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CONDUCTION ELECTRON SPIN RESONANCE IN GRAPHITE INTERCALATION COMPOUNDS

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Abstract: This paper intends to briefly review on recent progress in understanding the conduction electron spin resonance (CESR) phenomenon in graphite intercalation compounds. Emphasis will be placed on the following points: (1) correct line shape analysis in anisotropic conductors; (2) possible mechanisms of spin-relaxation and reasons of the CESR linewidth temperature dependence; (3) origin of the g-factor value and reasons of its temperature dependence.

I. INTRODUCTION

Conduction Electron Spin Resonance (CESR) is one of the most powerful methods of the study of the dynamic properties of carriers in conductors. The analysis of CESR lineshape and linewidth may yield information on physical characteristics of the resonance and conductors: the electrical conductivity, the spin relaxation time, the gyromagnetic factor, the electron state density on the Fermi surface, as well as the carrier diffusion constant [1-13]. It is just natural, therefore, that this powerful techniques should have been extensively applied to graphite and graphite intercalation compounds (GICs) to study the electronic and other properties of these anisotropic conductors.

Graphite is a well known compound which consist of honeycomb layers of carbon atoms strongly linked by covalent bonds with only weak interlayer forces as evidenced by the in plane and out of plane carbon-carbon distances. Many significant features of the electronic properties of graphite, such as the large basal plane electroconductivity and the large anisotropy of electroconductivity, the "metallic" and "non-metallic" temperature dependence of electroconductivity along and perpendicular to the basal plane, respectively, steams from the fact that graphite is a quasi-two-dimensional semimetal [14, 15]. Accordingly, the electronic structure and properties of this material [14] are significantly different from those in an insulator, semiconductor, or metal.

Because carbon occupies a middle position in the order of electronegativity of the elements in the periodic table, graphite welcomes many chemicals as guests, or intercalants, making it possible to produce a large number of new metallic materials known as GICs [16, 17]. The intercalation process is usually accompanied by charge transfer between the intercalate species and the graphite layers. Similar to doped semiconductors they are classified as "donor" GICs or "acceptor" GICs depending on whether the inserted species donate or accept an electron. The intercalation process usually occurs without disrupting the integrity of the carbon sheets, but the interplanar bonds are weak and easily to be broken.

GICs consist of an alternating sequence of n -hexagonal graphite monolayers ($n = 1, 2 \dots$ is called the "stage" of the compound) and a monolayer of guest (intercalant) atoms or molecules (Fig. 1). The ability to vary the strength of interlayer interaction at the synthetic level, by varying the stage, suggests the possibility of systematically investigating phenomena unique to two dimensions, such as anomalous behavior of phase transitions (e.g. melting), highly anisotropic electron-phonon interactions, and Fermi-surface-driven lattice instabilities [16]. Researchers have also found new kinds of

phase transitions between stages [18], two-dimensional metals with electron mobilities higher than those of ordinary metals, such as copper [19], superconductivity [20], two-dimensional hydrogen hole band with a heavy mass [21], magnetic [22], charge density wave type [23] and commensurate-incommensurate type [24] phase transitions and etc. Because of these phenomena, GICs have completely changed the ordinary concept of metals and thus in recent years have aroused great interest among physicist, chemists and materials scientists.

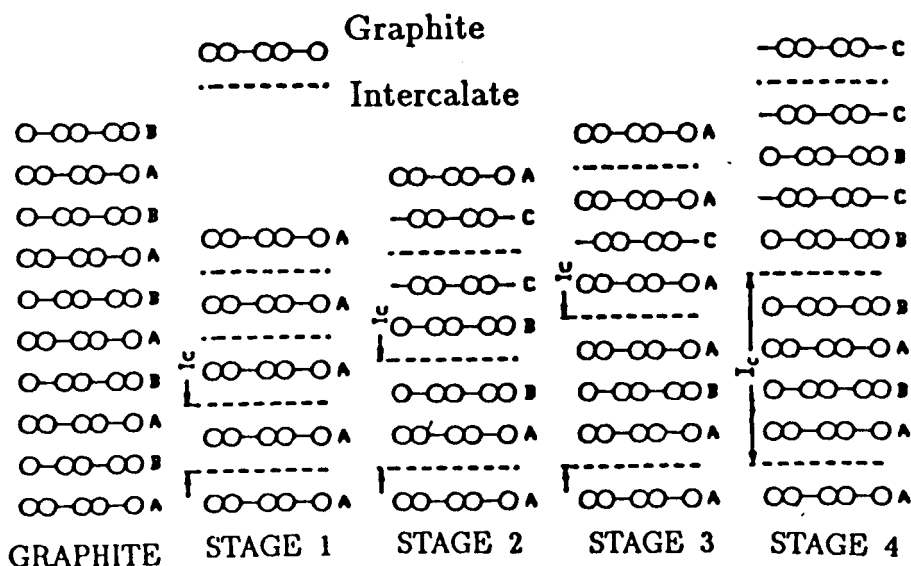


Fig. 1. Schematic diagram illustrating the staging phenomenon in graphite intercalation compounds. The intercalant layers are indicated by dashed lines and the graphite layers by solid lines connecting open circles, and indicating schematically a projection of the carbon atom positions. For each stage, the distance l_c between adjacent intercalate layers is indicated

In this article a short review on developments in the field of CESR in GICs with emphasis on the stage and temperature dependence of the g -factor, spin relaxation time and lineshape obtained for different donor and acceptor GICs is presented. These results are qualitatively discussed and compared with the existing theories.

II. EXPERIMENTAL DATA AND THEORIES

In GICs, as in other metallic systems, the resonant absorption is accompanied by another absorption process due to the eddy current induced by the hyperfrequency electromagnetic field. Both absorption are coupled and determine the field and current distributions in the medium. The direct magnetic resonance absorption with the small variations of the strong conduction losses leads to the characteristic asymmetric Dysonian shape of the resonance line in the derivative absorption spectra (Fig. 2). But in GICs, as in anisotropic conductors, the Dyson theory [1] and currently used Feher-Kip [5] or Kodera [7] procedures, which have been developed to interpret the CESR spectra in isotropic metals are not appropriate. In this context the situation is analogous with the case of the CESR in graphite, which was considered in [25] in detail. In other aspects the CESR in GICs, such as the g -shift and linewidth values, its temperature dependence and the origin of resonance parameters may be

quite different from those in graphite. In the following subsections of this chapter the present state of the experimental and theoretical investigations of the CESR in GICs are reviewed.

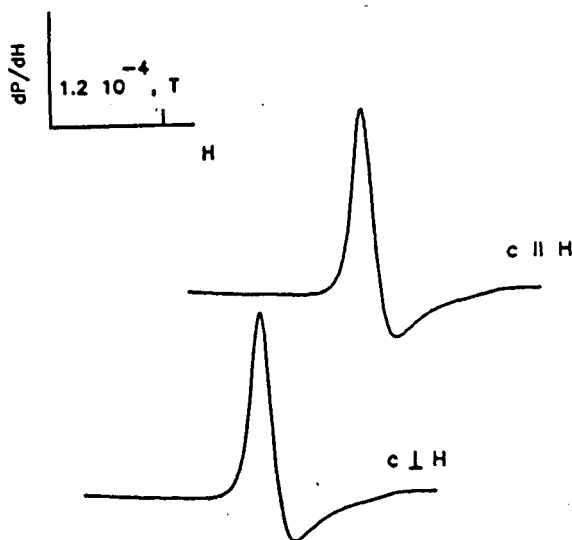


Fig. 2. Typical spin-resonance derivative curves for graphite intercalation compounds: $C_{10}HNO_3$ with dimensions $0.4 \times 0.4 \times 0.035 \text{ cm}^3$, $\nu = 9.52 \text{ GHz}$, $T = 300 \text{ K}$

CESR lineshape in GICs.

Due to the large anisotropy skin depths and conductivities, as well as anisotropy carrier diffusion, the application of the simple Dyson-Kaplan [1,2] theories to the case of GICs, as in the case of graphite [25], is not obvious. First, it was pointed out by Blinowski et al. [26] and Saint Jean et al. [27]. Following Kaplan [2] they have written the following, Bloch type, equation of the motion for the magnetization \mathbf{M} as

$$\begin{aligned} d\mathbf{M}/dt = (2\pi g \beta/h) [(\mathbf{M} + \mathbf{M}_0) \times (\mathbf{H} + \mathbf{H})] - \mathbf{M}_\parallel/T_1 - \\ - \mathbf{M}_\perp/T_2 + D_a(d^2\mathbf{M}/dy^2) + D_c(d^2\mathbf{M}/dz^2) \end{aligned} \quad (1)$$

where M_\parallel and M_\perp are the longitudinal and the transverse components of \mathbf{M} ; the oscillating magnetic field and magnetization are $\mathbf{H} \exp(-i\omega t)$ and $\mathbf{M} \exp(-i\omega t)$, D_a and D_c are diffusion coefficients along the planes and the c -axis, respectively, and \mathbf{M}_0 is the equilibrium magnetization. The x and y axis situated in the basal plane, the z axis and external constant magnetic field \mathbf{H} situated along the c -axis. Neglecting quadratic and higher orders in the expansion of M_x and using the standard boundary condition that the component of the gradient in (1) vanishes at the surface of the sample, Blinowski et al. [26] and Saint-Jean et al. [27] have obtained a solution for the transverse part of magnetization $M_x(\omega)$. The power absorption, F , was calculated and the line shape asymmetry parameter A/B was estimated from dF/dH . The results were given graphically as a function of the dimensionless parameters $q = d/\delta_a$ and $p = l/\delta_c$ (d and l are the dimensions of GIC plate along the c -axis and in the basal plane, respectively; δ_c and δ_a are the skin depths, which are determined by the c -axis (σ_c) and the basal plane (σ_a) conductivities, respectively) for the following limiting cases:

- 1) Very slow diffusion limit: $T_{Da} \gg T_2$ and $T_{Dc} \gg T_2$.
- 2) Very rapid diffusion limit: $T_{Da} \ll T_2$ and $T_{Dc} \ll T_2$.
- 3) Mixed cases: a) $T_{Dc} \gg T_2$ and $T_{Da} \ll T_2$ or b) $T_{Dc} \ll T_2$ and $T_{Da} \gg T_2$.

Here $T_{Dc} = \delta_a^2/2D_c$ and $T_{Da} = \delta_c^2/2D_a$ are the average times of diffusion of electrons across the skin depth along and perpendicular to the c -axis, respectively.

The calculations clearly indicate [26, 27] that whatever the diffusion regime the A/B ratio is very sensitive to the value of p (except for very thin samples with $q = d/\delta_a \ll 1$). As long as p is not much bigger than q the penetration of the radio frequency field through the sample borders parallel to the c -axis may not be neglected and for p smaller than q this way of penetration may even be dominant.

In the limit $p/q \rightarrow 0$ (say, $p/q < 0.01$) practically all the microwave power is absorbed via the sample borders. Then A/B ratio does not depend on the diffusion regime along the c -axis and can be interpreted with the use of the one-dimensional Dyson formula involving σ_c and T_{Da} . This case corresponds to the experimental conditions for highly anisotropy acceptor GIC e.g. AsF_5 - graphite.

For less anisotropic GICs e.g. low stage donor compounds, one has typically both p and q of the order of 100 or more. In these conditions the power absorbed on the sample faces perpendicular to the c -axis, as well as that absorbed on the borders parallel to the c -axis can again be calculated from the one-dimensional theory. The observed A/B ratio depends however on the total power absorbed in the sample and might therefore be a complicated function of σ_a , σ_c , T_{Da} and T_{Dc} .

Unfortunately, the above calculations of Blinowski et al. [26] and Saint Jean et al. [27] are inapplicable for the qualitative analysis of the CESR experimental data. Such limitedness of their calculations is associated directly with the author's assumptions on uniform distribution of the microwave field around the sample and on the independence of this distribution on the sample dimensions. In [25], using the graphite as an example, it was shown, that this assumption does not hold in anisotropic conductors. Therefore, it can be said, that at present, the completed theory of the CESR lineshape in GICs is still absent.

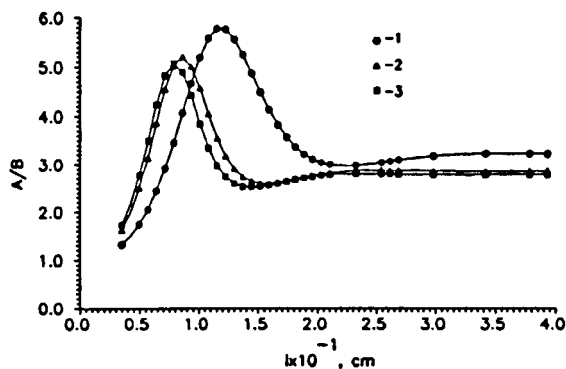


Fig. 3. The experimental (filled symbols) and theoretical (solid lines) values of the line asymmetry parameter A/B of the $\text{C}_{20}\text{HNO}_3$ plates with dimensions $l \times 0.4 \times 0.02 \text{ cm}^3$ as a function of sample width (l). The experimental curves 1, 2 and 3 correspond to 300 K, 220 K and 174 K, respectively. $\text{H} \perp c$, $\nu = 9.52 \text{ GHz}$. The theoretical curves at 300 K, 220 K and 174 K are one-dimensional Dyson's curves with $\sigma_c = 1.6, 2.74$ and $3.13 (\text{Ohm cm})^{-1}$, $R_a = (T_{Da}/T_2)^{1/2} = 1.2, 1.8$ and 2.1 , and $T_2 = 2.84, 2.1$ and 1.97 in the units of 10^{-8} s. , respectively

In acceptor GICs one may neglect the absorption of the microwave field through the basal planes and, consequently, the contribution to the CESR from regions adjacent to this planes due to the high conduction anisotropy ($\sim 10^5$). Only in this particular case the CESR line shape may be analyzed using the one-dimensional Dyson [1] expression with $\sigma = \sigma_c$ and $T_D = T_{Da}$ (and not σ_a and T_{Dc} !). In Fig. 3, as an example, for acceptor GICs $\text{C}_{20}\text{HNO}_3$, our experimental data for the dependence of the asymmetry parameter A/B on a sample width (l) are presented. From this figure it can be seen that really the experimental points are approximated by the theoretical curves $A/B(l)$ calculated on the basis of the one-dimensional Dyson [1] expression with $\sigma = \sigma_c$ and $T_D = T_{Da}$ very well.

g-factor of conduction electrons in GICs

Unlike pure graphite for which the shift of g -value from the free electron g -value at external magnetic field being along the c -axis, Δg_c , is about 0.05, GICs based on HOPG show only little anisotropy in the g -value. This was recognized, first, by Muller and Kleiner [28] for the donor type graphite-alkali metal compounds. Since this pioneering work, CESR was observed for a large class of donor and acceptor type GICs with well defined stages and even on residue compounds [29-36]. In all cases the spectra exhibit a single Dysonian lineshape with the g -factor around the free electron value and with a very small anisotropy in the field for resonance. At present no clear systematics of this anisotropy across the various systems exist.

In GICs, the theoretical derivations of Δg_c and Δg_a (the shift of g -value from the free electron g -value at external magnetic field being perpendicular to the c -axis) are limited. In the framework of the band structure of GIC's developed by Blinowski and Rigaux [37], Sugihara et al. have calculated Δg_i ($i = a, c$) for stage 2 [38] and 4 [39]. For stage 2, symmetry arguments previously developed by Dresselhaus et al. for three-dimensional graphite [40] have been used to determine the non-vanishing coefficients of the spin-orbit hamiltonian. Generalization to stage 4 is immediate. In this model, the magnetic field perpendicular to the layers was introduced following the Luttinger-Kohn formalism [41], the hamiltonian matrix with the spin-orbit interaction being developed to first order in perturbation. In both cases, the calculated average value of Δg_i ($i = a, c$) is strictly zero. These theoretical results are not in agreement with the experimental studies which exhibit small but finite values of Δg_i ($i = a, c$). Moreover, the application of this procedure to the first stage would result in a zero Δg_i ($i = a, c$), in contrast with the theoretical derivation for two-dimensional graphite [42].

The failure of this model is linked to the limitation to the first order in Luttinger-Kohn formalism. This approximation, used by McClure [43] to describe the case of three-dimensional graphite, is unjustified in GIC's. Indeed, in the case of three-dimensional graphite, McClure [43] has shown that the second order terms could be neglected since all the irreducible representation of the wave vector group were involved in the bands of interest near the Fermi level and the effect of the second order terms must be small compared to those already present in the hamiltonian [37]. For different reasons these conditions are not satisfied in GIC's: in the first stage, all the representation are not involved near Fermi level – whereas in the second stage, even if all the representations are present, the second order terms have to be taken into account to obtain a finite value of Δg_i ($i = a, c$).

To derive Δg_c in GIC's Fretigny and Saint-Jean [44] have developed a model in the framework of the Luttinger-Kohn analysis, including the second order terms in the hamiltonian matrix in the two-dimensional model of independants subsystems approximation. It was shown that the interband terms have to be included to obtain a coherent description of Δg_c . For both first and second stage GICs – the only which were considered – the Δg_c values are inversely proportional to the Fermi energy and must depended on stage index. The Fretigny-Saint Jean model [44] predicts negative and positive values of Δg_c respectively, for acceptor and donor compounds in qualitative agreement with the experimental results [28-36]. But good quantitative agreement was only found by comparison with the experimental data only for acceptor compounds. Nevertheless, in our last experiments, for instance with graphite-nitric acid [45], the independence of Δg_c – value on stage index has been found.

CESR linewidth in GICs

In GICs the CESR linewidth is determined by various factors, such as, the stage of GICs, the atomic number and aggregate state of the intercalate species, the temperature etc [28-36].

There is enough evidence now that the CESR linewidth in GICs increases significantly with the increase of the atomic number of the intercalate species. First, this was observed by Muller and Kleiner [28] for alkali metal GICs and recently for the XF_n fluoride GICs [46]. It implies that the carriers are not necessarily confined to the graphite layers and the scattering by the intercalants plays a significant role in the spin-relaxation process.

Almost for all GICs the linewidth is the smallest in the second stage and increases monotonically with the stage number for $n > 2$ [28-36]. The temperature dependence of the linewidth investigated in several donor and acceptor compounds reveals striking differences depending on intercalated species and on the stage. Generally the linewidth for $\mathbf{H} \parallel \mathbf{c}$ is larger than for $\mathbf{H} \perp \mathbf{c}$ but their temperature dependencies are similar. For acceptor compounds, for instance, with AsF_5 [35], SbCl_5 [34] and AlCl_3 [33] a decrease of linewidth is observed from helium to room temperature, similarly as in pure graphite. Abrupt changes of linewidth were observed in GICs with HNO_3 at about 250 K [29, 45].

In alkali metal GICs the situation is more complex. Rb-GICs of stage $n > 3$ [47] exhibit the same type of the temperature dependence of the linewidth as in acceptor compounds. In second stages of Rb [48] – and K [47] GICs, above 100 K, the linewidth is practically temperature independent. In first stage of alkali metal compounds the linewidth is larger at 300 K than at low temperature but the temperature dependence is not monotonic: in C_8Rb there is a broad maximum at about 200 K [47], in C_8K a broad minimum at about 50 K followed by a linear increase from 100 K is reported [48]. Finally higher stages of potassium compounds exhibit low temperature maxima than minima followed by the region of the linear increase [48].

The regions of the linear increase of the linewidth with temperature observed above 100 + 150 K for potassium compounds were qualitatively interpreted in terms of the Elliott theory with the help of the next expression for the temperatures above the Debye temperature (θ_D):

$$\Delta H \sim (\Delta g)^2 / \gamma m^* \cdot \mu(T) ,$$

where Δg is the g -shift, γ is the electronic gyromagnetic ratio, m^* is the carriers effective mass, and $\mu(T)$ is the in plane carriers mobility. This expression predicts a simple correlation between the CESR linewidth and the basal plane resistivity ρ_a ($\Delta H \propto \rho_a$). The decrease of the linewidth with temperature observed in other GICs and for potassium compounds at lower temperatures was generally attributed to the motional narrowing of the inhomogeneous broadening [29, 38, 39, 47]. Different physical origins of the inhomogeneous broadening were proposed. Murata and Suematsu [47] and Sugihara [38] suggested the spread of g -values at the Fermi energy in different bands. Khanna et al. [29] attributed the broadening to the effect of intercalated molecules whose motion is frozen at low temperatures. On the other hand Stein et al. [33] claimed in their recent paper that the CESR linewidth in acceptor as well in donor GICs can be entirely described by Elliott theory. To explain the decrease of the linewidth with increasing temperature, they involve the next expression obtained by Elliott for alkali metals below the Debye temperature:

$$\Delta H \sim (\Delta g)^2 \theta_D / \gamma m^* \cdot \mu(T) \cdot T^2 .$$

All above given interpretations of the CESR linewidth originating in GICs are purely qualitative and, at best, not justified experimentally. In individual cases they are in direct conflict with the experimental evidence. For instance, a systematic study of the CESR in first stage GICs with AsF_5 [49] at temperatures between 4.2 and 300 K have revealed that at a given temperature the linewidth is an increasing function of the in-plane conductivity (both for $\mathbf{H} \parallel \mathbf{c}$ and $\mathbf{H} \perp \mathbf{c}$). Whereas the opposite behavior results from the Elliott theory.

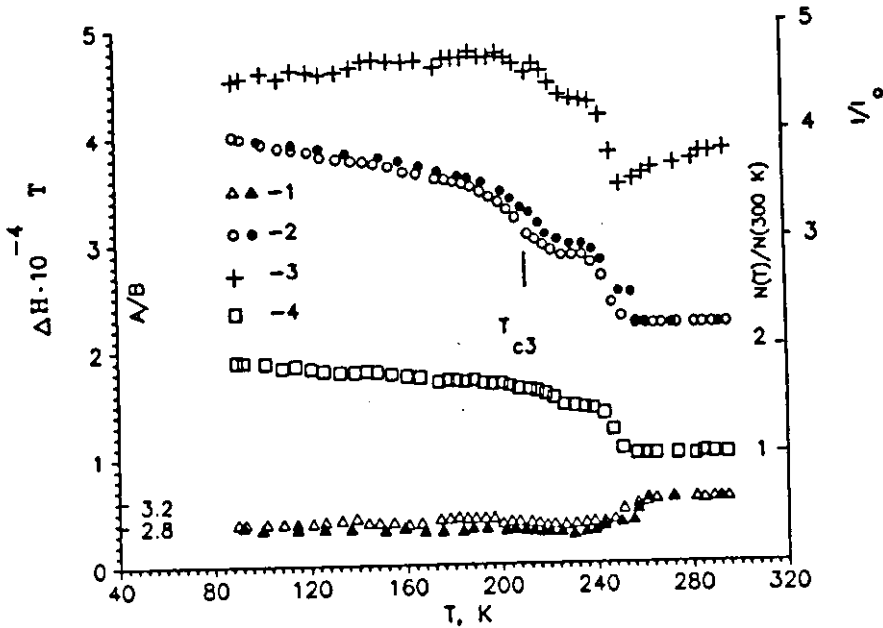


Fig. 4. Temperature dependence of CCSR line parameters of $C_{20}HNO_3$ plate with dimensions: $0.4 \times 0.4 \times 0.02$ cm, i.e., $A/B(T)$ (curve 1), $\Delta H(T)$ (curve 2), $I(T)/I_0$ (curve 3), where $I = (|A|+|B|) \times \Delta H^2$ and I_0 is the intensity of the Mn^{2+} ESR line in a standard sample $ZnS:Mn^{2+}$, and the relative spin concentration $N(T)/N(300 K)$ (curve 4). Unfilled (filled) symbols correspond to experimental values of parameters at cooling (heating) of the GIC. T_{c3} is the temperature of the third peak of the derivative $d(\Delta H)/dT$. $H \perp c$, $\nu = 9.52$ GHz

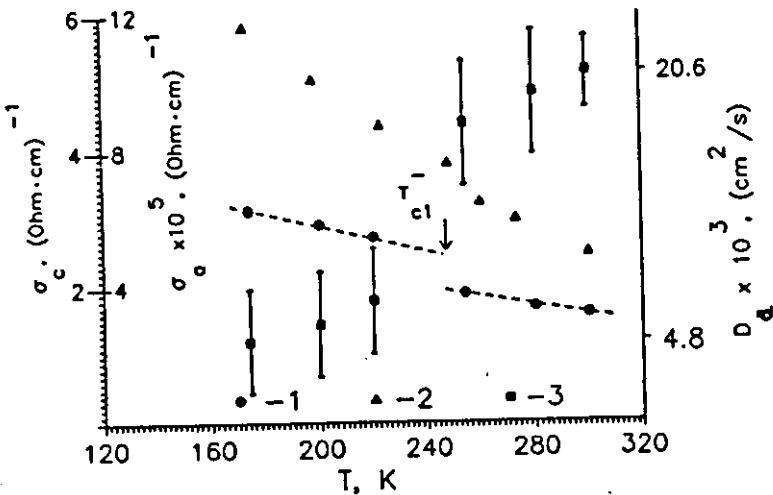


Fig. 5. Temperature dependence of σ_c (1), σ_a (2) and D_a (3) in $C_{20}HNO_3$. The dashed line corresponds to the linear function $\sigma_c = [(-6.52 \times 10^{-3} / K)T + 3.56] (\text{Ohm} \cdot \text{cm})^{-1}$ and $\sigma_c = [(-8.46 \times 10^{-3} / K)T + 4.6] (\text{Ohm} \cdot \text{cm})^{-1}$ for $T > T_{c1}$ and $T < T_{c1}$, respectively

Examining GICs with HNO_3 by means of the CESR method, we obtained new experimental results related to the problem under consideration. In these synthetic metals during and after crystallization of the HNO_3 guest molecules, the simultaneous increase of concentration (N) was found and investigated (Fig. 4 and 5) [50]. In terms of graphite intercalation compounds tight binding model, the increase of N is directly connected with partial localization of the conduction π -electrons. Since the localized electrons are the perturbation centres for the conduction electrons, it has been proposed that the increase of their concentration is the main reason for the decrease of the in-plane spin carriers mobility and the "nonmetallic" increase of the CESR linewidth observed during and after crystallization of the guest layers.

III. CONCLUDING REMARKS

In this brief review it is clearly demonstrated that CESR technique can provide useful informations on the spin relaxation time, the gyromagnetic factor, the spin carriers diffusion constant and electroconductivity. But several fundamental problems connected with the CESR in materials under consideration have not been invoked here: for instance, (1) the dependence of the CESR linewidth on GICs stage; (2) the contribution of the surface relaxation to the CESR linewidth; (3) the "bottle-neck" regime of the cross-relaxation between localized and conduction electron subsystems; (4) the correlation between spin relaxation and the c-axis electroconductivity and (5) the possibility of the anisotropic electronic relaxation. Also, it will be noted, that the very interesting field of ESR application to the study of GICs with magnetic ions and impurities is beyond the scope of this review.

All CESR results being considered in this article were obtained using CW conventional spectrometers. At low temperatures the observation of the electron spin echo opens new possibilities for studies of GICs [51]. Such investigations might also yield valuable information about the electronic states, wave functions and relaxation processes. Furthermore, as usual, the efficiency of the CESR technique is highly increased when used together with other techniques.

Acknowledgments

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