ELECTRON SPIN RESONANCE STUDY OF CARBON NANOTUBES

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Introduction

Since the discovery of carbon nanotubes [1] and methods of their production [2] there have been published a number of papers on electronic properties of these interesting materials. Theoretical band–structure calculations have predicted that nanotubes can be semimetals, narrow– or broad–band gap semiconductors, depending on their diameter and the degree of helical arrangement [3,4]. In papers [5–7] a conduction electron spin resonance (ESR) of multiwall carbon nanotubes (MWCNs) was clearly observed and some conclusions on similarity and difference of electronic properties of the observed tubules and those of graphite were made. On the other hand, MWCNs are characterized by perfect rolled–up carbon layers, lack of 3D ordering and increased interlayer distance (0.34 nm). From this point of view the nanotubes are similar to quasi–two–dimensional graphites (QTDGs) and their electronic properties can be treated within the scope of the approaches used for QTDGs [8–10].

In the present paper it is shown that the main fraction of the ESR signal in tubules studied is associated with conduction carriers and the temperature behaviour of the ESR parameters is explained in terms of the QTDG band model.

Experimental

MWCNs were produced by an arc–discharge method and then conditioned for a proper registration of ESR spectra. According to HREM data, the samples selected mostly consisted of multiwall tubules with outer diameters of 4–40 nm. ESR was measured with a Varian E–109 spectrometer operating at 9.3 GHz and equipped with appropriate temperature adapters. The intensity of the resonance magnetic field was measured by an E–500 NMR gaussmeter and the frequency of an UHF field by an HP–5342A counter. The temperature measurement error did not exceed 2% and absolute error of g–factor was less than 10^{-4}.

Results and Discussion

ESR spectra for the investigated MWCNs at different temperatures are shown in Fig.1. For the sample studied the registered g–factor value at room temperature was 2.0160. With temperature decreasing g–factor and the line width increased. The ESR intensity increased slightly in the temperature range of 100–550 K and corresponded to a paramagnetic susceptibility $\chi_P \approx 0.9 \cdot 10^{-8}$ emu/g at 300 K. Such a dependence of the χ_P value on temperature implies that the ESR signal in these carbon tubules is mainly conditioned by conduction carriers of semimetallic or narrow band–gap semiconducting materials with degeneracy temperature T_0 of about 500 K. Nevertheless the total paramagnetism of carbon tubules is $\chi_P = \chi_{PC} + \chi_{PL}$, where χ_{PC} is the contribution of conduction carriers (Pauli paramagnetism), χ_{PL} is that of local moments which follows the Curie law and which is remarkable at T<50 K.

It was accepted that the registered g–factor of MWCNs is a result of motional averaging of two principal g–factors: along (g_1) and normal (g_3) to the carbon layers, the first being close to that of the free electron (g_0=2.0023). Hence, from the experimental data of g–factor it is possible to estimate the g_3 value and g–shift $\Delta g = g_3 - g_0$. The Δg value depends on a contribution of 2D conduction electrons and is connected with the Fermi level and band structure. The experimental data on temperature dependence of the Δg values are shown in Fig.2 by points. The temperature behaviour of g–shift for carbon tubules resembles that for QTDGs [9]. It has turned out that the absolute values and temperature dependence of Δg and χ_{PC} are easily explainable in terms of the band model of QTDG [9] with 2D band parameter γ_0=3 eV and the effective spin–orbit energy interaction $\lambda_{eff} = 2.4 \cdot 10^{-5}$eV. As seen in Fig.2 at T>200K there is a satisfactory agreement between the experimental data and calculated g–shift for conduction carriers (curve 1). At low temperatures (T≈100 K) the difference between the calculated Δg and experimental data becomes noticeable. This difference is due to the presence in the tubules of a certain fraction of unpaired electrons localized on the layer defects and to the strong exchange interaction between the conduction electrons and localized centers [11]. For the latters g–shift is close to zero while the susceptibility increases as T→0 in accordance with the Curie law. Allowance for the effect of the localized centers has made it possible to fit the calculated curve to the experimental points in the entire temperature range (Fig.2, curve 2).

As the fitting parameters in the calculations there were used the degeneracy temperature T_0 of conduction carriers and the susceptibility of localized centers χ_{PL}. For MWCNs studied the best approximation was achieved with T_0=490 K and $\chi_{PL}=0.01\cdot10^{-8}$ emu/g. The estimated carriers density for MWCNs is $1.3\cdot10^{11}$cm^{-2}. Hence it may be concluded that the density of localized centers is only a small fraction (<3%) of the carriers density, although their influence on g–shift at low temperatures is quite substantial.

Conclusion

The ESR signal in the sample of MWCNs studied in the range of 100–550 K is mainly associated with 2D conduction carriers and a low density of localized centers. The g–factor and ESR intensity of the conduction carriers can be explained in terms of the band model of quasi–two–dimensional graphite, the Fermi level is been shifted into the valence band due to acceptor action of the layer defects.

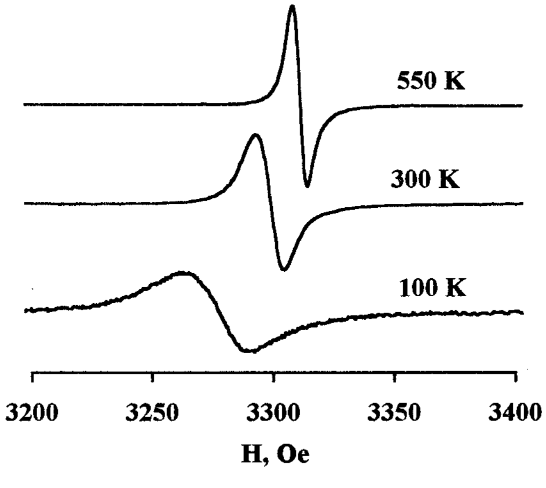

Figure 1. ESR spectra for MWCNs measured at different temperatures.

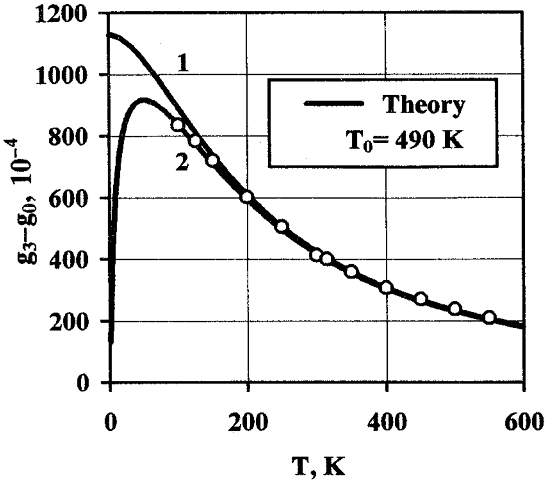

Figure 2. The temperature dependence of the g–shift for MWCNs. Points – experiment; lines – calculations in accordance with the theory of Ref. (9): 1– g–shift for 2D conduction carriers, 2 – additional effect of localized centers.

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