Abstract

It is obvious that the size of the sample can affect the properties of the material from which it is made. The appearance of quantum effects in very small samples constitutes the main barrier of miniaturization in the electronics. In the case of carbon materials it is known that nanocarbons, such as carbon nanotubes, or graphene show different properties than graphite. Less is known about the properties of intermediate sizes. Until now there were no systematic studies of this problem. This doctoral thesis should fill the gap.

The main research method used in this work is the electron paramagnetic resonance (EPR). Measurements of the conductive samples are subject to the additional effects such as skin effect causing the asymmetry of the EPR signal or reduction of the quality factor of the goodness or resonator. Therefore the effect of sample size on the EPR spectrum was a problem that required detailed research. Electrical conductivity of carbon materials is related to the sp2 hybridization, which indicates the presence of flat or curved graphene layers in the material's structure. Their arrangement varieties from the $ABAB$ in hexagonal graphite through $ABCABC$ stacking in rhombohedral graphite up to the turbostratic arrangement observed in materials subjected to grinding. Moreover, powders of these materials tend to have strong shape anisotropy having the form of small plates. Therefore, considering the size effects, it is necessary to take into account both the size of the specimen and its thickness (the number of graphene layers). The results showed that the study of the size effects forces us to separate the effects resulting from the used method (EPR), associated with skin depth and the influence of the sample on the quality factor of the resonator from the actual change of material properties. Illustration of possible problems, falsifying research results, presents study of a solid, thick sample of anthracite.

Three groups of carbon materials were studied. The first one consisted of materials with an ordered crystalline structure: graphene and nanographite, which properties are compared with those of graphite. The second group included anthracite that contained nearly $50\,\%$ of amorphous phase in which nanocrystallites of turbostratically ordered graphite with a diameter of about $2\,nm$ and a thickness of 4 graphene layers are dispersed. Anthracite, which can undergo graphitization, has an isotropic electrical conductivity characteristic for granular materials. The studied samples were of different sizes and shapes. The third group are higher antraxolites of different sample sizes. This amorphous carbon material is unable to undergo graphitization, but has a high, isotropic, and weakly dependent on temperature electrical conductivity characteristic for defected metals. The shape and temperature dependence of the EPR spectra of the studied materials are strongly influenced by defects generated in the grinding process. Unpaired electrons located on the defects are exchange coupled to conduction electrons, and this interaction affects the process of spin relaxation and averages spectrum parameters.

The analysis of spin relaxation processes was carried out with the Hasegawa-Barnes model. The results were unexpected. While in the amorphous materials a decrease in particle

size, as predicted, caused the increase in the spin relaxation rate, in crystalline materials the relaxation rate decreased with decrease of the grains lateral dimension. More monotonic character shows the dependence of the spin relaxation rate on the contribution of the Curie-type magnetic susceptibility to the EPR magnetic susceptibility of the studied specimens, the value which is proportional to the number of spins localized on defects. The obtained data showed that the increase in the number of defects decreases the rate of paramagnetic relaxation, which is the highest for a single crystal of graphite and the lowest for solid anthracite. This result is a confirmation of correctness of Huber's and his colleague's theory concerning the influence of fluctuations of orbital moment of electrons located on p_z orbitals on the width of the EPR resonance line of graphite. In the case of the higher anthraxolite, the tendency of material to agglomerate makes particles smaller than $250\,nm$ almost impossible to obtain. However, for the specially crafted sample we were able to observe the effect of electron localization on very small grains whose size due to agglomeration could not be measured, but estimates indicate that the diameter was no more than $10-20\,nm$.