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MAGNETIC RESONANCE & RELATED PHENOMENA

Extended Abstract

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SPIN RESONANCE ON ATOMIC AND BAND ELECTRONS IN INCOMMENSURATE SYSTEMS: A COMPARISON STUDY

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Abstract

A short review of our recent EPR experimental and theoretical reseach work results of the phase transitions and incommensurate states in dielectric improper ferroelastics of the type $ABF_6.6H_2O$ (A -divalent and B - fourvalent metal) and conductive acceptor graphite intercalation compounds (GICs) are presented with more emphasis on early unknown common properties of this incommensurate materials.

A lack of the generally accepted translational symmetry in incommensurate states removes some limitations for the crystal structure organization. Therefore, incommensurate systems are potential carriers of new physical properties.[1] Magnetic resonance methods are powerful techniques for studing of such systems.[2] In this review our recent investigation results of incommensurate phases of dielectric crystals $ABF_6.6H_2O$ and conductive acceptor GICs are presented.

It has been found and investigated by means of 3d-ions EPR and conduction ESR (CESR):

- the incommensurate phases of the crystals $MgBF_6.6H_2O$ (B- Si, Ge, Ti) and of the mixed ferroelastics of the type $(Mg,Zn)BF_6.6H_2O$;[3]
- the order parameter of the paraelastic phase - incommensurate phase transition in above mentioned crystals, which is a rotation angle of the complex ions around the crystal C-axis relative to their position in the paraelastic phase;

two anti-phase lattice displacement modulation waves of the type: $F(x,T) = F_o(T)\cos w(x) \pm dF(T)$, where $F_o(T)$ and $w(x)$ are the modulation wave amplitude and phase; the critical temperature dependence of the parameters $F_o(T)$ and $dF(T)$ near the phase transition temperature;

- the succession of modulated states in crystals $MgBF_8.6H_2O$[3,4] and in GICs $C_{5n}HNO_3$,[3,5] which can not be unambiguously reduced to the well known "devil's staircase" of discreate changes in the modulation wave vector;

- the influence of defects on phase transitions and incommensurate states;

- the "nonmetallic" temperature dependence of the GICs CESR line width and the decrease of spin carriers mobility during and after incommensurate crystallization of the "guest" molecules subsystem;[5]

- the current carriers injection phenomenon at incommensurate crystallization of "guest" molecule layers in acceptor GICs[5];

- effect of "guest" molecules subsystem dimension on phase transitions and incommensurate states in GICs $C_{5n}HNO_3$ ($n = 2 \div 5$), including the GIC stage index (n) dependence of phase transition temperatures;

- the "devil's staircase" type process, realizing at graphite intercalation from gase phase.[6]

This results of the investigations will be discussed in details at the Congress.

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CONDUCTION ESR AND CURRENT CARRIER INJECTION PHENOMENON AT INCOMMENSURATE CRYSTALLIZATION OF "GUEST" MOLECULE LAYERS IN ACCEPTOR GRAPHITE INTERCALATION COMPOUNDS

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Abstract

In acceptor graphite intercalation compounds (GICs) was found and investigated the simultaneous increase of conductivity, conduction ESR (CESR) line width and spin carriers concentration (N). It was shown by means of the CESR method that the increase of N is directly connected with the partial localization of the conduction electrons. It has been proposed, that the increase of localized electrons concentration is the main reason for the decrease (the increase) of the in plane spin carriers mobility and nonmetallic increase (the CESR line width).

The systematic investigation of the effect of temperature on the CESR spectra of GICs were realized with the 2D CESR line shape analysis procedure developed by authors.[1,2] Conductivities σ(c) and σ(a) of investigated GICs have also been measured. As a result, we established

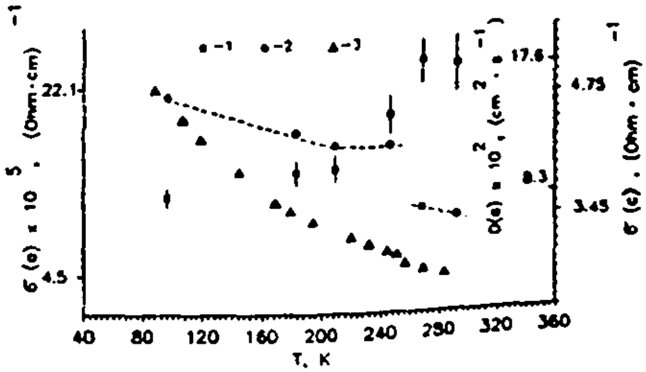

Fig.1 Temperature dependence of D(a)-1, σ(c)-2 and σ(a)-3 in $C_{10}HNO_3$

an earlier unknown phenomenon: if layers of "guest" molecules undergo an aggregate or a 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 σ(a) increase in spite the decrease (!) of the charge carrier mobility (Fig.1). CESR measurements of charge carrier concentration (N) vs. temperature show (Fig.2) that this unusual "nonmetallic " behaviour of GICs results from the increase of the current carrier concentration 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 the current carrier concentration in π-bands indicates that in some GICs phase transitions are "triggers" for the process of reoxidation of graphite layers.

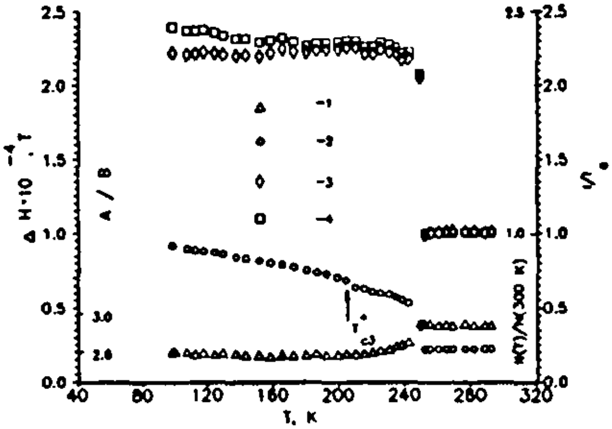

Fig.2. CESR line shape parameters in $C_{10}HNO_3$ vs. T. 1,2,3 and 4 correspond to A/B, $\Delta H_{1/2}$, $I=(A+B)\cdot\Delta H^2$ and $N(T)\sim(I/I_0)\cdot(\sigma(c))^{1/2}$, respectively.

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CONDUCTION ELECTRON SPIN RESONANCE IN ANISOTROPIC CONDUCTORS: GRAPHITE AND ITS ACCEPTOR INTERCALATION COMPOUNDS

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Abstract

The results of experimental investigations and theoretical analysis of the current carriers ESR line shape in anisotropic conductors (graphite and its acceptor type intercalation compounds) are presented.

The effects of sample size, electromagnetic configuration, magnetic field modulation frequency and temperature on the line-shape and intensity of the conduction electron spin resonance (CESR) was investigated in graphite and its acceptor type intercalation compounds. The theoretical analysis of the line-shape are carried out in limits of the two-dimensional modification of the Dyson - Kaplan model and within this model the qualitative explanation of the all observed peculiarities of the experimental curves were obtained. In graphite to achieve a quantitative conformity it requires, in addition, to take into consideration the dependence of the ratio of the mean values of this amplitude at the nonequivalent faces on a sample size. Using this model, we propose an experimental procedure to determine the two - dimensional diffusion constant of current carriers and c- axis resistivity from CESR spectra of anisotropic conductors.[1]

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CONDUCTION ELECTRON SPIN RESONANCE AND AN *IN SITU* STUDY OF THE KINETICS AND PLANAR INTERCALATE DIFFUSION CONSTANT IN ACCEPTOR GRAPHITE INTERCALATION COMPOUNDS

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Abstract

The results of an *in situ* conduction ESR (CESR) studies by two - zone vapour transport method, of the intercalation process of nitric acid molecules into highly oriented pyrolytic graphite (HOPG) are presented.

The application of the newly, developed procedure[1] of CESR *in situ* experiments of HOPG intercalation has allowed us to study individual reactions steps (Fig.1) and to discover two essentially different intercalation mechanisms: a slow diffusion of the intercalate through sides parallel to the c-axis in the whole thikness of a sample and a relatively faster nucleation of a new phase in the near surface galleries. Each of these intercalation mechanisms is characterized by an " induction period " during which graphite takes up comparatively little intercalant and by the index (n) of the stage appearing of its own. In the HOPG plates with protected ba-

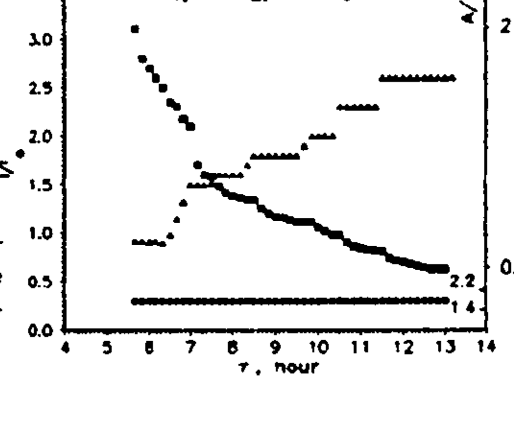
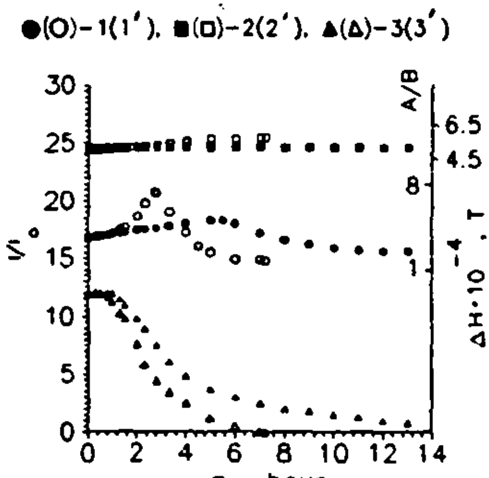


Fig.1. CESR line shape parameters of the (HOPG+HNO_3) system vs exposure time (τ). 1, 2 and 3 corresponds to ΔH, A/B and $I/I_0 = (A+B)\cdot\Delta H^2$.

sal planes the second of the above - mentioned intercalation mechanisms is ineffective. This fact suggests that the near surface intercalation is probably due to the formation of charge density waves in surface layers during the initial period of the intercalation. By assuming that the centres of perturbation of conduction electron spin wave functions are situated preferentially at the edges of the Dumas - Herold islands, the decrease of CESR line width vs. exposure time (Fig. 2) can be attributed to the decrease in the number and the increase size of intercalate islands as the intercalate concentration increases. Because of this, after formation the initial stage of GIC, the increase of the basal plane conductivity vs. exposure time may be due to the increase of charge carrier mobility, rather than the increase of its concentration.

Fig.2. CESR line shape parameters of graphite vs. exposure time (T) 1(1'), 2(2') and 3(3') correspond to A/B, ΔH and $1/I_o = (A+B)\cdot\Delta H^2$ for plate with protected (unprotected) basal plane. I_o is the ESR line intensity of a standard sample $ZnS:Mn^{2+}$.



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