

Materials Science Forum  
Volumes 91-93 (1992) Pt. 1

# Intercalation Compounds ISIC-6

Pt. 1



Guest Editors: D. Tchoubar and J. Conard

Trans Tech Publications

## X-RAY PHOTOELECTRON SPECTROSCOPY AND ESR STUDIES OF PHASE TRANSITIONS AND INCOMMENSURATE STATES IN GRAPHITE INTERCALATION COMPOUNDS $C_{10}HNO_3$

A.M. Ziatdinov, N.M. Mishchenko and Yu.M. Nikolenko

Institute of Chemistry, Far-Eastern Branch Academy of Sciences  
690 022 Vladivostok, USSR

### ABSTRACT

ESR data of graphite intercalation compounds  $C_{10}HNO_3$  point at change of quantity and mobility of spin carriers at intercalate crystallization ( $T < 250$  K). Crystallization (melting) of intercalate is a multistages process with a "global" temperature hysteresis. Reversible temperature variations of line shapes of core C1s, N1s and O1s X-ray photoelectrons at phase transitions can be explained in assumption of formation of the charge density waves (CDW) in surface layers of this compounds.

### INTRODUCTION

The intercalation of ions and molecules into graphite leads both to anomalous changes in graphite properties and to rise of new properties: superconductivity, two-dimensional magnetism, structural incommensurability, etc. [ 1 ]. Particularly, in graphite intercalation compounds (GIC) with nitric acid  $C_{5n}HNO_3$  ( $n = 1, 2, \dots$ ) two-dimensional liquid-like layers  $HNO_3$  lower  $T_c \approx 250$  K are ordered and form quasitwo-dimensional crystal which, for  $n=2$ , is incommensurable with carbon net along one of its crystallographic directions [ 2-4 ]. Therefore,  $C_{10}HNO_3$  compounds draw a special attention as object suitable for study of various problems of physics and chemistry of low-dimensional systems, especially of two-dimensional crystallization (melting) in periodic external potential. The present paper gives an account of the results of ESR studies in GIC  $C_{10}HNO_3$  unknown peculiarities of parameter variations of line shapes of conduction electrons and electron spectroscopy for chemical analysis (ESCA) studies of the changes in electronic structure of the surface layers at intercalate "freezing". In case of ESR studies we also conducted a detailed analysis of dependence of the shape of resonance line of GIC on geometrical sizes of sample.

EXPERIMENT

Synthesis of GIC  $C_{10}HNO_3$  for ESR-studies was conducted on HOPG plates with different width (l), height (h) and thickness (d), where  $l \times d$  - square of a side of a sample perpendicular to  $\bar{c}$ -axis. Two series of samples were synthesized. In the first series l changed in the interval  $0.05 \pm 0.225$  cm at constant  $h=0.5$  cm and  $d=0.01$  cm. In another series d changed in the interval  $0.1 \pm 0.34$  cm at constant  $h=0.5$  cm and  $l=0.225$  cm. Accuracy of determination of sizes of the plates was  $\sim 5 \cdot 10^{-3}$  cm. Synthesis of compounds for ESCA was conducted on the plates with  $d=0.05$  cm and  $h \times l=0.9 \times 0.9$  cm. Samples were synthesized in "steaming" nitric acid with density  $\rho = 1.565$  g/cm<sup>3</sup>. GIC stage was controlled by diffraction method. According to data of uncontact measurements of electroconductivity of GIC plates at 300 K  $\sigma_a \approx 1.5 \cdot 10^4$  Ohm<sup>-1</sup>·cm<sup>-1</sup>. According to literary data in  $C_{10}HNO_3$   $\sigma_c \approx 2$  Ohm<sup>-1</sup>·cm<sup>-1</sup> [ 5 ]. ESR measurements in X(Q)-band were conducted in the rectangular (cylindrical) resonator with mode  $TE_{102}$  ( $H_{011}$ ) at 2.5 (100) kHz modulation and at  $T = 100 \pm 300$  K. In the rectangular resonator structure of electromagnetic field of  $TE_{102}$  mode has such a form that at conventional setting of resonator a constant magnetic field  $\bar{H}$  is parallel to electrical component ( $\bar{E}$ ) of microwave field (MWF). GIC plates were placed in the resonator in such a way that basic and two lateral sides ( $h \times d$ ) were parallel to magnetic component ( $\bar{H}$ ) of MWF. In  $T_c$  area temperature changed gradually with a step  $\Delta T \approx 0.2^\circ$  and was kept up with accuracy  $\approx 0.1$  / hour.

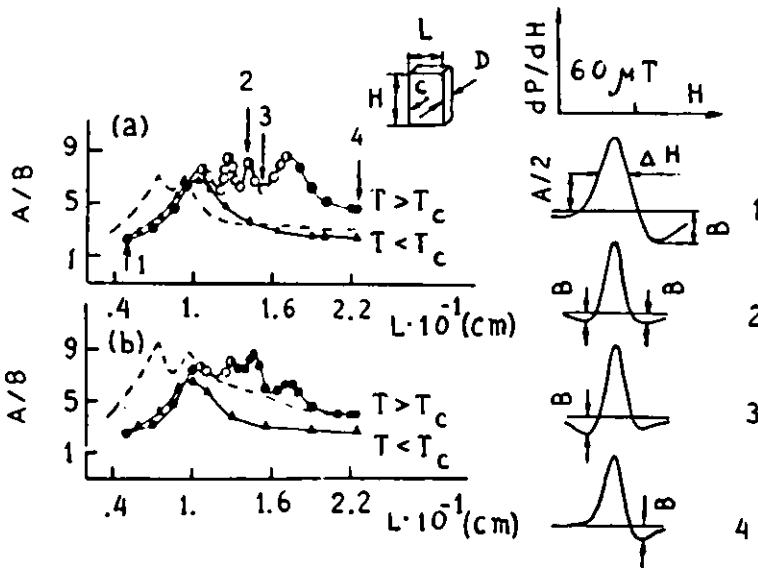


Fig.1 A/B parameter of the ESR first derivative absorption line A/B of  $C_{10}HNO_3$  at  $\bar{c} \perp \bar{H}$  ( a ) and  $\bar{c} \parallel \bar{H}$  ( b ) for  $T > T_c$   $T < T_c$  on width (l) of plates. A/B(l) dependence of ESR lines of conduction electrons of HOPG plates ( shading line ) is shown for comparison. GIC plate dimensional parameters is shown in the upper part. ESR signals for l values marked by pointers are shown, also. Line shapes kind of 2,3 and (1,4) correspond to half-pointed, light and dark points.  $d = 10^{-2}$  cm,  $h = 0.5$  cm.  $f=9.52$  GHz.

ESCA measurements of C1s, N1s, and O1s electrons spectra of GIC  $C_{10}HNO_3$  plates were conducted with application of  $MgK_{\alpha}$ -radiation in the interval 170-300 K, with residual pressure in a chamber of energy analyzer  $\sim 5 \cdot 10^{-8}$  Torr. Resolution for  $4f_{7/2}$  gold peak was 1.4 eV. Variations of binding energies of C1s and N1s electrons were determined relative to energy of O1s electrons which was supposed to be constant. Accuracy of temperature maintenance in ESCA-experiments was  $\sim 2^\circ$ /hour.

## RESULTS

ESR signal of  $C_{10}HNO_3$  with axial angular dependence relative to  $\bar{c}$ -axis and  $g_{11} = 2.0023 \pm 0.0002$  and  $g_{12} = 2.0028 \pm 0.0002$  is observed in both GIC phases from all plates. At  $T < T_c$  shapes of lines have a "normal" phase - in the sense that A peak is situated in smaller magnetic fields relative to B peak and A/B(l) curve has one gentle sloping maximum at  $l_{max} = 0.1$  cm (Fig. 1). At  $T > T_c$  A/B(l) dependence has a four peaked shape. At  $\theta = 90^\circ$  ( $\theta$  - angle between  $\bar{c}$  and H) A/B(l) maximum is observed at  $l_{max} = 0.105, 0.125, 0.140$  and  $0.170$  cm. Plates with  $l_{max}$  have a shape of line symmetrical relative to A peak. For plates with  $l$  from three adjoining each other areas between  $l_{max}$ . A peak of line situated in larger magnetic fields in comparison with B peak - that has a "reversed" phase (Fig. 1). At  $\theta \rightarrow 0^\circ$  A/B(l) dependence remains with four peaks, however, number of areas with a "reversed" phase decreases to one. In both GIC phases at  $l \rightarrow 0$  shape of a line aims at Lorentzian. At  $l, h = \text{const}$  A/B and "phase" of the shape of a line don't depend on d.

On the basis of A/B(l) dependence (Fig. 1) for temperature studies in X-band we selected plates with  $l = 0.18$  cm for which A/B variation at phase transition is close to maximum and samples with  $l > 0.22$  cm and corresponding A/B values from "plateau" of A/B(l) curves. Regime of passage of phase transition was selected basing on the studies of temperature dependence of time  $\Delta T(T)$  from the moment of gradual variation of temperature on  $\Delta T$  to saturation of peak intensity of ESR signal. At cooling; (heating) at  $T_c^-(T_c^+) = 250 \pm 0.5$  ( $253 \pm 0.5$ ) K dependence of  $\Delta T(T)$  has a clear maximum (Fig. 2). This temperature was taken for temperature of phase transition, later on.

At  $T > T_c$  width ( $\Delta H$ ), integral intensity ( $I = (A+B) \cdot \Delta H$ ) and A/B of a line don't depend on temperature (Fig. 2). At  $T_c$  all parameters of a line experience a leap. In crystalline phase of intercalate  $\Delta H(I)$  increases (decreases) as temperature decreases. Simultaneously A/B of samples with  $l$  ( $l > 0.22$  cm) decreases to  $3.4 \pm 0.1$  ( $3. \pm 0.2$ ) in saturation obtained at  $T \sim 100$  K. Curve

$H(T)$  in the interval  $T_c - 10^\circ < T < T_c$  has a peculiarity: it consists of several linear sections with different tangents of inclination. It's notable that one of them observed at  $(T_c - 2.7)K < T < (T_c - 1.9)K$  is parallel to abscissa axis. Integral intensity of a signal does not change in this interval of temperature too. At temperature increase values of parameters of ESR line change in a reverse consequence, however, with a "global" temperature hysteresis. It's interesting that transitions between corresponding linear sections of  $\Delta H(T)$  curve of the present sample take place at the same values of parameters of the line apart from a direction of temperature variation. At powers of MWF far from saturation and at the same T,  $\Delta H$  value in Q-band  $\sim 15\%$  more than one in X-band.

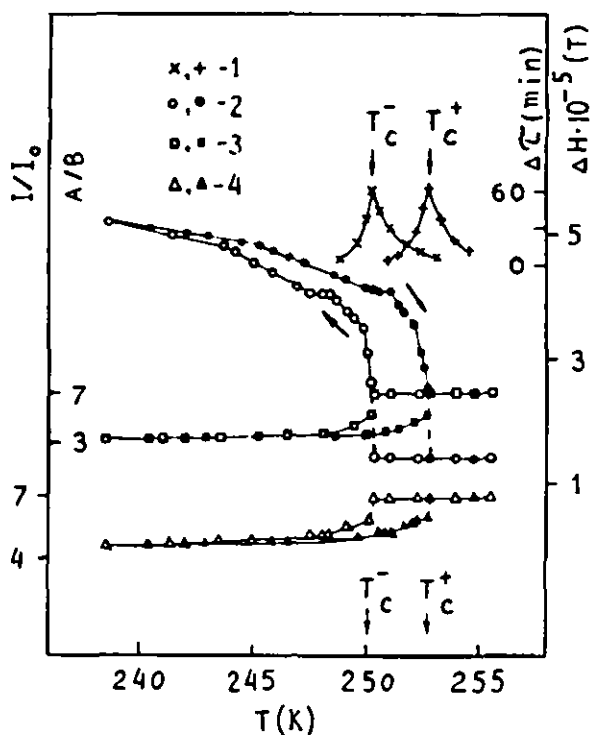


Fig.2  $\Delta\tilde{C}$  ( 1 ) and parameters of ESR line of  $C_{10}HNO_3$   $\Delta H$ ( 2 ),  $A/B$ ( 3 ) and  $I/I_0$  ( 4 ), where  $I_0$ - intensity of a standard signal, or temperature at crystallization ( melting ) of intercalate. Light ( dark ) points correspond to experimental values of parameter at cooling ( heating ) of GIC. A typical ESR line with parameters  $d = 10^{-2}$  cm,  $h = 0.5$  cm,  $l = 0.13$  cm,  $f = 9.52$  GHz.

At  $T > T_c$  binding energy ( full width on half maximum -  $\Delta E$  ) of one-peak lines of core C1s, O1s and N1s electrons  $C_{10}HNO_3$  don't depend on temperature, they are correspondingly:  $285.0 \pm 0.1$  ( $2.4 \pm 0.1$ )eV,  $533.0 \pm 0.1$  ( $2.6 \pm 0.1$ )eV and  $407.3 \pm 0.1$  ( $2.2 \pm 0.1$ )eV. At  $T_c$  all lines widen unevenly and the spectra of C1s electrons has a shape with two peaks. These peaks of C1s spectrum are situated on different sides of corresponding carbon line observed at  $T > T_c$ .  $\Delta E(T)$  curve of C1s electrons has two gentle sloping sections ( Fig. 3 ). A smooth transition between these parts takes place at such temperatures when restricted rotations of  $HNO_3$  molecules [ 6 ] are " frozen " ( "refrozen" ) at cooling (heating) of a compound studied. It is interesting that in the same temperature interval two-step temperature dependence line width of ESR of  $C_5HNO_3$  was discovered [7,8]. Width of unevenly

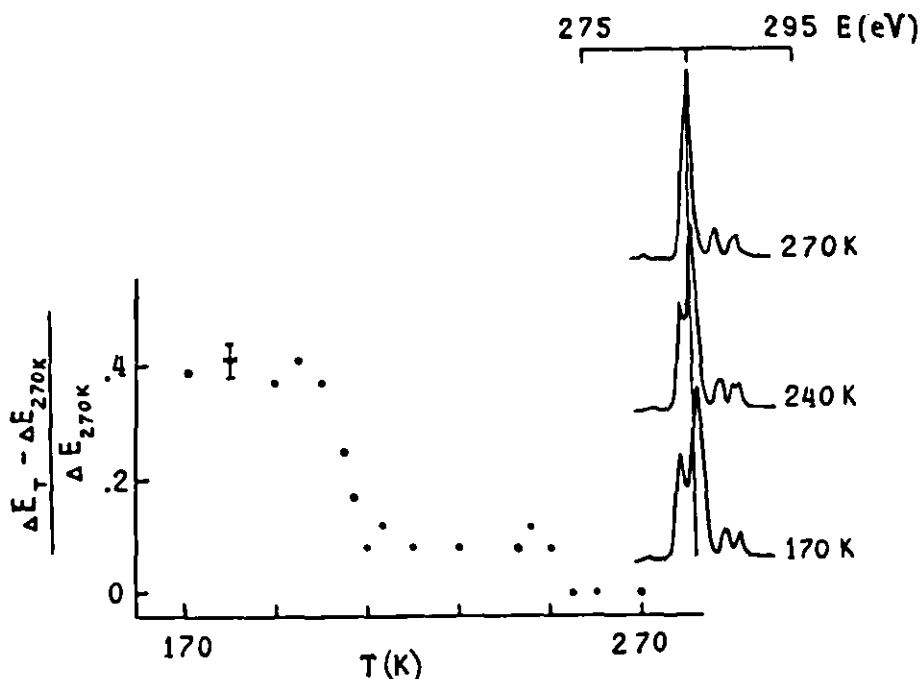


Fig.3 Temperature dependence of a line shape and relative increase of full width on half maximum  $(\Delta E_T - \Delta E_{270}) / \Delta E_{270}$  of ESCA spectrum of C1s electrons of GIC  $C_{10}HNO_3$ .

widened line of N1s electrons increases at temperature decrease and at  $T < 200K$  has a weakly expressed shape with two peaks and  $\Delta E = 2.8 \pm 0.2$  eV. At  $T < T_C$   $\Delta E$  of O1s electrons doesn't depend on temperature, and equal to  $3.0 \pm 0.1$  eV. All described variations of spectra are reverse in temperature in limits of accuracy of the experiment.

#### DISCUSSION.

Multipeaked shape of  $A/B(l)$  curve with areas of "reversed" phase of the line shape with going out at large  $l$  on the "plateau" with  $A/B > 2.55$  testifies high mobility of spin carriers at  $T > T_C$  [ 9 ]. And vice versa, one-peaked  $A/B(l)$  dependence, aimed at  $\approx 3$  at large  $l$  is typical for weakly diffusion spins in metals [ 8 ]. At phase transitions mobility of spin carriers in ESR time scale decreases and only weakly diffusion spins are present in crystalline phase of intercalate. Invariability of values of  $g$ -tensor of spin carriers at changes of aggregate states of intercalate and their closeness to  $g$ -factor of free electrons testifies that density of their probability on intercalate molecules

is small and doesn't change at phase transition. A very weak frequency dependence of  $\Delta H$  ( according to [ 10 ] being almost the same when frequency decrease up to 1.3 GHz. ) indicates that it's growth at lower  $T_c$  isn't conditioned by increase of degree of axis scattering and (or) values of g-tensor. " Non-metallic " behaviour of  $\Delta H(T)$  at GIC cooling lower  $T_c$  and correlation of  $\Delta H$  and value of reverse spin concentration allow us to hypothesize that observed ESR signal is a result of incomplete dynamic spectra averaging due to fast cross-relaxation transitions between to or more subsystems of spins weakly connected with a lattice ( electronic "bottlenecked" effect [ 11 ] ). In limits of this hypothesis widening of the line and A/B aiming at temperature decrease at values typical for weakly diffusion spins are considered to be a consequence of decrease in probabilities of averaging cross-relaxation transitions due to decrease in spin concentration (opening of "bottleneck").

Temperature variations of line shapes of core electrons are typical only for incommensurate phase of  $\alpha$ -modification of GIC with nitric acid. It proves interpretation of this properties of GIC basing on of just this peculiarity of its nature. Apparently it's necessary to exclude explanations proceeded from incommensurate modulation of covalent bonds between atoms of carbon and intercalate lower  $T_c$  because ionic interaction between sublattice [ 8, 9, 11 ]. At the same time observed variations of line shapes of core electrons can be explained by presence of CDW in surface layers of GIC.

In fact, unhomogeneous distributions of intercalate molecules kind of one-dimensional lattice of stripped domains is realized in  $C_{10}HNO_3$  lower  $T_c$  [ 2 ]. In acceptor GIC intercalate layer contains both neutral molecules and negative charged fragments [ 1, 12 ] Therefore, its crystallization and formation of mass density wave may lead to modulation of concentration of negative charge in a layer. Exciting influence of this layer on  $\pi$ -electronic graphite subsystem may initiate instability kind of CDW with a wave vector parallel to carbon planes through electron-phonon interaction. According to [ 13 ] CDW presence leads to appearance of additional energetic correction for formation of a "hole" in its core shells. It leads to widening of X-ray photoelectronic line of core-shell electrons of several atoms with transformation of their forms up to two-peaked shape at increase of CDW amplitude. At  $T < T_c$  conductivity of  $C_{10}HNO_3$  plates increases  $\sim 20\%$  [ 12 ]. It allows to assume formation in this GIC at  $T < T_c$  of CDW localized only in its surface layers.

In conclusion it's necessary to note that one-dimensional conductor  $1T-TaS_2$  is the only known compound which experiences temperature variations of X-ray photoelectron lines of core electrons of the type observed in  $C_{10}HNO_3$ . The described peculiarity of spectrum connects crystals of this compound with Peierls phase transition into state with anomalous large CDW amplitude on the surface [ 14 ]. Besides, X-ray photoelectron studies with angular resolution of valent zone of GIC  $C_8Cs$  proved presence of CDW of a new type born by interaction between sublattice of carbon and intercalate with a wave vector parallel to carbon planes and localized in surface layers of GIC only [ 15 ].

#### REFERENCES

- 1 Dresselhaus M.S., Dresselhaus G.: Adv.in Phys., 1981,30,139-326

- 
- 2 Samuelseen H.J., Moret R., Fuzellier H., Klatt M.  
Lelaurain M., Herold A.: Phys. Rev. B., 1985,32,417-427
  - 3 Clark R., Hernandez P., Honma H., Montague E.: Synth.  
Met., 1985,12,27-32
  - 4 Bottomley M.J., Parry G.S., Ubbelohde A.R.: Proc. Roy.  
Soc. London, 1964,A297,291-302
  - 5 Ubbelohde A.R.: Proc. Roy. Soc. London, 1972,A231,445-454
  - 6 Battalan F., Rosnman I., Magerl A., Fuzellier H.: Phys.  
Rev. B., 1985,32,4810-4813
  - 7 Lauginie P., Conard J., Estrade H., Guerard D., El Makhini M.,  
Lagrange P., Fuzellier H., Furdin G., Vasse R.: 14-th Biennial  
Conf. on Carbon. Extended abstracts. Penn. State Univ., 1979,  
312-313
  - 8 Lauginie P.: Unpublished date
  - 9 Kodera H.J.: Rhys. Soc. Japan, 1970,28,89-98
  - 10 Genaro A.M., Sartori J.C., Retori C., Barbers G.E.: 6-th Intern.  
Symp. on Interc. Comp.(ISIG-6). Abstracts Orlean, France, 1991, 11
  - 11 Barnes S.E.: Adv. in Phys., 1981,30,801-938
  - 12 Solin S.A.: Adv. in Chem. Phys., 1982,49,455-532
  - 13 Bishop M.F., Bose S.M., Lange P., Prutzer S.: Phys. Rev.  
B., 1987,36,9341-9244
  - 14 Hughes H.P., Pollak R.A.: Phys. Mag., 1976,34,1025-1034
  - 15 Lagues M., Fischer J.E., Marchan D., Fretigny C.: Solid  
St. Comm., 1988,67,1011-1015