Mol. Cryst. and Liq. Cryst., 2000, Vol. 340, pp. 191-196
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Printed in Malaysia

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

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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 (σ_c) at preservation of the « metallic » temperature dependence of the conductivity along carbon layers (σ_a) is found. The analysis of the experimental data has shown that in the GIC studied the σ_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 2nd stage of α - modification of GICs with HNO_3 with the general formula $C_{5n}HNO_3$ (n=1,2,3,..). According to the data of various physical methods[1-12], 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~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 $T_{i\text{-}c}$ ~210 K[9]. In spite of numerous publications devoted to studies of various properties of $C_{5n}HNO_3$[1-12], 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 (σ_a) and the c-axis (σ_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 σ_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 σ_a - and σ_c - conductivities equal to $(1.2\pm0.2)\cdot10^4$ S/cm and (7.7 ± 0.5) S/cm, respectively. They were in the shape of rectangular parallelepipeds with the dimensions: width (*l*)×height (*h*)×thickness (*d*), where *h*×*l* is the basal plane area. The effect of temperature on σ_a – and σ_c – conductivities were studied using the plate of size 0.4×0.4×0.02 и 0.04×0.4×0.02 cm^3, respectively. Accuracy in determining the size of plates was $\sim5\cdot10^{-4}$ cm.

Synthesis of GIC $C_{10}HNO_3$ was carried out in liquid nitric acid with density $\rho \sim 1.565$ g/cm^3. The GIC stage was analyzed by X-ray diffractometer.

The measurements of the σ_a– conductivity of $C_{10}HNO_3$ were carried out by the contactless Wien bridge method analogous to that described in ref.[13].

The measurements of the σ_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[14]. The essence of this method of σ_a-determination consists in the following. In the interval $l/\delta_c < 2$ (δ_c is the skin-depth governed by the σ_c - conductivity) the asymmetry parameter of the first derivative 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 δ_c and, consequently, the value of σ_c, unambiguously, by measuring the values of A/B and *l*.

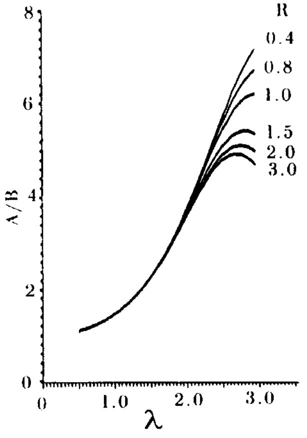

FIGURE 1 The asymmetry parameter of the first derivative of absorption line, A/B, vs. the $\lambda=L/\delta$ (L is the sample size, δ is the skin-depth). $R=(T_D/T_2)^{1/2}$ (T_D is the spin diffusion time across the skin-depth δ, and T_2 is the spin-relaxation time).

The CESR measurements were carried out using an X-band E-line spectrometer in a rectangular cavity with TE_{102} mode in the conventional setting of the resonator. The constant magnetic field ($\mathbf{H}_0$) modulation frequency and amplitude were 2.5 kHz and ~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 ~0.1 deg/h.

RESULTS

Outside of an interval of existence of an incommensurate phase of $C_{10}HNO_3$ the σ_a - and σ_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 σ_a – conductivity continues to increase monotonously, while the temperature dependence of the σ_c - conductivity is absent. The temperature dependence of the σ_c - conductivity is restored only below the "lock-in" phase transition temperature.

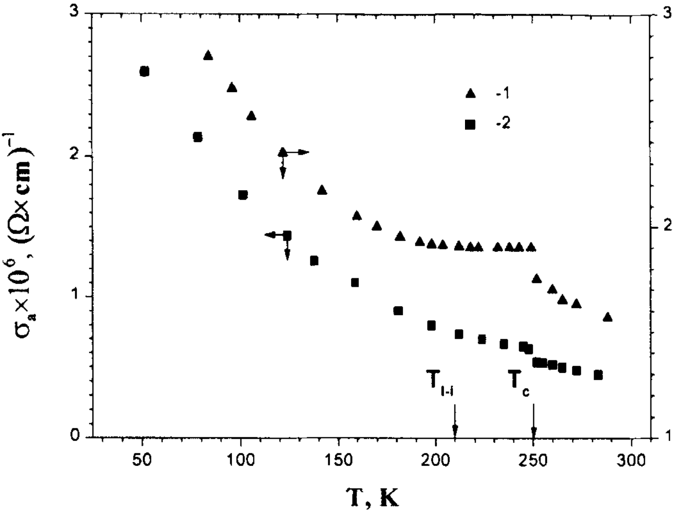

FIGURE 2 Temperature dependencies of the σ_c (1) – and σ_a (2) - conductivities in $C_{10}HNO_3$.

Over the entire temperature range of the investigations the CESR spectrum of $C_{10}HNO_3$ consist of single asymmetric line determined by Dyson mechanism[15]. The CESR spectrum is axial with respect to the c– axis and is characterized by $g_{\parallel}=2.0023\pm0.0002$, $g_{\perp}=2.0028\pm0.0002$. At room temperature, the CESR line width is equal to $\Delta H_{\parallel}=(0.38\pm0.02)\times10^{-4}$ T and $\Delta H_{\perp}=(0.36\pm0.02)\times10^{-4}$ T. Here, $g_{\parallel}$ $(\Delta H_{\parallel})$ 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~250 K, the width of the CESR 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 ~3 times. At microwave field power levels being far from saturation and the same temperature, the CESR linewidths in the Q – and X – bands coincide, indicating that the line is homogeneously broadened.

DISCUSSION

According to Sugihara[16-19] the main contribution to the σ_c - conductivity of the lowest stage (n = 1÷3) GICs is from the mechanism of a charge transfer through conduction paths (conducting channels). The value of this contribution to the σ_c - conductivity is described as[19]

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

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_I 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 σ_a - conductivity[19,20].

At presence of coupling of the graphite bands across the intercalant, the tight-binding calculations of the **c**-axis conduction lead to[20,21].

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

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 Markiewich [20,21]

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

where $d_0 \cong 0.71$ Å.

With neglecting the temperature changes in d_I and V_0, from Exps. (1) and (2) the conclusion follows that in GICs in some temperature interval σ_c - conductivity can remain constant - at presence of temperature dependence of the σ_a - conductivity (and, hencive, $\Gamma \propto \Gamma_a$), only if within this interval the complete mutual compensation of temperature changes in Γ and B^2 (the band model) or in Γ and N_c (the conduction path model) takes place. Within the framework of the band model of the σ_c - conductivity in GICs it is not possible to find the physically reasonable mechanism, which could provide the temperature changes in Γ and B required for the constancy of this conductivity. And on the contrary, in the conduction path model of the σ_c - conductivity it is possible to specify the reason for the ratio N_c/Γ (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/Γ and, according to Exp. (1), the σ_a – conductivity may be independent on temperature. In such GIC phases any change in N_d directly results in change of σ_a - conductivity. At the same time, the change in N_d can have an effect on the σ_c - conductivity only at its decrease and, moreover, this decrease should be so considerable that contribution of Γ_l to Γ may not be neglected. Thus, it is possible to explain absence of temperature dependence of the σ_c – conductivity in an incommensurate phase of $C_{10}HNO_3$, while temperature dependence for the σ_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 (~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[22,23], 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[9], 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 $C_{10}HNO_3$[10] 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 σ_a – conductivity increase, which can occur at constant value of the σ_c – conductivity. From above consideration it follows also, that in some phases of GICs the «metallic» temperature dependence of σ_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 σ_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 $SbCl_5$[24], in which the intercalate subsystem at T≈210 K undergoes a phase transition into the structural incommensurate phase[25]. In all these GICs the absolute value of temperature coefficient of σ_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 σ_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).

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