



## Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl19>

## Electrical Conductivity and Conduction ESR in Incommensurate Phase of Graphite Intercalation Compounds with Nitric Acid

Albert M. Ziatdinov<sup>a</sup>

<sup>a</sup> Institute of Chemistry, Far Eastern Branch of the Russian Academy of Sciences, 159, Prosp. 100-letiya, 690022, Vladivostok, Russia

Version of record first published: 24 Sep 2006

To cite this article: Albert M. Ziatdinov (2000): Electrical Conductivity and Conduction ESR in Incommensurate Phase of Graphite Intercalation Compounds with Nitric Acid, *Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals*, 340:1, 191-196

To link to this article: <http://dx.doi.org/10.1080/10587250008025465>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Electrical Conductivity and Conduction ESR in Incommensurate Phase of Graphite Intercalation Compounds with Nitric Acid

ALBERT M. ZIATDINOV

*Institute of Chemistry, Far Eastern Branch of the Russian Academy of Sciences,  
159, Prosp. 100-letiya, 690022 Vladivostok, Russia*

Electrical conductivity and conduction ESR (CESR) of the second stage of graphite intercalation compound (GIC) with nitric acid ( $C_{10}HNO_3$ ) in its incommensurate phase (210 K < T < 250 K) are studied. Absence of the temperature dependence of the c-axis conductivity ( $\sigma_c$ ) at preservation of the « metallic » temperature dependence of the conductivity along carbon layers ( $\sigma_a$ ) is found. The analysis of the experimental data has shown that in the GIC studied the  $\sigma_c$ -conductivity realized by means of the non-band mechanism, as which one there can be mechanism of the transport of free charge carriers through the narrow high conductive paths (channels).

**Keywords:** graphite intercalation compounds;  $HNO_3$ ; electrical conductivity

### INTRODUCTION

The compound  $C_{10}HNO_3$  investigated belongs to the 2<sup>nd</sup> stage of  $\alpha$ -modification of GICs with  $HNO_3$  with the general formula  $C_{5n}HNO_3$  ( $n=1,2,3,\dots$ ). According to the data of various physical methods<sup>[1-12]</sup>, in these GICs the two-dimensional liquid-like layers of  $HNO_3$  are ordered and form a two-dimensional crystal at temperatures below  $T_c \sim 250$  K. Layers of  $HNO_3$  may be incommensurate 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  $T_{i-c} \sim 210$  K<sup>[9]</sup>. In spite of numerous publications devoted to studies of various properties of  $C_{5n}HNO_3$ <sup>[11-12]</sup>, till now the conductivity peculiarities in an incommensurate phase of these GICs have not received sufficient attention. This paper is devoted to the results of the basal plane ( $\sigma_a$ ) and the c-axis ( $\sigma_c$ ) electrical conductivity studies in incommensurate phase of  $C_{10}HNO_3$ , as well as the results of investigation of the conduction ESR (CESR) signal transformation at intercalate subsystem crystallization. The data on the  $\sigma_c$ -conductivity obtained have been analyzed within frameworks of its existing theoretical models.

## EXPERIMENTAL

All HOPG plates required for GICs synthesis (for electrical conductivity and CESR measurements) were cut out of a single bar with the  $\sigma_a$  - and  $\sigma_c$  - conductivities equal to  $(1.2 \pm 0.2) \cdot 10^4$  S/cm and  $(7.7 \pm 0.5)$  S/cm, respectively. They were in the shape of rectangular parallelepipeds with the dimensions: width ( $l$ ) $\times$ height ( $h$ ) $\times$ thickness ( $d$ ), where  $h \times l$  is the basal plane area. The effect of temperature on  $\sigma_a$  - and  $\sigma_c$  - conductivities were studied using the plate of size  $0.4 \times 0.4 \times 0.02$  и  $0.04 \times 0.4 \times 0.02$  cm<sup>3</sup>, respectively. Accuracy in determining the size of plates was  $\sim 5 \cdot 10^{-4}$  cm.

Synthesis of GIC C<sub>10</sub>HNO<sub>3</sub> was carried out in liquid nitric acid with density  $\rho \sim 1.565$  g/cm<sup>3</sup>. The GIC stage was analyzed by X-ray diffractometer.

The measurements of the  $\sigma_a$ - conductivity of C<sub>10</sub>HNO<sub>3</sub> were carried out by the contactless Wien bridge method analogous to that described in ref.<sup>[13]</sup>.

The measurements of the  $\sigma_c$ - conductivity of GICs investigated were carried out also by the contactless method with the help of a CESR technique by using the procedure suggested by Saint Jean and McRae<sup>[14]</sup>. The essence of this method of  $\sigma_a$ -determination consists in the following. In the interval  $l/\delta_c < 2$  ( $\delta_c$  is the skin-depth governed by the  $\sigma_c$  - conductivity) the asymmetry parameter of the first derivative

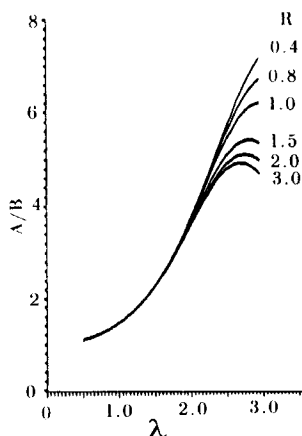


FIGURE 1 The asymmetry parameter of the first derivative of absorption line,  $A/B$ , vs. the  $\lambda = L/\delta$  ( $L$  is the sample size,  $\delta$  is the skin-depth).  $R = (T_D/T_2)^{1/2}$  ( $T_D$  is the spin diffusion time across the skin-depth  $\delta$ , and  $T_2$  is the spin-relaxation time).

of absorption line,  $A/B$ , (which is determined as the ratio of the maximum peak height,  $A$ , to the minimum peak height,  $B$ , both measured with respect to the zero line of the resonance derivative) does not depend on spin carrier mobility (Fig. 1). This enables one to determine the value of  $\delta_c$  and, consequently, the value of  $\sigma_c$ , unambiguously, by measuring the values of  $A/B$  and  $l$ .

The CESR measurements were carried out using an X-band E-line spectrometer in a rectangular cavity with TE<sub>102</sub> mode in the conventional setting of the resonator. The constant magnetic field ( $H_0$ ) modulation frequency and amplitude were 2.5 kHz and  $\sim 0.1$  mT, respectively. The temperature was varied by regulating the rate and temperature of a nitrogen gas flow through the quartz dewar with the sample. The temperature was maintained with an accuracy of  $\sim 0.1$  deg/h.

## RESULTS

Outside of an interval of existence of an incommensurate phase of  $C_{10}HNO_3$  the  $\sigma_a$  - and  $\sigma_c$  - conductivities increase at decreasing the temperature (Fig. 2). As is seen from Fig. 2, at the commensurate – incommensurate phase transition both conductivities steeply increase. Below  $T_c$  the  $\sigma_a$  - conductivity continues

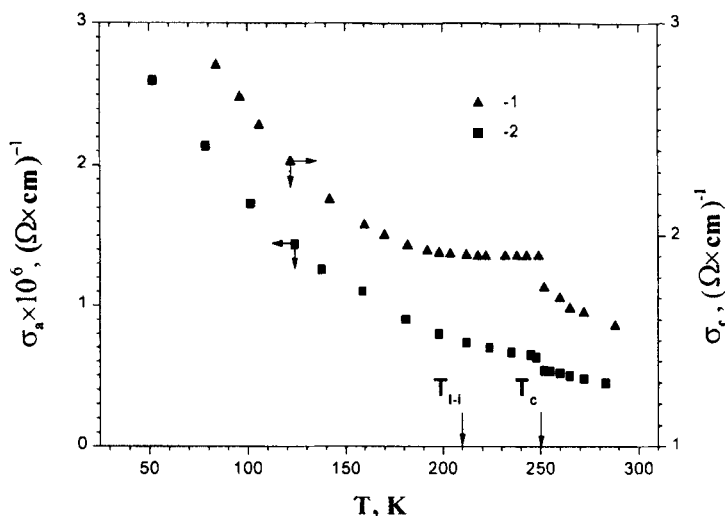


FIGURE 2 Temperature dependencies of the  $\sigma_c$  (1) – and  $\sigma_a$  (2) - conductivities in  $C_{10}HNO_3$ .

to increase monotonously, while the temperature dependence of the  $\sigma_c$  - conductivity is absent. The temperature dependence of the  $\sigma_c$  - conductivity is restored only below the “lock-in” phase transition temperature.

Over the entire temperature range of the investigations the CCSR spectrum of  $C_{10}HNO_3$  consist of single asymmetric line determined by Dyson mechanism<sup>[13]</sup>. The CCSR spectrum is axial with respect to the  $c$ - axis and is characterized by  $g_{||}=2.0023\pm0.0002$ ,  $g_{\perp}=2.0028\pm0.0002$ . At room temperature, the CCSR line width is equal to  $\Delta H_{||}=(0.38\pm0.02)\times10^{-4}$  T and  $\Delta H_{\perp}=(0.36\pm0.02)\times10^{-4}$  T. Here,  $g_{||}(\Delta H_{||})$  and  $g_{\perp}(\Delta H_{\perp})$  are values of the  $g$  - tensor (the line width) at  $H_0$  parallel and perpendicular to the  $c$ - axis, respectively. Down to  $T_c\sim 250$  K, the width of the CCSR line measured at half the height of the peak A is independent on temperature. At the intercalate crystallization the line width undergoes a stepwise increase approximately in  $\sim 3$  times. At microwave field power levels being far from saturation and the same temperature, the CCSR linewidths in the Q - and X - bands coincide, indicating that the line is homogeneously broadened.

## DISCUSSION

According to Sugihara<sup>[16-19]</sup> the main contribution to the  $\sigma_c$  - conductivity of the lowest stage ( $n = 1 \div 3$ ) GICs is from the mechanism of a charge transfer through conduction paths (conducting channels). The value of this contribution to the  $\sigma_c$  - conductivity is described as<sup>[19]</sup>

$$\sigma_c = \frac{16e^2}{\hbar^3} m^* d_l V_0^2 \left( \frac{N_c}{\Gamma} \right), \quad (1)$$

where  $V_0$  is the matrix element of the scattering potential,  $N_c$  is the number of conduction paths per unit cell,  $m^*$  is the effective mass of carriers,  $d_l$  is the distance between nearest neighbor layers with an intervening intercalate layer,  $e$  is the charge of electron,  $\hbar$  is Planck's constant, and  $\Gamma/\hbar$  - is a sum of the relaxation rates due to phonon and impurity scattering:  $\Gamma = \Gamma_{ph} + \Gamma_i$ . At high temperatures it is possible to consider  $\Gamma/\hbar$  with a good accuracy to be equal to the relaxation rate of current carriers in the graphite basal plane  $\Gamma_a/\hbar$  associated with the  $\sigma_a$  - conductivity<sup>[19,20]</sup>.

At presence of coupling of the graphite bands across the intercalant, the tight-binding calculations of the c-axis conduction lead to<sup>[20,21]</sup>

$$\sigma_c \propto K \frac{e^2}{\pi \hbar^3} d_l \left( \frac{B^2}{\Gamma} \right), \quad (2)$$

where  $K$  includes both numerical and energy-related factors,  $B$  is the c-axis interaction energy or resonance integral linking graphite states separated by an intercalate layer, and other designations have the same sense as in Exp. (1). According to Markiewicz<sup>[20,21]</sup>

$$B = B_0 \exp(-d_l/d_0),$$

where  $d_0 \cong 0.71 \text{ \AA}$ .

With neglecting the temperature changes in  $d_l$  and  $V_0$ , from Exps. (1) and (2) the conclusion follows that in GICs in some temperature interval  $\sigma_c$  - conductivity can remain constant - at presence of temperature dependence of the  $\sigma_a$  - conductivity (and, hence,  $\Gamma \propto \Gamma_a$ ), only if within this interval the complete mutual compensation of temperature changes in  $\Gamma$  and  $B^2$  (the band model) or in  $\Gamma$  and  $N_c$  (the conduction path model) takes place. Within the framework of the band model of the  $\sigma_c$  - conductivity in GICs it is not possible to find the physically reasonable mechanism, which could provide the temperature changes in  $\Gamma$  and  $B$  required for the constancy of this conductivity. And on the contrary, in the conduction path model of the  $\sigma_c$  - conductivity it is possible to specify the reason for the ratio  $N_c/\Gamma$  (which determines these conductivity according to Exp. (1)) can be independent on temperature in some GICs phases. Such reason can be high concentration of defects  $N_d$  in these

phases, when in a first approximation  $\Gamma/\hbar$  is determined only by processes of scattering of current carriers on defects, i. e.  $\Gamma/\hbar \cong \Gamma_l/\hbar \propto N_d$ . If, besides,  $N_c \propto N_d$ , it is obvious, that in GIC phases with the high content of defects, the ratio  $N_c/\Gamma$  and, according to Exp. (1), the  $\sigma_a$  - conductivity may be independent on temperature. In such GIC phases any change in  $N_d$  directly results in change of  $\sigma_a$  - conductivity. At the same time, the change in  $N_d$  can have an effect on the  $\sigma_c$  - conductivity only at its decrease and, moreover, this decrease should be so considerable that contribution of  $\Gamma_l$  to  $\Gamma$  may not be neglected. Thus, it is possible to explain absence of temperature dependence of the  $\sigma_c$  - conductivity in an incommensurate phase of  $C_{10}HNO_3$ , while temperature dependence for the  $\sigma_a$  - conductivity takes place, by occurrence of new structural defects in a sample at the incommensurate crystallization of intercalate, which concentration decreases with temperature. Let us note, that the significant CESR signal broadening ( $\sim 3$  times) at the intercalant subsystem crystallization also indirectly confirms the point of view about more defective structure of  $C_{10}HNO_3$  in its incommensurate phase.

It is known<sup>[22,23]</sup>, that in the modulated phases of crystals, alongside with the orientational domains, wide domain walls between the translational domains ("stripe-domains") and structural solitons can take place. As the "lock-in" transition temperature is approached, the concentration of these structural imperfections decreases. According to the X-ray data<sup>[9]</sup>, the similar structural imperfections can take place in  $C_{10}HNO_3$  below the intercalant crystallization temperature. The research data by the method of quasielastic neutron scattering of  $C_{10}HNO_3$ <sup>[10]</sup> confirm this conclusion and, besides, testify the decrease of the "stripe-domain" concentration, as the "lock-in" transition temperature is approached. Hence, if in an incommensurate phase of  $C_{10}HNO_3$   $\Gamma_{ph} \gg \Gamma_l$  and some part of high-conductive paths (channels) formed at intercalate crystallization is caused by "stripe-domains" or structural solitons in intercalate layers, then the decrease of their concentration at approach to the "lock-in" - transition temperature can result in the  $\sigma_a$  - conductivity increase, which can occur at constant value of the  $\sigma_c$  - conductivity. From above consideration it follows also, that in some phases of GICs the «metallic» temperature dependence of  $\sigma_a$  - conductivity first of all can be determined not by the decrease in amplitudes of thermal oscillations of atoms in carbon and intercalate layers, but the in plane intercalant structural ordering.

Before in the literature the problem of searching and analysis of possible anomalous features of electrical conductivity in incommensurate phases of the GICs was not considered. At the same time, our analysis of the literature has shown, that among GICs, for which the temperature dependence of  $\sigma_c$  - conductivity was studied, there are some compounds with structural incommensurate phases. They are acceptor GICs of 3-d, 4-th and 6-th stages with  $SbCl_5$ <sup>[24]</sup>, in which the intercalate subsystem at  $T \approx 210$  K undergoes a phase transition into the structural incommensurate phase<sup>[25]</sup>. In all these GICs the absolute value of temperature coefficient of  $\sigma_a$  - conductivity decreases at incommensurate phase transition and it remains small (in compounds of 3-d

and 4-th stages it is absent in fact) in a broad temperature range ( $\Delta T \approx 100$  K) below the phase transition temperature. These facts suggest, that the temperature invariance of the  $\sigma_c$  - conductivity revealed by us in an incommensurate phase of  $C_{10}HNO_3$  can be a characteristic feature of all structural incommensurate phases of acceptor GICs.

### Acknowledgments

The author is grateful to N.M. Mishchenko and V.V. Sereda for help in experiments and to L.B. Nepomnyashchii (Scientific Research Centre for Graphite, Moscow) for providing the HOPG samples. This work was supported by the Russian Foundation for Basic Research (grant № 97-03-33346).

### References

- [1] M. Bottomley, G.S. Parry, and A.R. Ubbelohde, *Proc. Roy. Soc. (London)*, **A 279**, 291(1964).
- [2] D.E. Nixon, G.S. Parry, and A.R. Ubbelohde, *Proc. Roy. Soc. (London)*, **A 291**, 324(1966).
- [3] A.R. Ubbelohde, *Carbon*, **6**, 177(1966).
- [4] A.R. Ubbelohde, *Proc. Roy. Soc. (London)*, **A 304**, 25(1968).
- [5] K. Kawamura, T. Saito, and T. Tsuzuku, *Carbon*, **13**, 452(1975).
- [6] A. Avagadro and M. Villa, *J. Chem. Phys.*, **66**, 2359(1977).
- [7] S.K. Khanna, E.R. Falardeau, A.J. Heeger, and J.E. Fischer, *Solid State Comm.*, **25**, 1059(1978).
- [8] A. Dvorkin and A.R. Ubbelohde, *Carbon*, **16**, 291(1978).
- [9] E.J. Samuelson, R. Moret, H. Fuzellier, M. Klatt M. Lelaurain, and A. Herold, *Phys. Rev. B*, **32**, 417(1985).
- [10] F. Batallan, I. Rosenman, A. Magerl and H. Fuzellier, *Phys. Rev. B.*, **32**, 4810(1985).
- [11] A.M. Ziatdinov and N.M. Mishchenko, *J. Phys. Chem. Solids*, **58**, 1161(1997).
- [12] A.M. Ziatdinov and N.M. Mishchenko, *Solid State Comm.*, **97**, 1085(1996).
- [13] L. A. Pendry, C. Zeller and F.L. Vogel, *J. Mat. Sci.*, **15**, 2103(1980).
- [14] M. Saint Jean and E. McRae, *Phys. Rev. B*, **43**, 3969(1991).
- [15] F.J. Dyson, *Phys. Rev.*, **98**, 349(1955).
- [16] K. Sugihara, *Phys. Rev. B.*, **29**, 5872(1984).
- [17] K. Sugihara, *Phys. Rev. B.*, **37**, 4752(1988).
- [18] K. Sugihara, *J. Phys Soc. Jpn.*, **62**, 624(1993).
- [19] M. Suzuki, C. Lee, I.S. Suzuki, K. Matsubara, and K. Sugihara, *Phys. Rev. B.*, **54**, 17128(1996).
- [20] R.S. Markiewicz, *Solid State Comm.*, **57**, 237(1986).
- [21] R.S. Markiewicz, *Phys. Rev. B.*, **37**, 6453(1988).
- [22] A.O. Bruce and R.A. Cowley, *J. Phys.*, **C11**, 3577(1978).
- [23] P. Bak, *Rep. Prog. Phys.*, **45**, 587(1982).
- [24] C. Uher and D.T. Morelli, *Mat. Res. Soc.*, **20**, 163(1983).
- [25] H. Homma and R. Clarke, *Phys. Rev. B*, **31**, 5865(1985).