DIAMAGNETISM OF SOME QUASI–TWO–DIMENSIONAL GRAPHITES AND MULTIWALL CARBON NANOTUBES

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Introduction

Due to the energy band structure features, graphitic materials have the highest diamagnetic susceptibility (DMS) after superconductors [1]. Among graphites the maximum DMS value is observed in turbostratic carbons, or quasi–two–dimensional graphites (QTDGs), having the perfect 2D layer structure along with an increased interlayer distance ($d_{002}\geq 0.34$ nm) and lack of azimutal ordering between the layers. It was shown that DMS of such materials may be explained in terms of the band model of QTDG [2,3]. Recently a high diamagnetism has also been obtained on multiwall carbon nanotubes (MWCNs), for which the DMS value may exceed or be close to that of perfect graphite [4,5]. The DMS of carbon tubules has been discussed in some theoretical works [6–8], but so far no explanation of its temperature dependence has been done. Since in the MWCNs there is no 3D ordering between relatively perfect rolled up layers and $d_{002}\geq 0.34$ nm, it was suggested to treat their magnetic properties also in the framework of the QTDG band model [9].

In the present paper the results of investigation of DMS of some QTDGs and MWCNs are discussed, and comparisons between the experimental data and calculations in terms of the chosen band model are given.

Experimental

For the experimental investigations, samples of QTDGs having different types of texture have been selected. Pyrolytic carbon (PC) with planar texture was obtained by deposition from vapour phase. PAN–based carbon fibre (CF) with "fibrous" type of texture was produced at 2800°C. Isotropic classy carbon (GC) was prepared under specific conditions. All the samples had no 3D ordering and $d_{002}\geq 0.34$ nm. To study MWCNs, the deposits formed on the cathode by the arc–discharge method set forth in the paper [10] have been selected. According to HREM data the deposits consisted of MWCNs with diameters of 6–30 nm and small portion of nanoparticles. The magnetic susceptibility in the temperature range 4–950 K was measured by the Faraday method using an electronic balance Cahn–2000.

Results and Discussion

DMS of carbon layers and crystallites in graphites is highly anisotropic and can be represented by two main components χ_1 and χ_3, where χ_1 is the susceptibility along the layer which is close to the atomic susceptibility $\chi_a = -0.3\cdot 10^{-6}$ emu/g and is actually independent of the structure perfection and temperature, χ_3 is that in the normal direction to the layer. The latter is responsible for the high average DMS of carbon materials. The value $\chi_{or}=\chi_3-\chi_1$ is the orbital contribution of 2D conduction carriers which is highly sensitive to the structure and temperature changes.

For many polycrystalline QTDGs with an axial texture their χ_{or} may be represented as:

$$\chi_{or}=\chi_z+2\chi_y-3\chi_1, \quad (1)$$

where χ_z is the DMS along and χ_y is that across the texture axis z. It should be noted that at any temperature the χ_z and χ_y values are interrelated by the linear equation:

$$\chi_z+\chi_y=2\chi_1+F\cdot(\chi_z-\chi_y), \quad (2)$$

where $F=\langle 2-\sin^2\theta\rangle/\langle 3-2\sin^2\theta\rangle$ is independent of temperature, and θ is the angle between the normal to the layer and texture axis of the sample. Hence, from the experimental data of χ_z and χ_y it is easy to find the χ_1 value for a polycrystalline sample if its DMS anisotropy is not too low.

Earlier it was shown [3] that the 2D carriers band diamagnetism of QTDGs can be explained in terms of the QTDG band model with the fitting parameter T_0 (the degeneracy temperature of conduction carriers) taking into account the "smearing" of density of states due to electron non–thermal scattering by structure defects. This "smearing" is formally taken into account by using the effective temperature $T_{eff}=T+\delta$ instead of the lattice temperature. If the type of layer defects remains invariable for QTDGs with intrinsic structure defects, the value of δ is $\approx 0.5T_0$.

Fig.1 presents temperature dependence of χ_{or} for PC, GC and CF. The lines in Fig.1 show the calculated approximation in the framework of the QTDG band model [2,3]. The chosen T_0 values for conduction carriers correspond to the best agreement between the experimental and calculation data. The additional

temperature δ is $\approx 0.5T_0$ for all the studied samples.

The temperature dependence of DMS for MWCNs samples is shown in Fig.2. The relative temperature dependence of $\chi_z-\chi_1$ and $\chi_y-\chi_1$, where χ_z and χ_y are DMS values along and across the rod cut out coaxially from a black central part of the cathode deposit is the same and well described in terms of the QTDG band model with T_0 =270 K and with $\delta = 0.5T_0$. These parameters are also completely valid for the theoretical approximation of the $\chi_{or} = \chi_z+2\chi_y-3\chi_1$. It is obvious that the nature of DMS in both principal directions of the rod is the same and the difference in absolute values between $\chi_z-\chi_1$ and $\chi_y-\chi_1$ is a consequence of the angle distribution of nanotubes layers, that is their texture. It has turned out that at all the measurement temperatures the relation between χ_z and χ_y values are well described by Eq. (2) with $\chi_1 = -(0.35\pm0.2)\cdot10^{-6}$ emu/g. The estimated average texture parameter $\langle\sin^2\theta\rangle$ for the layers is equal to 0.62. From this it is easy to show that the nanotube axes are oriented normal to the deposit axis rather than along it.

The experimental data on DMS temperature dependence of MWCNs given in the literature [4,5] are also well described within the QTDG band model.

Conclusion

It is shown that DMS of MWCNs is well described in the framework of the QTDG band model, same as for carbon materials with a pronounced 2D structure, and the diamagnetism of MWCNs has a band nature.

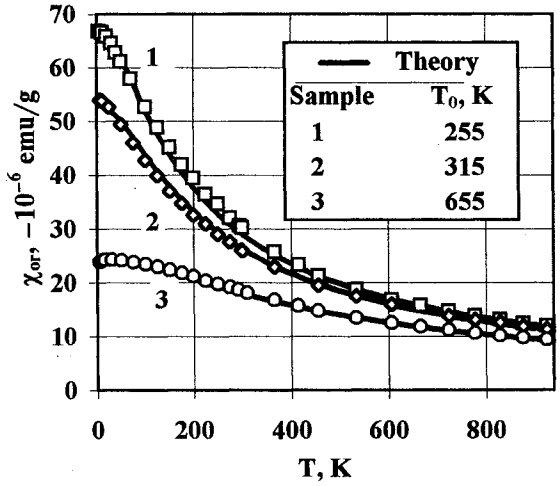

Figure 1. χ_{or} *vs.* temperature for QTDGs: (1) pyrolytic carbon, (2) glassy carbon, (3) carbon fibre. Points – experiment, lines – calculation in the framework of the QTDG band model.

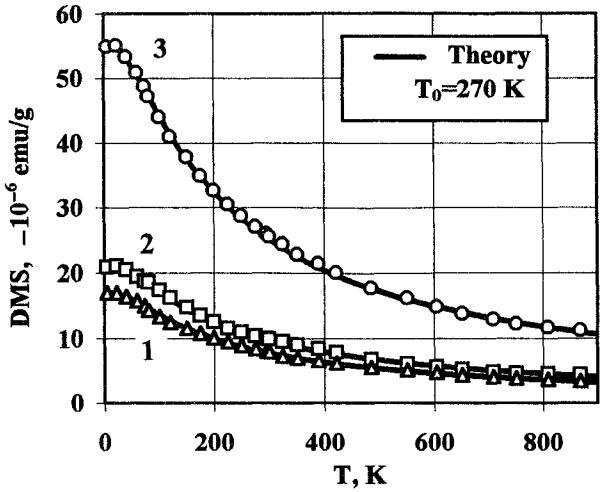

Figure 2. DMS *vs.* temperature for the sample rod cut out coaxially from the cathode deposit central part: (1) $\chi_y-\chi_1$, H normal to the rod axis; (2) $\chi_z-\chi_1$, H along the rod axis; (3) $\chi_{or}=\chi_z+2\chi_y-3\chi_1$. Points – experiment, lines – calculation with the given T_0 (for χ_{or} the 2D band parameter γ_{0eff}=2.85 eV).

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