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Abstracts



X-Ray Photoelectron Spectroscopy of Activated Carbon Fibers Treated with Chlorine

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The results of X-ray photoelectron spectroscopy (XPS) study of the activated carbon fibers (ACF) processed with chlorine are presented in the paper. Initial carbon fibers have been prepared from the PAN-fibers activated with water vapour. According to the data of X-ray diffraction ACFs consist of nanometric graphite particles and some amount of aliphatic fragments. Elimination of these fragments has been performed by high vacuum evacuation at temperature ≈ 800 °C. Later on the samples were placed in the atmosphere of gaseous chlorine for some hours.

The XPS spectra for C1s-electrons of initial ACF and spectra for C1s- and Cl2p-electrons after the fibers treatment with chlorine are presented in Fig.1.

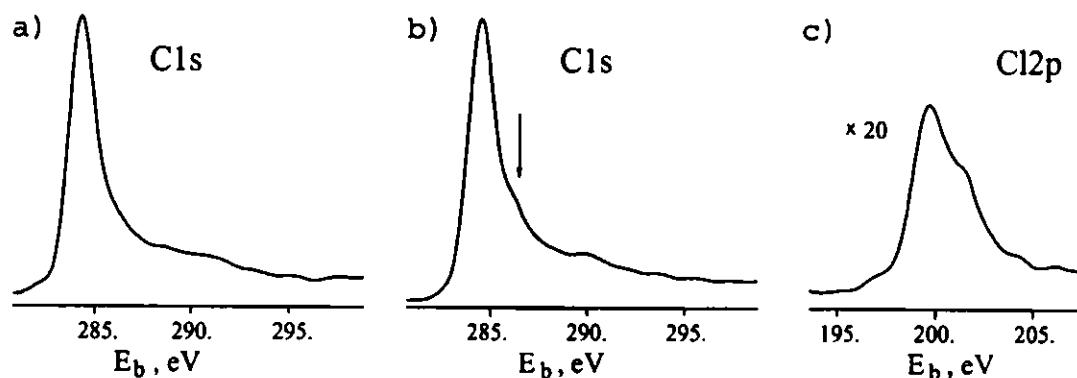


Fig.1. The XPS spectra (after smoothing) for C1s-electrons of initial ACF (a), and spectra for C1s- (b) and Cl2p-electrons (c) after the fibers treatment with chlorine.

The spectrum for carbon of initial fibers is a single asymmetric line with additional excitation signals $\pi \rightarrow \pi^*$. After chlorination an additional signal shifted by ≈ 1.5 to 2 eV with respect to main peak on the binding energy (E_b) scale arises in the C1s electron spectrum (see Fig. 1b, arrow). The value of E_b for the maximum of Cl2p-electron spectrum is equal to 199.8 ± 0.1 eV, which is close to E_b of the core electrons of chlorine covalently bound with carbon atoms in the series of organic compounds^{1,2}. Observed changes in the C1s electron spectrum and E_b of chlorine core electrons indicate to the covalent binding of chlorine and carbon atoms. Taking into account nearly complete elimination of aliphatic fragments and significant decrease of oxygen content in the sample after preliminary high vacuum evacuation at high temperature, one may conclude that chlorine forms covalent bonds with edge atoms of nanometric graphite particles.

References:

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2. C.D. Wagner, J.F. Moulder, L.E. Davis, W.M. Riggs, *Handbook of X-ray photoelectron spectroscopy*, Perking-Elmer Corporation, Physical Electronics Division, USA, 1978, 58.

Magnetic Properties of Graphite Intercalation Front: Conduction ESR Study

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The conduction ESR (CESR) technique is one of the most powerful methods for studying the graphite intercalation process, because shapes and intensities of the CESR signal both from non-intercalated and intercalated regions of graphite plate vary strongly during the intercalation. This work is devoted to the results of an *in situ* CESR study of HNO₃, SbF₅, Br₂ and F₂ molecules intercalation into narrow graphite slab.

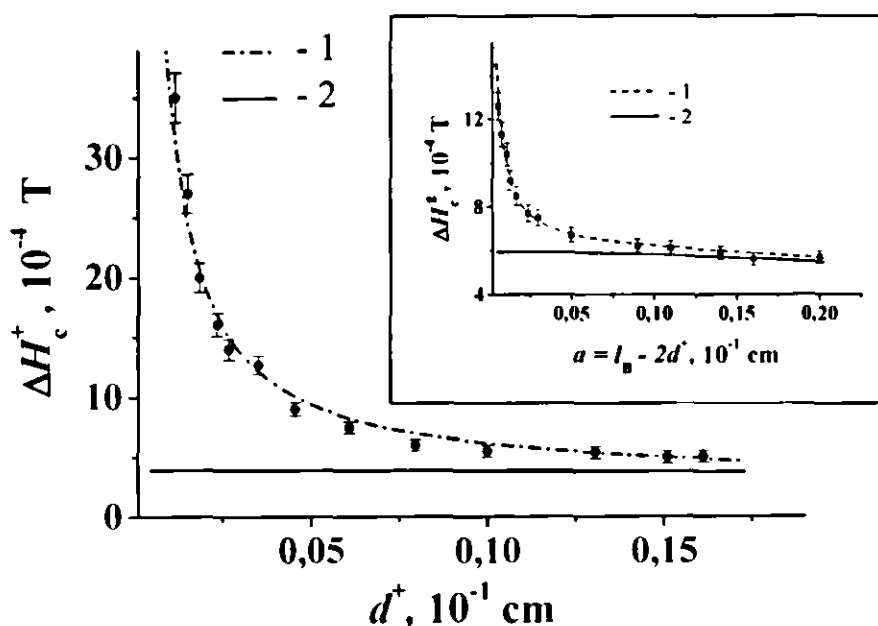


Figure. The experimental (dots) and theoretical (lines) values of CESR linewidth, ΔH_c^+ (ΔH_c^E), vs. average thickness, d^+ (a), of intercalated (non-intercalated) parts of narrow graphite slab. The dashed (solid) lines were calculated with the non-zero (zero) values of average spin reorientation probabilities during the collisions of current carriers with the front of graphite intercalation by antimony pentafluoride molecules.

In all experiments the narrowing (broadening) of the CESR signal at the beginning (at the end) of intercalation of narrow graphite slab have been clearly detected. Under the assumption that the CESR signal evolution is caused by the advance of a boundary separating the intercalated and non-intercalated parts of graphite, the average value of spin reorientation probability ε during the collision of current carriers with this interface and the constant of two-dimensional diffusion of intercalate molecules into graphite galleries have been extracted from experimental data by calculations. It was found that the value of ε depends on the nature of intercalate, experimental conditions and the side of collision of current carriers with the front of reaction.

Graphite Nanoparticles: ESR and Magnetic Susceptibility Data

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The presence of open edges around the peripheral region can result in occurrence of specific features in nanographites, which are different from bulk graphite and their closed-surface counterparts. In this report, we present ESR and magnetic susceptibility (MS) data for nanographites - the structural blocks of activated carbon fibers (ACFs), in order to clarify their structure and electronic properties.

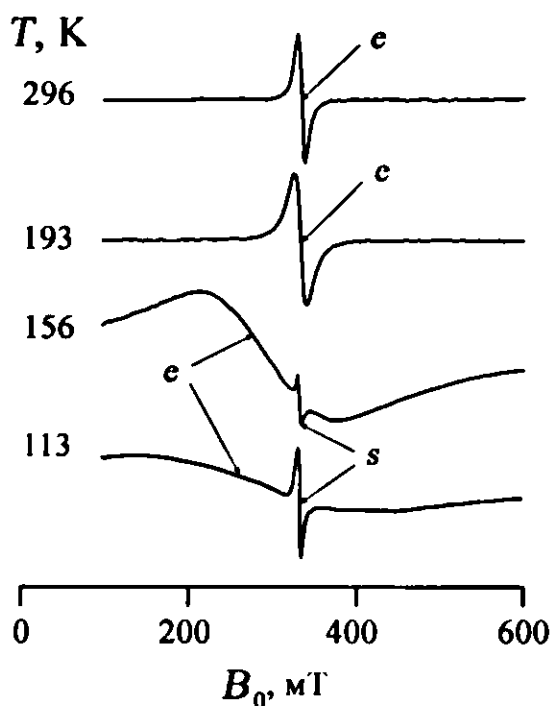


Fig. 1. The ESR spectra of ACFs. (e – and s – the signals from conduction and localized electrons, respectively).

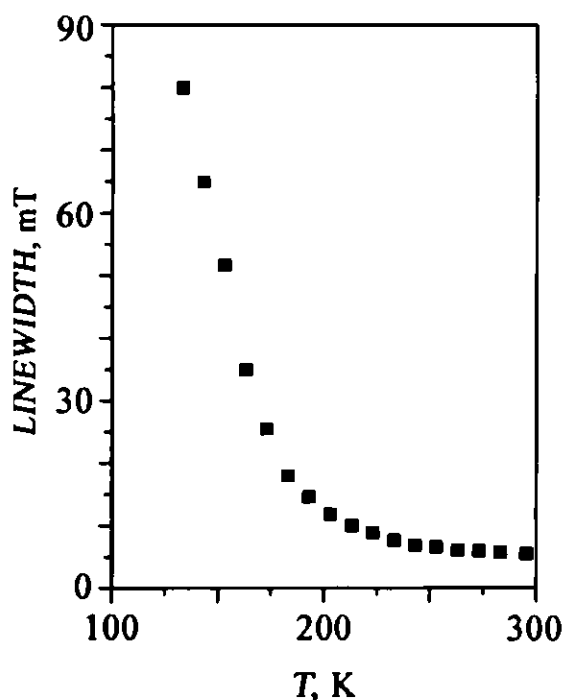


Fig. 2. The CCSR linewidth of pure ACFs vs. temperature.

At temperatures above ≈ 150 K only signal from conduction electrons with a linewidth ≈ 6 mT is observed (Fig. 1). Below ≈ 150 K, a second narrow signal from localized spins appears with a linewidth $\approx 0,2$ mT. The g values are estimated at $g=2,0027(3)$ and $2,0033(3)$ for the signals from conduction electrons and localized states, respectively. At lowering the temperature, the CCSR signal linewidth rapidly increases (Fig. 2) at constant values of the g -factor and integral intensity. From MS data, it follows that approximately one localized spin per 2500 carbon atoms are presented in fibers at low temperatures. From comparison of integral intensities of signals from conduction electrons and localized spins the density of states near the Fermi level in nanographites was estimated. Such calculations show, that it is more than one order of magnitude larger than in bulk regular graphite at the same value of Fermi energy. The results obtained unambiguously indicate the presence of an additional band around the Fermi energy in nanographites that was proposed theoretically.

Investigation of Inhomogeneous Phases in Mixed Crystals

 $\text{Mg}_x\text{Zn}_{(1-x)}\text{TiF}_6 \cdot 6\text{H}_2\text{O} : \text{Mn}^{2+}$ by EPR*Peter G. Skrylnik and Albert M. Ziatdinov*

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The mixed crystals of improper ferroelastics $\text{Mg}_x\text{Zn}_{(1-x)}\text{TiF}_6 \cdot 6\text{H}_2\text{O} : \text{Mn}^{2+}$ have been studied by EPR. The $\text{MgTiF}_6 \cdot 6\text{H}_2\text{O}$ (MFTH, $x=1$) crystals undergo transition of the first order from monoclinic ferroelastic phase to structurally inhomogeneous phase above $T_C^+ = 311 \pm 0.3$ K ($T_C^- = 300 \pm 0.3$ K), as concluded on the basis of analysis of temperature and angular dependences of experimental parameters and numerical calculations. In this phase studied crystals consist of two types of regions characterized by homogeneous and inhomogeneous structural organization. In the latter both the angle of $\text{Mg}[\text{H}_2\text{O}]_6^{2+}$ octahedra rotation around crystal C_3 axis and their axial distortion along C_3 are modulated parameters. The assumption was expressed that at $T_{i2} = 370$ K these crystals may undergo phase transition from inhomogeneous phase to incommensurate phase. The mixed crystals $\text{Mg}_x\text{Zn}_{(1-x)}\text{TiF}_6 \cdot 6\text{H}_2\text{O} : \text{Mn}^{2+}$ ($x=0.64, 0.34, 0.2$; denoted as MZT1, MZT2 and MZT3) have been investigated as well, with special attention paid to inhomogeneous phase, observed at temperatures above ferroelastic phase transition. There is evident qualitative difference between spectra of mixed crystals with $x > 0.5$ (lineshape with two peaks, being similar to MFTH spectra) and $x < 0.5$ (one peak lineshape) (Fig. 1), as well as in their temperature dependences.

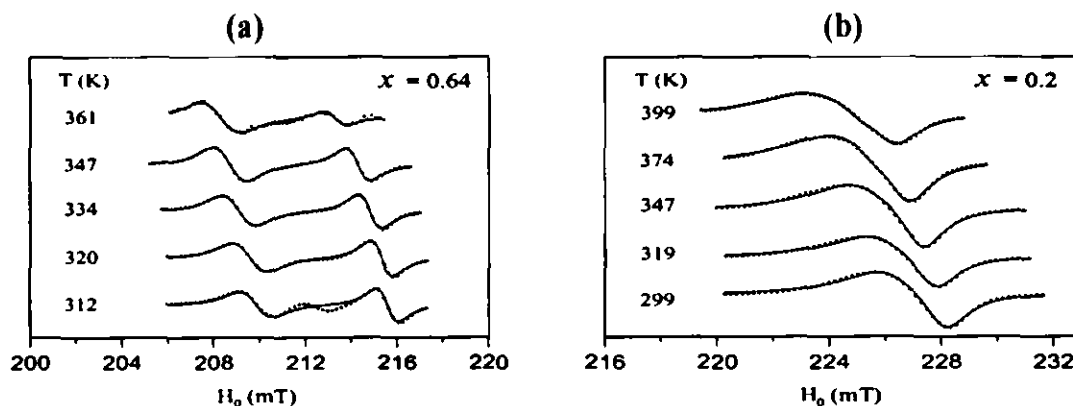


Fig. 1. EPR spectra of mixed crystals $\text{Mg}_x\text{Zn}_{(1-x)}\text{TiF}_6 \cdot 6\text{H}_2\text{O} : \text{Mn}^{2+}$ ($x=0.64$ (a) and $x=0.2$ (b)). Dots and solid lines correspond to experimental and theoretical calculated spectra, respectively.

Overall lineshape character is preserved within entire temperature range of inhomogeneous phase for all mixed crystals studied, though parameters of lineshape are temperature dependent. Within the frameworks of the model utilized for MFTH the successful description of experimental Mn^{2+} EPR spectra of MZT1 crystals has been reached (Fig. 1a), therefore nature of inhomogeneous phase being similar to MFTH is supposed. On the contrary, experimental spectra of MZT2 and MZT3 crystals are not described by that model, which confirms their qualitative difference from MFTH and MZT1 (i.e. $x > 0.5$) crystals. Therefore, we proposed a qualitative model for description of considered mixed crystals with $x < 0.5$. The essence of the model is that axial fine structure parameter D of particular paramagnetic centre (connected with trigonal distortion of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ octahedra), which influences the position of line in the spectrum, is determined by configuration of nearest neighbouring sites (octahedral aqua complexes connected via hydrogen bonds) occupied by particular ions (Mg^{2+} or Zn^{2+}). Taking into account the probability of different configurations in mixed crystals, the resulting lineshape can be calculated. The rhombic distortions of the octahedral complexes, resulting from the strain caused by significant amount of Zn^{2+} ions, should be taken into account in the calculation model as well. These theoretical calculations are in good agreement with experimental results (Fig. 1b).