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PHASE TRANSITION INDUCED CHANGE OF CHARGE CARRIER CONCENTRATION IN GRAPHITE INTERCALATION COMPOUNDS

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Graphite intercalation compounds (GICs) are a wide class of synthetic metals and consist of an alternating sequence of n hexagonal graphite monolayers (n is the stage index) and a monolayer of "guest " atoms or molecules (intercalate). The compounds $C_{10}HNO_3$ investigated belong to second stage of α-modification of GICs with nitric acid of the general formula $C_{5n}HNO_3$ ($n=1,2,3,...$). According to the data of various physical methods, in this GICs the two-dimensional liquid-like layers of HNO_3 are ordered and form a two-dimensional crystal at temperatures lower than T ~ 250 K. Layers of HNO_3 may be incommensurable with a carbon net along one of its crystallographic direction and they undergo a structural phase transition of the incommensurate phase - commensurate phase type at T ~ 210K.

The systematic investigation of the effect of temperature on the conduction electron spin resonance (CESR) spectra of GICs were realized with the 2D CESR line shape analysis procedure developed by present authors [1,2]. Conductivities σ_c and σ_a of investigated GICs have also been measured. As a result, we established an earlier unknown phenomenon: if layers of "guest" molecules undergo an aggregate or structural phase transition, such as in GICs with nitric acid, then with a temperature decrease lower than a critical phase transition region, σ_c and the σ_a increase in spite of the decrease (!) of the charge carrier mobility [1,2]. CESR measurements of charge carrier concentration (N) vs. temperature show (Fig. 1) that this unusual "nonmetallic" behaviour of GICs results from the increase of the current carrier concent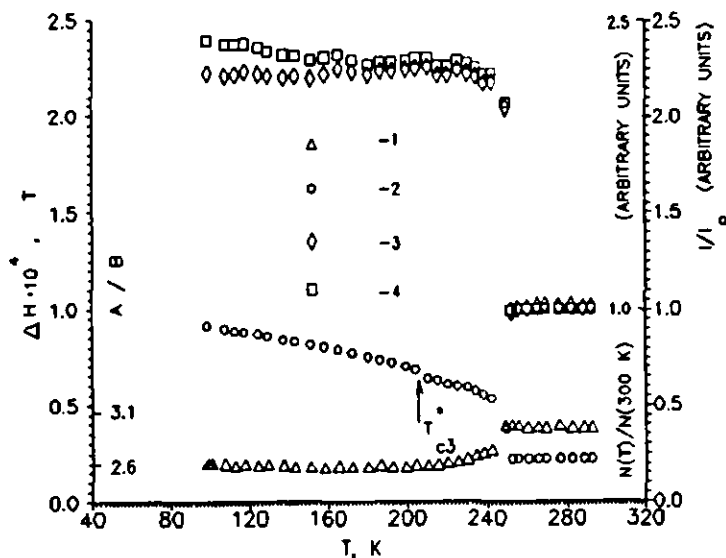ration in π - bands. Thus, one can conclude that in this synthetic metals, in the solid phase of the intercalate (in all the temperature range of investigation), the negative sign of the temperature coefficient of electroconductivity is due to the increase in N. In terms of the GICs tight binding model, the increase of current carriers concentration in π-bands indicates that in some GICs, phase transitions are "triggers" for the process of graphite layers reoxidation.

Fig. 1. CESR line shape parameters in $C_{10}HNO_3$ vs. T. 1, 2, 3 and 4, correspond to A/B, ΔH, $I=(A+B)\cdot\Delta H^2$ and $N(T) \sim (I/I_0)\cdot(\sigma_c)^{1/2}$, respectively. $v=9.5$ GHz.

The theoretical curves CESR line shape of asymmetry parameters $A/B(\lambda=l/\delta)$, where l and δ are wide and skin depth of samples, calculated from the Dyson theory shows that A/B is independent of the diffusion for $\lambda \leq 2.5$. Thus measurements of A/B on samples of the dimension comparable to the skin depth provide a good mean to determine λ and consequently the c-axis conductivity at the frequency used in the measurement [3]. Our investigations of σ_c in $C_{10}HNO_3$ by aforesaid procedure show that in incommensurate phase of this GICs the temperature dependence of c-axis electroconductivity is absent (Fig. 2). In terms of the c - axis conduction path mechanism this phenomenon may be
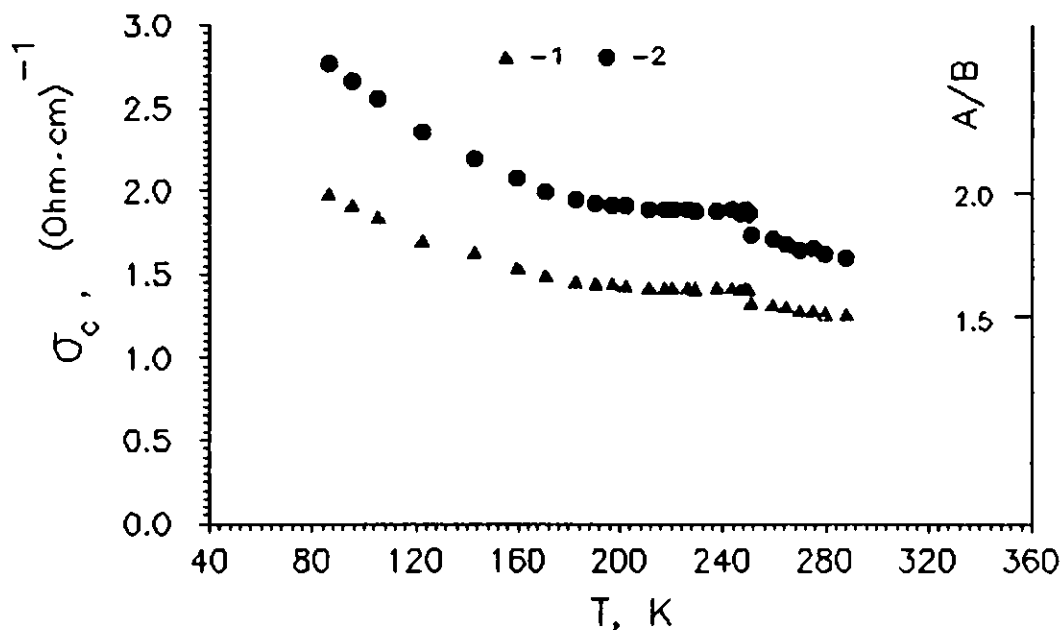

Fig. 2. Temperature dependence of CESR line shape asymmetry parameter $A/B(1)$ in $C_{10}HNO_3$ thin sample with l = 0.04 cm and σ_c (2) . v = 9.5 GHz.

explained as a consequence of full compensation of the increase of current carriers scattering rate in the basal plane by the simultaneously decrease of the conduction path channels density. Another more preferably explanation of this fact may be given in terms of the c-axis band conduction: if in incommensurate phase of GICs the small undulation of assentially cylindrical Fermi surface of GICs disappears, then the c-axis band conduction caused by undulation disappears also.

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CONDUCTION ELECTRON SPIN RESONANCE IN GRAPHITE AND ITS INTERCALATION COMPOUNDS

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ABSTRACT

This paper intends to briefly review on our recent developments in understanding the conduction electron spin resonance (CESR) phenomenon in graphite and acceptor graphite intercalation compounds (GICs).

NEW ASPECTS OF THE THEORY OF CESR PHENOMENON IN GRAPHITE AND GICs

The theoretical analysis of the experimentally observed effects of sample size, microwave electromagnetic field configuration, constant magnetic field orientation and modulation frequency, temperature and stage index on the lineshape and intensity of the CESR signal were performed in graphite and its acceptor intercalation compounds. The calculations of the CESR lineshape in graphite and GICs were carried out in the framework of the 2D modification of the Dyson–Kaplan theory and within this model the qualitative explanation of basic peculiarities of the experimental data were obtained [1]. As for graphite and GICs with nitric acid synthesized in strong concentrated acid, to achieve a quantitative agreement it is necessary, in addition, to take into consideration the presence of the spin relaxation mechanism similar to the surface spin relaxation mechanism or/and (for graphite) the dependence of the ratio of a mean value of the microwave amplitude at the nonequivalent sample faces on a sample size. Basing on these conceptions, we proposed the new procedure to determine from CESR lineshape parameters: the basal plane and c–axis electroconductivity, the spin carrier diffusion constant and the density of states at the Fermi surface. We believe that the origin of the similar temperature dependencies of the basal plane electroconductivity and CESR linewidth is due to the fact, that the spin – orbit interactions in the vicinity of intercalate domain walls, graphite crystallites and sample surface are the main CESR relaxation mechanisms in graphite and acceptor GICs and their contributions increase with the in–plane conductivity increase. In GICs with nitric acid synthesized in strongly concentrated acid for the interpretation of the CESR data, it is necessary to take into consideration the presence of the small concentration of the localized spins, in addition to the surface relaxation effects. In the latter case the contribution of the surface relaxation ef-

fects and concentration of the localized spins undergo the step-wise changes at the aggregate phase transition in the intercalate subsystem of GICs.

APPLICATIONS OF THE CESR TECHNIQUE

1. Using the CESR technique we carried out a detailed study of the intercalate melting-crystallization phase transition in GICs $C_{5n}HNO_3$ (n = 1 - 7) [2]. As a result we have found: two-step nature of the 2D intercalate layers melting; decrease of density of spin carriers, planar and c-axis electroconductivity and increase of the spin relaxation time at the intercalate melting; larger phase transition temperature for a larger "n" in series of samples with even and odd stage index. We also found that in incommensurate phase of GICs under consideration the temperature dependence of the c-axis electroconductivity is absent. This fact was interpreted in the terms of the c-axis band conduction as a direct consequence of the disappearing of the small undulation of the Fermi surface in incommensurate phase. Basing on obtained data we set up a model for the 2D melting in these GICs.

2. We realized an *in situ* CESR study of intercalation of SbF_5, HNO_3, Br_2 and F_2 molecules into graphite plates by the two-zone vapor transport method. The experiments were made with the graphite plate c-axis along and perpendicular to the direction of the microwave magnetic field. This allows to vary the skin-depth and, consequently, the CESR method time resolution of the different intercalation phases more than 15 fold. The application of the developed by author procedure of these experiments allows to find and study individual reaction steps, two essentially different intercalation mechanisms, constants of the 2D diffusion of the intercalate through the sample after insertion of it into graphite, rate of the advance of the stage index change front occurring at the interface between initial and previous stages. The presence of the high-ohmic barrier in the direction perpendicular to the initial intercalation and the stage index change fronts has been established. The obtained data have been successfully applied to the elaboration of a theory of physical reasons of graphite intercalation.

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