defects and carriers that are degenerate at 77 K. It can be seen from the figure that here $\sigma_s = 0.45 \cdot 10^{-4}\,\Omega^{-1}$ and is independent of n_s. This value of σ_s can be qualitatively explained by assuming that the scattering is from the boundary of two-dimensional crystallites, i.e., $l \approx 0.4 L_a$ (Ref. 7), where L_a is the crystallite diameter, and the boundary line of each crystallite captures one electron from the valence band. Then $n_s \approx 4/(\pi L_a^2)$ and $\sigma_s \approx 0.5 \times 10^{-4}\,\Omega^{-1}$.

The author thanks L. N. Bulaevskiĭ for a helpful discussion of the work.

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Translated by J. G. Adashko