Planar diffusion constant D_a in acceptor-graphite intercalation compounds

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The planar carrier diffusion constant D_a of first-stage AsF$_5$-graphite intercalation compounds is determined through analysis of the conduction-electron spin-resonance (CESR) spectra using an analytical procedure specifically adapted to highly anisotropic conductors. This study was carried out at 9 GHz, and for $10 < T < 300$ K on samples of different sizes. Whatever the sample size, D_a decreases as T rises. Two significant results were observed: D_a based on CESR data is always larger than that obtained from planar conductivity measurements using Einstein's formula and depends somewhat upon sample dimensions.

I. INTRODUCTION

Conduction-electron spin resonance (CESR) is a powerful technique for studying the dynamic properties of carriers in conductors. Quite naturally, it has been applied to graphite intercalation compounds (GIC's) concerning the electronic properties of both donor[1-4] and acceptor compounds.[5-13] An extensive presentation of these results can be found in Ref. 13.

Many attempts have been made to extract the transport coefficients of these highly anisotropic conductors from the CESR studies. However, in spite of the fact that many interesting experimental results have been obtained, satisfactory quantitative results are rare. Indeed, in most cases the interpretation of the experiments is based on an unadapted model of line shape, Blinowski et al.[14] having shown that the Feher-Kip line-shape analysis procedure currently used, based on the Dyson formula with σ_a and D_c, is completely unjustified in the case of GIC's.

To obtain the correct line-shape analysis in the case of anisotropic conductors of finite dimensions, these authors have extended the Dyson theory by taking into account the anisotropy of both conductivity and diffusion, and the finite sample dimensions. Using this model, they have proposed a proper analysis of the experimental CESR spectra in GIC's which leads to a precise determination of the physical characteristics related to the resonance: the electrical conductivity, the spin relaxation, the gyromagnetic factors, and the carrier diffusion constant.[14-18]

In this paper we report the temperature and dimension dependences of the planar diffusion constant D_a deduced from the quantitative analysis of CESR measurements. In particular, two surprising results are presented: the planar diffusion constant determined from CESR measurements is always larger than that obtained from planar conductivity measurements using Einstein's formula and secondly the values seem to depend on the sample dimensions.

The experimental CESR study has been based on first-stage AsF$_5$ GIC's, nominally formulated C$_8$AsF$_5$. The determination of the diffusion constant requiring measurements on a set of chemically and structurally similar samples of width comparable to and larger than the skin depth, several samples with different geometrical l dimensions were investigated in the 10–300-K temperature range.

This paper is organized as follows. The procedure used to determine the diffusion constant D_a from the CESR spectra is presented in Sec. II. Experimental details and CESR experimental results are described in Sec. III. In Sec. IV the planar diffusion constant values are reported and discussed.

II. DETERMINATION OF D_a FROM CESR SPECTRA

In GIC's, as in metallic systems, the derivative absorption spectrum presents a characteristic asymmetric (Dysonian) resonance line shape, characterized by three experimental parameters: the line asymmetry ratio A/B, the linewidth ΔH, and the resonant field H_{res}. Figure 1 shows the theoretical spectrum dP/dH as a function of the dimensionless variable X. To interpret quantitatively these experimental parameters, a theoretical line-shape model has been developed[14-18] which extends the Dyson-Kaplan theory[19,20] and includes the anisotropy of conductivity and diffusion, and the finite dimensions of the sample. We underline that this model is more general than the previous Kahn model[21] which is restricted to anisotropic media without diffusion processes.

In the particular case of acceptor GIC's, the conductivity anisotropy, σ_a/σ_c may exceed 10^6, where σ_a and σ_c are, respectively, the planar and c-axis conductivities. Consequently, the skin depth $\delta_a = c/2\pi\sqrt{\nu\sigma_c}$ for the microwave penetration through the faces parallel to the c axis is much larger than the skin depth $\delta_c = c/2\pi\sqrt{\nu\sigma_a}$ for the faces perpendicular to the c axis. For the usual geometrical dimensions (l,d) of samples (Fig. 2), we have
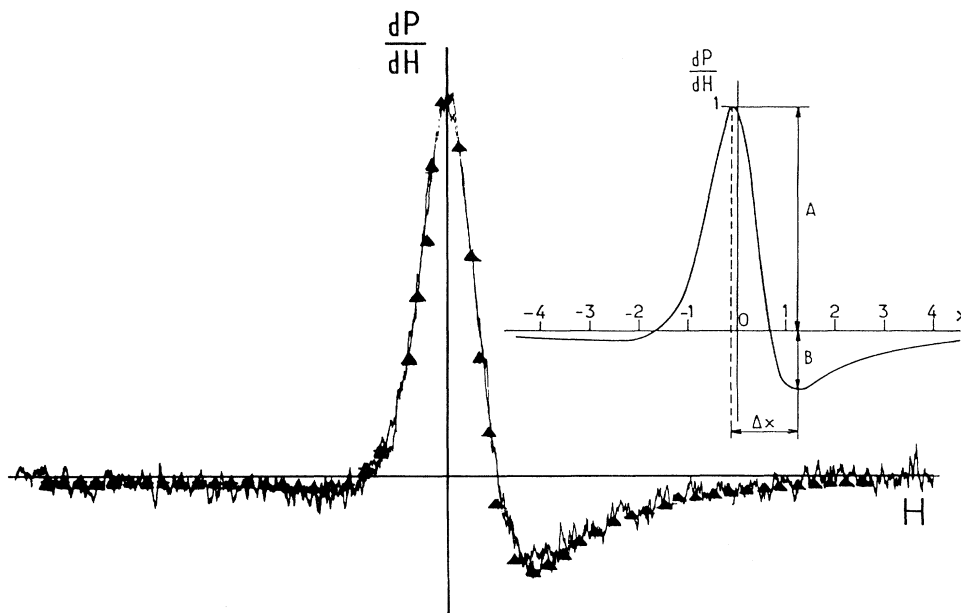
FIG. 1. Experimental Dysonian spectrum observed for the sample with $l=2$ mm; $T=300$ K. ▲: Theoretical spectrum dP/dH calculated for $\lambda=6.4$ and $R=0.75$. Inset: Definitions of theoretical CESR parameters. $X=g\mu_B T_2(H-H_0)/\hbar$.

$\lambda=1/\delta_a \ll \mu=d/\delta_c$. In this case, we have previously shown that practically all the microwave power is absorbed by the sample faces (zx) parallel to the c axis and that the CESR spectra can be completely interpreted in the framework of the one-dimensional Dyson theory, involving the c-axis conductivity σ_c and the in-plane diffusion constant D_a.[14−18]

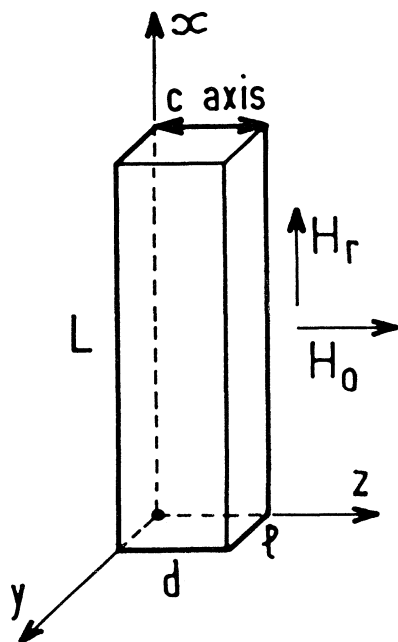The validity of this theoretical model has been verified

FIG. 2. Experimental configuration.

by extensive study of CESR experiments performed on samples with different sizes. In particular, the observed dimension dependence of the line shape has been completely interpreted using this model.[16,18] More recently, a quantitative analysis of CESR data obtained at 4 and 9 GHz on narrow samples ($\lambda<2.5$) allowed showing the frequency dependence of the c-axis conductivity in C_8AsF_5.[17]

In the framework of this model, the line asymmetry ratio A/B of the absorption derivative depends on two parameters $\lambda=1/\delta_a$ and $R=\sqrt{T_D/T_2}$, where $T_D=\delta_a^2/2D_a$ is the time required for the carriers to diffuse across the skin depth δ_a and T_2 is the spin relaxation time. The theoretical curves of the asymmetry ratio $A/B(\lambda,R)$ and those of the theoretical linewidth $\Delta x(\lambda,R)$, numerically calculated from the Kodera expressions in Ref. 22, are, respectively, reported in Figs. 3 and 4 for several values of R.

For sample widths comparable to the skin depth ($\lambda<2.5$), the magnetic field inside the sample is almost uniform and A/B does not depend on R. For samples with $2.5<\lambda<6$, the distribution of the rf field and consequently A/B, depends in a complex way on both λ and R. $A/B(\lambda)$ exhibits a sharp maximum which occurs in the region of $\lambda=3-4$ for all R. Finally, for $\lambda>6$, the spins which leave the skin depth relax before reaching the middle of the sample so the microwave field distribution depends on the diffusion. Then $A/B(\lambda)$ is nearly constant and exhibits a regular increase of A/B with decreasing R. Similar strong variations and complex features with λ and R are observed on the theoretical linewidth.

From these theoretical data, we have proposed the following procedure to analyze quantitatively the CESR spectra.
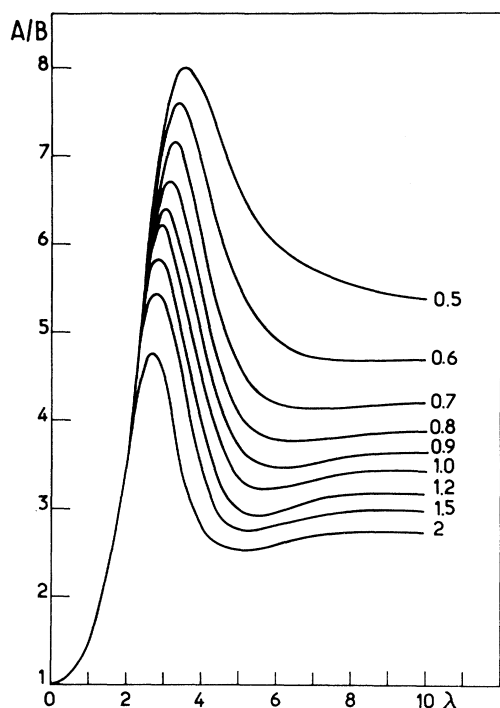
FIG. 3. Theoretical dependence of A/B vs λ. The values of R are indicated on each curve.

For narrow samples, $\lambda < 2.5$, A/B is independent of the diffusion. Thus measurements of A/B on samples in which l is comparable to the skin depth provide a good means to determine λ and consequently the c-axis conductivity at the frequencies used in the measurement. The c-axis conductivity is deduced from the value of λ with the use of the following formula:

$$\sigma_c = \left[\frac{\lambda}{l}\right]^2 \frac{c^2}{4\pi^2 \nu} . \tag{1}$$

This procedure does not permit determining the value of R, however the spin relaxation time may be evaluated us-
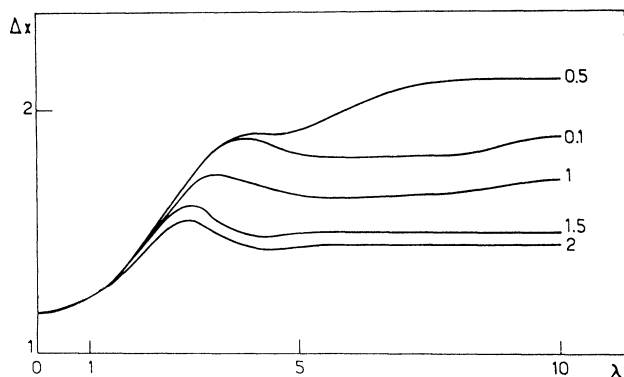

FIG. 4 Theoretical dependence of Δx vs λ. The values of R are indicated on each curve.

ing the theoretical linewidth Δx which is independent of R for this class of samples, $T_2^{-1} = (g\mu_B/\hbar)\Delta H/\Delta x(\lambda)$ where μ_B is the Bohr magneton and g the gyromagnetic factor. Notice that for these narrow samples, the diffusion constant cannot be evaluated.

For wide samples, $\lambda > 2.5$, the reduced dimension cannot be determined from the experimental value of A/B because A/B depends simultaneously on λ and R. However, the c-axis conductivity σ_c determined from the experimental line shape of narrow samples is assumed identical for a given series.[17,18] Thus we deduce the values of λ for the samples with various widths l by using the proportionality between λ and l.

The parameter R may therefore be estimated from the best agreement between the experimental and theoretical values of A/B measured on wide samples. The spin relaxation time T_2 and the planar diffusion constant D_a may be determined. T_2 is estimated by comparing the experimental linewidth ΔH to the theoretical linewidth $\Delta x(\lambda, R)$ calculated for the parameters λ and R obtained from the line-shape analysis, using the relation

$$T_2^{-1} = \frac{g\mu_B}{\hbar} \frac{\Delta H}{\Delta x(\lambda, R)} . \tag{2}$$

Notice that it is essential to introduce Δx to discuss correctly the relaxation process.[18] For instance, if the relaxation process is studied as a function of l, $T_2(l)$ is monotonic whereas $\Delta H(l)$ may not be so. The differences arise from the necessity of introducing Δx which, in our experiments, varies from 1.2 to 2.1.

From the determination of R and T_2, D_a is extracted by using the relation

$$D_a = \frac{c^2}{8\pi^2 R^2 \nu T_2 \sigma_c} . \tag{3}$$

Thus this procedure allows analyzing the experimental spectra and determining the complete set of dynamic parameters of carriers: σ_c, T_2, and D_a, provided that CESR measurements are performed on samples with different l dimensions corresponding to narrow and wide samples.

III. EXPERIMENTAL DETAILS AND CESR RESULTS

A. Experiments

All CESR spectra presented here were obtained for first-stage AsF_5 compounds synthetized following the method of Falardeau, Hanlon, and Thomson.[23] The graphite used was Union Carbide highly oriented pyrolitic graphite (HOPG), type ZYB. After intercalation, the stage and the homogeneity of the compounds were confirmed by x-ray diffraction analysis[24,25] and the samples were encapsulated in quartz tubes filled with helium gas to avoid degradation.

We have systematically studied the effects of the geometrical sample dimensions on the carrier diffusion constant by using a series of rectangular parallelepipedic samples with different dimensions: $0.5 < l < 2$ mm, $L = 10$ mm, and $d = 0.4$ mm (Fig. 2).

All CESR spectra were obtained with the standard

CESR reflection method using a 9-GHz VARIAN E 115 spectrometer. The sample geometry and the field configurations are presented in Fig. 2. The measurements were made for the static magnetic field H_0 parallel or perpendicular to the c axis. In GIC's, the line shape is very sensitive to the experimental measurement conditions:[15] in order to eliminate passage and saturation effects over the whole temperature range, measurements were made at a low microwave power of 10 μW and at a small field modulation frequency of 35 Hz. The CESR experiments were carried out between 10 and 300 K. The temperature regulater used permitted controlling the sample temperature to within an accuracy of ± 1 K. All measurements were made during the heating process; the initial cooling took one hour from room temperature to 10 K.

Details concerning the direct σ_a and σ_c measurements on samples synthesized in the same reactors as the CESR samples have been presented elsewhere.[24,26]

B. Experimental CESR results

All CESR spectra obtained on C_8AsF_5 present an asymmetric Dysonian line shape characterized by the asymmetry ratio A/B and the linewidth ΔH. Figure 1 shows a typical experimental spectrum.

Measurements performed on the ZYB series (Fig. 5) show a nonmonotonic variation of A/B with l. For instance, at $T=100$ K, A/B varies from about 3 for $l=0.5$ mm up to 8 for $l=1$ mm and decreases to about 3.5 for $l=2$ mm. While not shown, the asymmetry ratio corresponding to $l=1.5$ mm is constant and equal to 7 ± 0.5.

As regards the temperature variations, A/B is seen to be temperature independent between 10–200 K. Above 200 K, the sense and amplitude of these variations depend on the sample width l. For instance, the asymmetry ratio A/B corresponding to samples with $l=0.5$ and 1 mm decreases whereas those corresponding to $l=1.5$ and 2 mm are constant and increasing, respectively, as the temperature rises.
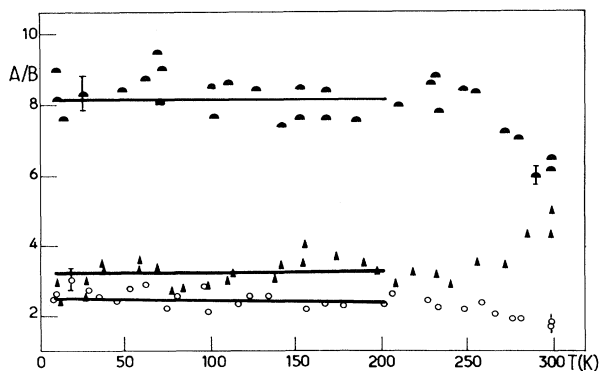

FIG. 5. Finite l-dimension effects on the line asymmetry ratio A/B. ○, $l=0.5$ mm; ●, $l=1$ mm; ▲, $l=2$ mm. For a given l, the solid lines represent the average values for all samples studied over the 10–200-K range.
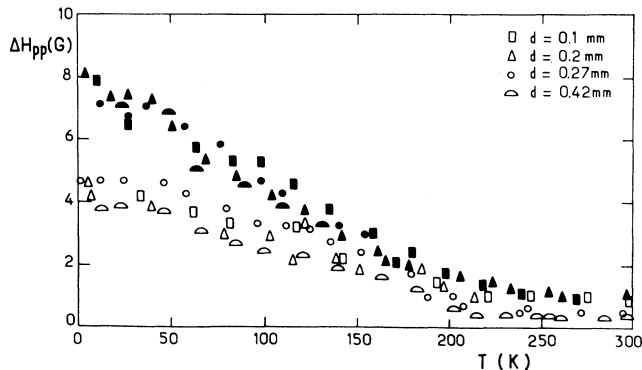

FIG. 6. Temperature dependence of the linewidth observed for samples with $l=2$ mm. Open symbols: $H_0\|c$, solid symbols: $H_0\perp c$.

The linewidth exhibits the same temperature behavior, for each configuration of the external field ($H\|c$ and $H\perp c$), whatever the sample dimensions: $\Delta H_\|$ and $\Delta H_\perp$ decrease with increasing temperature, varying typically from a few tens of gauss at low temperature to 0.5 G at room temperature. Figure 6 illustrates this temperature dependence: the CESR linewidths are measured on samples of $l=2$ mm at 9 GHz.

IV. EVALUATION OF THE IN-PLANE DIFFUSION CONSTANT AND DISCUSSION

The above experimental results can be completely interpreted in the framework of the proposed procedure. At 9 GHz, the sample with $l=0.5$ mm can be considered as "narrow" while the others are "wide." The quantitative determination of the c-axis conductivity and the spin relaxation time have been presented previously.[17] In this paper the focus will be placed on the carrier diffusion constant.

Whatever the sample studied, D_a decreases with increasing temperature. This feature is illustrated in Fig. 7. For instance, D_a corresponding to the sample ZYB $l=2$ mm, varies from 6×10^4 cm^2 s^{-1} at 10 K to 2×10^3 cm^2 s^{-1} at 300 K. At high temperature, the values of the diffusion constant are identical for all samples. In contrast, when the temperature decreases, the variations of $D_a(T)$ seems to depend on the sample width l. As shown in Fig. 7, D_a increases more rapidly when the sample is narrow. For example, at $T=10$ K, the diffusion constant obtained for the sample $l=1$ mm is equal to 2.5×10^5 cm^2 s^{-1} whereas that corresponding to $l=2$ mm is around 0.6×10^5 cm^2 s^{-1}.

These variations of D_a with the temperature can be compared to the decrease of the planar conductivity measured by McRae et al.[26] on corresponding samples, these two parameters being related by the Einstein formula:

$$D_a = \frac{I_c\sigma_a}{N(E_F)e^2} = \frac{I_c 9\pi\gamma_0^2 b^2\sigma_a}{8E_F e^2} \; ;$$

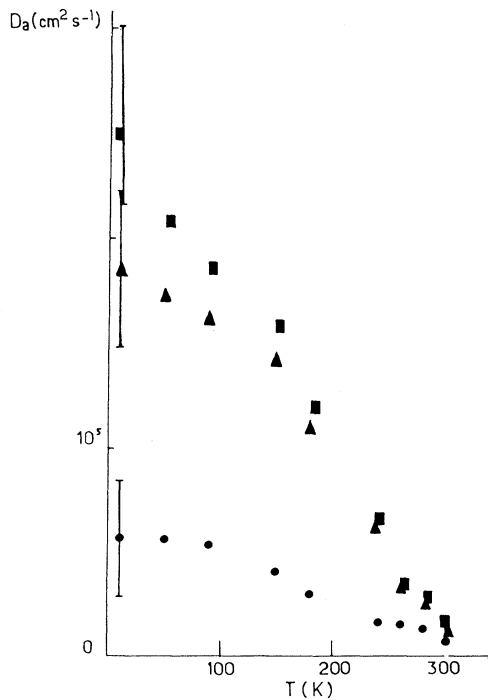the latter expression can be derived from the former us-

FIG. 7. Temperature dependence of the planar diffusion constant. ■, $l=1$ mm; ▲, $l=1.5$ mm; ●, $l=2$ mm.

ing the relationship for $N_{2D}(E_F)$ deduced from the Blinowski model.[27] In the numerical calculations we take $\gamma_0=2.62$ eV, $b=1.42$ Å, $I_c=8.08$ Å, and $E_F=1.28$ eV.

Our results indicate however that this simple relation cannot be unambiguously applied to GIC's. Indeed, the values of D_a obtained from CESR results are systematically larger by 1 order of magnitude than those deduced from the direct measurements of conductivity. Table I, which presents the different values of D_a obtained for the $l=2$ mm sample illustrates this important result. We underline that the fact that D_a determined from CESR is both width dependent and greater than that based on σ_a was confirmed on several series of samples.

Differences between transport coefficients obtained from analysis of conductivity and CESR have been mentioned previously by Davidov et al.[12] in their studies of fluorine compounds. They observed a significant difference between the product $\rho_a\rho_c$ extracted from conductivity studies and from the diffusion time T_D. However, two comments should be made. First, these authors compare a parameter which mixes the conductivities σ_a

and σ_c. Second, the conductivity introduced by Davidov et al. is measured using a four-contact dc technique whereas this conductivity depends drastically on the frequency as we have previously shown.[17] From this point of view, the present procedure is more valid because the independent determination of σ_c at the CESR frequency allows directly comparing the planar coefficients D_a obtained from conductivity and diffusion time measurements.

Diffusion processes have long been studied in numerous other fields (see, for example, the review in Ref. 28) and discrepancies between the values of diffusion constants (or jump or "attempt" frequencies) evaluated using different experimental probes have been largely discussed. A long-standing problem exists, for instance, in the case of the β-alumina superionic conductors[29] in which, as in our case concerning the AsF$_5$ GIC's, an order of magnitude difference exists between diffusion constants evaluated not only from magnetic resonance (NMR) and conductivity studies, but also using measurements of internal friction, tracer diffusion and ir vibration.[30]

Returning to the analysis of Kodera himself, we note such a difference in the value of diffusion constant determined in these two ways was observed when he applied his numerical treatment to the experimental data on phosphorous-doped silicon.[22] In his case, the value of D_a determined from conductivity data was from 1 to 3 orders of magnitude less than that calculated from CESR data. While no confirmed explanation could be proposed, this author put forward two suggestions. The first was that Dyson's theory having been developed for metals in which the electrons are degenerate may not be applicable for semiconductors. Second, in the case of his samples the observed ratio A/B being very close to that expected for stationary spins, it is relatively insensitive to T_D such that a reliable value of R, and thus the diffusion constant, is difficult to ascertain.

Neither of these propositions seems applicable to our results. At the present time, we have no explanation which allows understanding such a reproducible experimental result.

We suggest however, that the underlying reason may be due to the localized moments observed in graphite layers. In a recent paper, Davidov et al.[12] observed by spin-echo techniques performed on AsF$_5$ GIC's the presence of localized moments in the graphite layers and suggested the existence of traps. A precise analysis of the spin relaxation time confirms this assumption.[18] While the exact nature of these traps remains to be determined, it seems reasonable to assume that they are related with

TABLE I. Planar diffusion constant D_a based on CESR and direct planar conductivity measurements, for sample $l=2$ mm.

T (K)	10	50	90	150	180	240	260	280	300
$10^{-5}D_a$ (cm^2 s^{-1}) (CESR)	0.2–0.96	0.2–0.96	0.2–1	0.13–0.7	0.1–0.47	0.05–0.47	0.05–0.3	0.05–0.3	0.03–0.1
$10^{-3}D_a$ (cm^2 s^{-1}) (conductivity)	2.5	2.1	1.8	1.3	1.1	0.8	0.7	0.6	0.6

the complex transport-ordering correlations observed in AsF$_5$ GIC's.[25,26]

The density of trapped carriers is certainly much smaller than that of conduction spins, no experimental results in acceptor compounds indicating a significant proportion of localized spins. Then, it is easy to demonstrate, using the Hasegawa model,[31] that the hyperfrequency power is mainly absorbed by the conduction spins.[18] Consequently, the theoretical line-shape model is not affected by the trapped carriers and the quantitative analysis procedure presented in Sec. II remains applicable. However, the diffusion constant introduced in the Bloch equations is a phenomenological constant which, in homogeneous materials, represents the spin diffusion. In the presence of traps, this simple parameter is certainly insufficient to describe the real complex diffusion processes. Furthermore, the Einstein relation obtained for homogeneous systems has to be modified to take into account the existence of localization processes. Thus, in acceptor compounds, identifying the diffusion constant determined from CESR measurements with that deduced from planar conductivity seems to be unjustified, more complete theories of CESR line-shape and diffusion processes, including the trap distributions, being required to obtain a valid comparison.

V. CONCLUSIONS

We have indicated in the present paper a precise analytical methodology for analyzing CESR spectra in highly anisotropic materials which permits extracting the planar diffusion constant D_a. In the specific case of AsF$_5$ GIC's, this procedure has allowed showing both that D_a is strongly dependent on sample width and that the value thus obtained is larger than that based on direct planar conductivity measurements. We suggest that these results are linked to the existence of carrier traps. Many experimental efforts will be necessary to characterize precisely the nature of such traps. At the same time, theoretical work should be carried out to include the trap distributions. Whatever the results of these future developments, the features of D_a presented in this paper already point out that acceptor graphite intercalation compounds are not usual two-dimensional metallic systems.

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