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ABSTRACTS

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NMR STUDY OF Mn - DECORATED GRAPHENE OXIDE

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Graphite and graphene oxides are usually prepared by oxidizing graphite with $KMnO_4/H_2SO_4$ according to the method of Hummers and Offeman. [1] Recently it has been discovered [2] that graphene synthesized by reduction of graphene oxide reveals Mn^{2+} ions, which originate from potassium permanganate used in the process of the sample preparation. These ions do not exist as a separate phase but form paramagnetic charge-transfer complexes with the graphene planes, which should affect structural, electronic and magnetic properties of graphene important for its applications, e.g., for graphene electronics. One can suggest that similar impurities occur in the precursor graphene oxide. In the present communication, we report on NMR study of Mn-decorated graphene oxide (GO) produced by the Hummers method [1].

The experimental and theoretical temperature dependences of the second moment M_2 of the ^{1}H spectra and ^{1}H spin-lattice relaxation rate R_1 in Mn-GO are shown in Fig.1 and Fig.2.

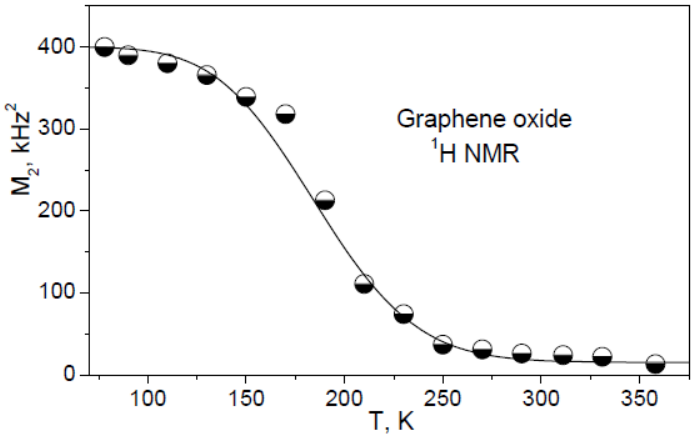

Figure 1. Temperature dependence of the second moment M_2 of the ^{1}H spectra in graphene oxide.

The calculated parameters, which fit the experimental data, are given in Table.

Table. Calculated parameters that describe proton mobility and relaxation via paramagnetic centers. Here γ_H = 26,752196 rad×kHz /G.

ΔM_2, kHz^2	τ_0, s	$\overline{E}_a$, kcal/mol	σ_E, kcal/mol	τ_{0e}, s	E_{ae}, kcal/mol	$\gamma_H^2\langle H_L^2\rangle$, (rad×kHz)^2
385	10^{-13}	5.00	0.2	4×10^{-10}	0.1	1000

Our ^{1}H measurements support the conclusion that Mn^{2+} ions are attached to the graphene oxide planes, herewith being positioned close to the hydrogen atoms. Since graphene oxide is

built of aromatic islands of variable size, which are separated from each other by aliphatic 6-membered rings containing C–OH and epoxy groups and double bonds, and since the distribution of functional groups in every oxidized aromatic ring is not identical and both the oxidized rings and aromatic entities are distributed randomly [3], we suggested in our calculations that proton mobility in graphene oxide is inhomogeneous and is characterized by a normal distribution of the activation energies.

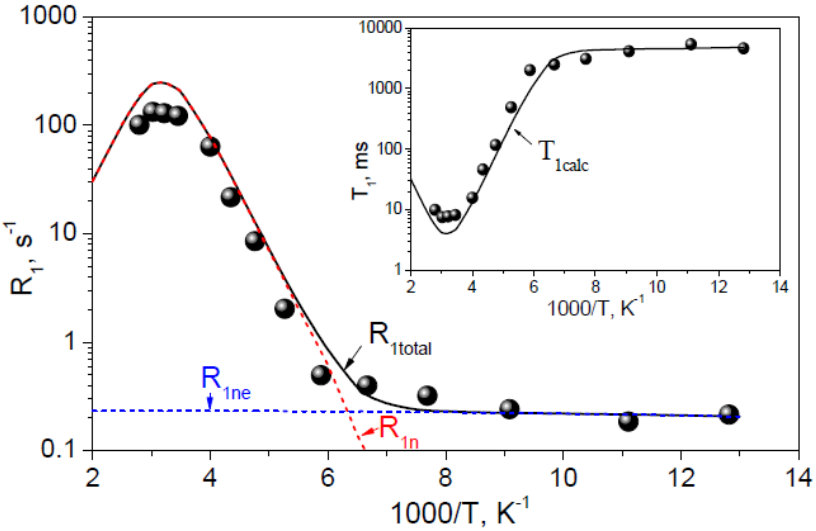

Figure 2. Dependence of ^{1}H spin-lattice relaxation rate R_1 in graphene oxide in semi-logarithmic scale on reciprocal temperature. Filled circles - experiment, red dash line – contribution of motion of hydrogen atoms, blue dash line - contribution of paramagnetic centers, black solid line – total calculated R_1. Temperature dependence of ^{1}H spin-lattice relaxation time T_1 is shown in inset.

An attempt was made to extract an average value for the Mn-C and Mn-H distances. We calculated R(Mn-C) = 4.57 Å and R(Mn-H) = 4.7 Å, much longer than the sum of covalent radii of Mn and C, 2.27 Å, and Mn and H, 1.87 Å. However, we note that since the number of paramagnetic ions is several orders of magnitude smaller than the number of H and C atoms, the real distances between them would vary in a wide range, from those corresponding to covalent bond to much longer distances to the distant atoms.

Since water diffusion at high temperature averages out all dipole-dipole interactions between diffusing H_2O molecules and OH groups, the corresponding value of the second moment at 358 K reflects the dipole-dipole coupling among the protons of fixed hydroxyl groups. For two neighboring OH groups, the value of M_2 = 13 kHz^2 at T = 358 K yields separation between two hydrogen atoms as 2.82 Å. This is in good agreement with the structural model of graphene oxide [3], in which two hydroxyl groups neighbor each other. We note, however, that owing to inhomogeneity of the positioning of these groups, the distance between the hydrogen atoms is likely variable.

References

1. W.S. Hummers, and R.E. Offeman, *J. Am. Chem. Soc*. **80**, 1339 (1958).
2. A. M. Panich, A. I. Shames, A. E. Aleksenskii, A. Dideikin, *Solid State Commun.* **152**, 466 (2012).
3. H. He, Th. Riedl, A. Lerf, and J. Klinowski, *J. Phys. Chem.* **100**, 19954 (1996).