

Diamagnetism of quasi-two-dimensional graphites

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The temperature dependence of the diamagnetic susceptibility of quasi-two-dimensional graphites is studied in the temperature interval 4.2–1000 K. At low temperatures, the large diamagnetic susceptibility, in comparison with the exponentially small value predicted by current theories, is attributable to the effect of scattering of electrons by the structural defects on the “smearing” of the energy spectrum near a conic singularity.

Because of the structural features of the bond structure, graphites have the highest diamagnetic susceptibility after superconductors which is measured along the crystallographic c axis. Among graphites the quasi-two-dimensional graphites have the maximum diamagnetic susceptibility which is characterized by a sufficiently perfect graphite layer structure in the absence of azimuthal order between the layers (pyrocarbons¹ produced at a temperature of 2100 °C, for example). The diamagnetic susceptibility of a 3D ordered graphite has been explained² on the basis of the familiar band model,³ whereas in the case of quasi-2D graphites the low-temperature measurements and theoretical estimates of the diamagnetic susceptibility differ appreciably.

In a first approximation of quasi-2D graphites, we can use a band model of a 2D graphite which is a gap-free semiconductor. In this semiconductor the linear dispersion law is satisfied in the region where the filled band comes in contact with the vacant band^{3,4} (Fig. 1). In an actual quasi-2D graphite, the chemical potential is shifted forward the valence band because of acceptor action of the inherent quasi-2D graphite layer defects.

The band contribution to the diamagnetism of a 2D graphite, in which the strong interband effects were taken into account, was calculated for the first time by McClure.⁵ This contribution is described by the equation

$$\chi = -1.46 \times 10^{-3} \gamma_0^2 \operatorname{sech}^2(E_F/2kT)/T \text{ cm}^3/\text{g}, \quad (1)$$

where γ_0 is the band parameter (approximately equal to² 3 eV), E_F is the chemical potential, k is the Boltzmann constant, T is the temperature (K), and $\chi = \chi_c - \chi_a$ where χ_c is the diamagnetic susceptibility along the c axis, and χ_a is the diamagnetic susceptibility along the layer); here χ_a is equal to the atomic diamagnetism ($-0.4 \times 10^{-6} \text{ cm}^3/\text{g}$).

The value of χ is determined by the number of electrons that occupy the state near the conic point ($E=0$) and hence depends strongly on E_F and T . At $T > T_0$, where $T_0 = E_{F_0}/k$ is the degeneracy temperature of the current carriers, we have $\chi(T) \sim 1/T$, in satisfactory agreement with the experimental data of Ref. 1. In contrast, the calculated value of the diamagnetic susceptibility decreases exponentially in

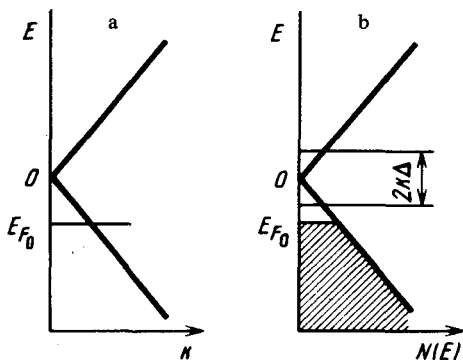


FIG. 1. (a) The dispersion law $E(k)$ for a 2D-graphite model; (b) the state density $N(E)$.

the limit $T \rightarrow 0$, while the experimental value increases. Although these circumstances stimulated the continuation of theoretical research, Eq. (1) was proved to be valid for 2D graphite in a more general approach.⁶

In this letter we report the experimental results of χ for quasi-2D graphites measured over a broad temperature interval and we compare these results with theory.^{4,5} Furthermore, we estimate χ , taking into account the "smearing" of the state density near a singularity as a result of scattering of electrons by the layer defects. The quasi-2D graphites are represented by highly textured pyrocarbons which were obtained by deposition of hydrocarbon pyrolysis products on a plane substrate at 2100°C. The pyrocarbons had an interlayer distance $d_c = 0.343$ nm, indicating an absence of three-dimensional ordering.^{1,4} The diamagnetic susceptibility was measured by the Faraday method along the plane of deposition of the samples and perpendicular to it. An appropriate textural correction was introduced in the measurement of χ . The error of the measurement of the diamagnetic susceptibility was no greater than 2% and that of the temperature was 1.5%.

The results of the measurement of χ for pyrocarbons with various degrees of imperfection of the layers are represented by the experimental points in Fig. 2(a). The dashed curves are the results of calculations based on Eq. (1). At each temperature the values of E_F were determined from the electroneutrality equation. In low magnetic fields this equation for a 2D graphite is

$$\mathcal{F}_1(E_F/kT) - \mathcal{F}_1(-E_F/kT) = T_0^2 / 2T^2, \quad (2)$$

where \mathcal{F}_1 is the Fermi integral, $T_0 = a\gamma_0\sqrt{3\pi n_s}/2k$, $a = 0.246$ nm is the lattice constant, and n_s is the 2D density of the extrinsic carriers which was determined by measuring the Hall coefficient at 4.2 K. In a quasi-2D graphite, n_s is equal to the density of dispersing defects.⁴

Analysis of Eq. (1) has shown that for any permissible change in γ_0 and T_0 the calculated values of χ will always be lower than the experimental values at low temperatures. This discrepancy between theory and experiment can, in our view, be eliminated by introducing, by analogy with the incorporation of the broadening of the

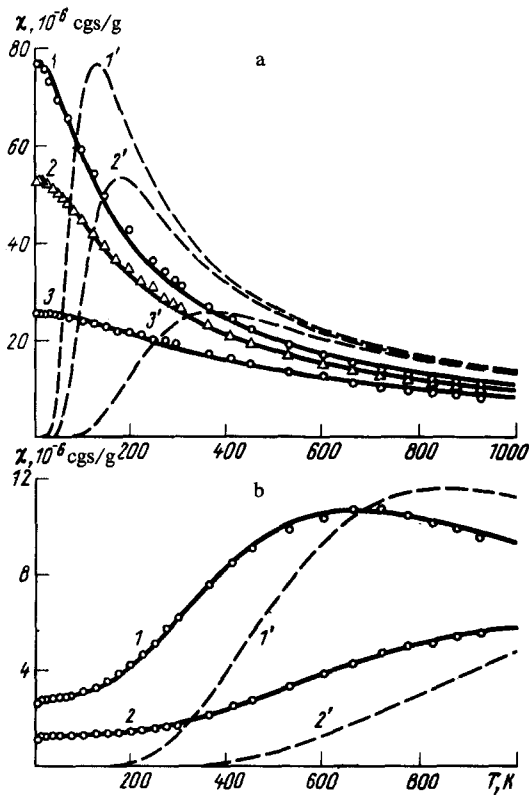


FIG. 2. The temperature dependence of χ for pyrocarbons (a) and for borated pyrocarbons (b) at various degeneracy temperatures of the current carriers (T_0, K): (a) 1—240; 2—330; 3—690 and (b) 1—1600; 2—2800.

Landau levels in the de Haas-van Alphen effect,⁷ in Eqs. (1) and (2) the effective temperature $T_e = T + \Delta$, instead of T , where $\Delta = \hbar/\pi k\tau$, and τ is the relaxation time. The parameter Δ formally takes into account the "smearing" of the spectrum near $E = 0$ [Fig. 1(b)] because of the finite value of τ . A rigid model of 2D graphite is used for calculations in the remaining part. From the relations for the conductivity of quasi-2D graphites given in Ref. 4 we easily see that at $T \ll T_0$

$$\hbar/\pi k\tau = (e^2/2\pi\hbar)(2T_0/\pi\sigma_s), \quad (3)$$

where σ is the 2D conductivity of the graphite layer. For a pyrocarbon with structural defects we have $\sigma_s = 0.45 \times 10^{-4} \Omega^{-1}$ and is independent⁴ of n_s . In this case $\Delta \cong 0.5 T_0$. At $\gamma_0 = 3$ eV this value of Δ corresponds to the best approximation of the experimental points by the theoretical curves upon the introduction of T_e [solid curves in Fig 2(a)]. The approximating values of T_0 in this case agree within 20% with the values of T_0 determined from the independent measurements of the Hall coefficient. At $T > T_0$ we took into account the additional scattering of electrons by phonons. For a 2D graphite we have $1/\tau_f = T/A$ (Ref. 8), where $A = 5 \times 10^{-11} K$, and $\Delta = 0.5 T_0 + 0.05T$.

The T dependence of χ behaves differently for borated pyrocarbons: χ goes

through a maximum at $T < T_0/2$ and decreases as $T \rightarrow 0$ [Fig. 2(b)]. This difference from pyrocarbons stems from the fact that n_s and τ in borated pyrocarbons are determined principally by the concentration of boron dissolved in the lattice. The transport cross section for scattering of carriers by boron ions is smaller than that for scattering of carriers by structural defects. For borated pyrocarbons $\sigma_s = 1.4 \times 10^{-4} \Omega^{-1}$ (Ref. 4) and $\hbar/\pi k\tau = 0.17T_0$; i.e., T_e is closer to T in borated pyrocarbons than it is in pyrocarbons. Equation (1) cannot, however, completely describe the experimental curve upon the introduction of T_e , since at $T < T_0/2$ the values of χ are always higher than the calculated values. The borated pyrocarbons seem to have regions in which the scattering of electrons by intrinsic structural defects remains dominant. Because these regions are small, they do not affect the conductivity appreciably but increase dramatically the diamagnetism of borated pyrocarbons at low temperatures. The theoretical curves can be brought to a good agreement with the experimental results at all T [solid curves in Fig. 2(b)] by assuming that χ in these regions is determined, as in the case of pyrocarbons, by Eq. (1), with $\Delta \cong 0.5T_0$, and that these regions correspond to $\sim 20\%$ in sample 1 and to $\sim 15\%$ in sample 2.

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¹E. Poquet, *J. Chim. Phys.* **60**, 566 (1963).

²M. P. Sharma, L. G. Johnson, and J. W. McClure, *Phys. Rev. B* **9**, 2467 (1974).

³J. C. Slonczewski and P. R. Weiss, *Phys. Rev.* **109**, 272 (1958).

⁴A. S. Kotosonov, *Zh. Eksp. Teor. Fiz.* **86**, 995 (1984) [*Sov. Phys. JETP* **59**, 580 (1984)].

⁵J. W. McClure, *Phys. Rev.* **104**, 666 (1956).

⁶S. A. Safran and F. G. DiSalvo, *Phys. Rev. B* **20**, 4889 (1979).

⁷F. Blatt, *Fizika élektronnoĭ provodimosti v tverdykh telakh* (The Physics of Electronic Conductivity in Solids), Mir, Moscow, 1971.

⁸J. Bok, *Physica* **105B**, 491 (1981).

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