

# Magnetic resonance in graphite intercalation compounds

Autor(en): **Estrade-Szwarckopf, H.**

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## MAGNETIC RESONANCE IN GRAPHITE INTERCALATION COMPOUNDS

H. Estrade-Szwarckopf

Centre de Recherche sur les Solides à Organisation Cristalline  
Imparfaites, C.N.R.S., 45045 Orléans Cedex, France.

A review is presented of NMR and EPR studies of graphite intercalation compounds, with emphasis on alkaline intercalates. The relevance of these data for the electronic band structure of these compounds and the relation with informations obtained from other experiments are discussed.

### 1. Introduction

Graphite intercalation compounds (G.I.C.) are interlamellar ones in which the graphite layers keep their internal identity whereas the interlayer space is occupied or not by the inserted molecules or atoms.

The ability of graphite to give such a great variety of G.I.C. is due to two essential properties:

1 - thanks to the amphoteric character of the C-element and/or to the semi-metallic character of the graphite, insertion of both electron-donors or-acceptors is possible: in those cases the Fermi level of the new compounds are respectively high-or -low energy shifted (Fig. 1).

2 - the anisotropy of its cristallographic structure: on one hand the planar hexagonal bondings are very strong (the C-C in plane distance = 1.42 Å), and will be almost unchanged during the insertion; on the other hand the interplanar bonds are of Van der Waals type, weak and easily broken by the insertion (the carbone-carbone interplanar distance  $d \sim 3.35$  Å in pure graphite becomes  $d_1 = 3.7$  to  $5$  Å when inserted by alkali-metals or even  $12$  Å when inserted with salts).

G.I.C. present a very peculiar property: staging, that is to say in

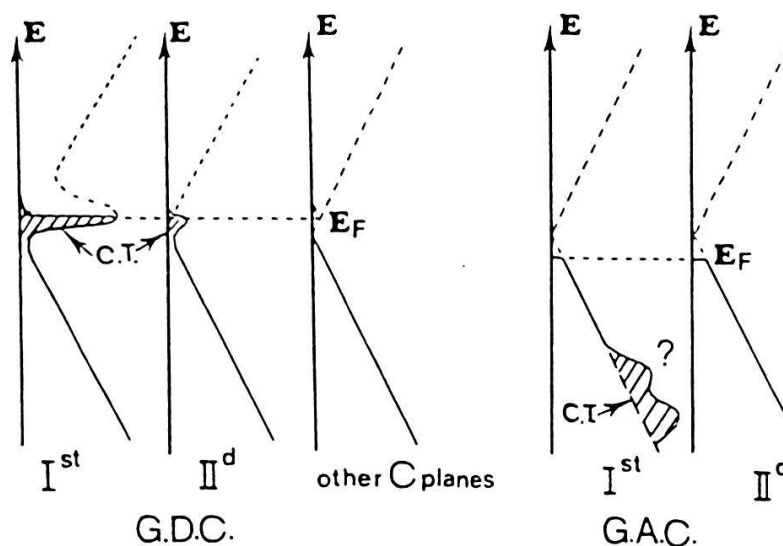


Fig. 1. Schematic band structure of graphite and G.I.C. of donors (GDC) or acceptors (GAC). from Conard, ...[18]

some cases the presence in the  $\vec{c}$ -direction of several carbon planes between inserted interlamellar spaces. Their number is called the stage. Depending on the preparation conditions, well defined stages may be obtained from 1 to 8 or 9 and even  $12 \pm 1$  in the case of potassium for instance. In that last case, the identity c-period becomes as high as  $\approx 42 \text{ \AA}$ . ( $I_c = (n-1) \times 3.35 + d_1$  where  $n$  is the stage) (Fig. 2).

A rough classification of the G.I.C. may be done depending on the inserted species:

- a) donor species as alkali- or alkaline earth metals ( $\text{LiC}_{6n}$ ,  $\text{KC}_8$ ,  $\text{KC}_{12n}$ ,  $\text{CsC}_8$ ,  $\text{CsC}_{12n}$ ,  $\text{BaC}_6$ , ...)
- b) acceptor species as salts (chlorides, fluorides...  $\text{SbF}_5$ ,  $\text{AsF}_5$ ,  $\text{NiCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{FeCl}_3$ , ...); acids (nitric, sulfuric...).

However more complicated compounds are now prepared and characterized in which several kinds of atoms or molecules are inserted. Apart from bialkaline ones as graphite-(Na + K), structurally similar to the monoalkaline compounds, ternary compounds have been synthesized as graphite-alkali + organic molecules (benzene, tetrahydrofuranne, ammoniac...) or alkali + hydrogen or

alkali + mercury or tantalum.

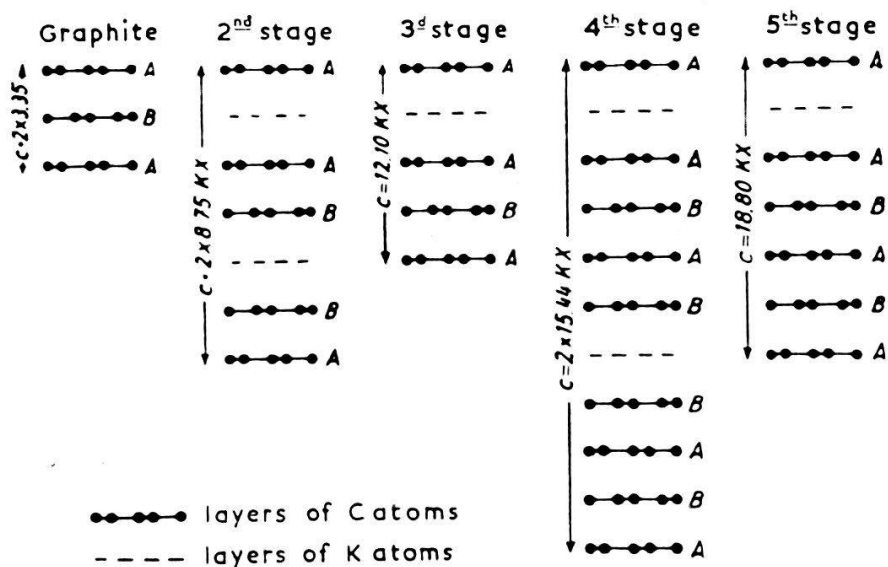


Fig. 2. Sequences of carbon hexagon networks and potassium atoms in various potassium/graphite compounds, viewed perpendicular to the c-axis.

Hundreds of such compounds are yet known (some of them since 1925!) and new ones are almost daily synthesized. The scientific interest for the G.I.C. increased about 7-8 years ago on one hand because of possible applications (high in-plane conductivity close to the copper value, anisotropy of this conductivity as high as  $10^6$  in acceptor-compounds, possibility of chemistry and catalysis in the very specific inter-lamellar space...) and on the other hand, for the physicists, a beautiful example in which low dimensional theories may be verified (physical transitions as melting, N.M.R. relaxation processes...).

This increasing interest for the G.I.C. may be illustrated by the increasing number of papers published on the subject. Fortunately, the bibliography is easily completed as, since 1975, an international meeting has taken place almost each year. Those annual meeting proceedings constitute the basic literature [1-7] and except for the special aim of this paper (N.M.R. and E.P.R. in G.I.C.) no precise reference will be given here.

Many groups devote their activity to those G.I.C. in Europe, U.S.A. and Japan. Almost all the available techniques of characterization of solids

may be and are applied to them. The aim of all those studies are like in all interesting solids, to increase our knowledge of their properties and of origin of those properties. They may then result in improving those properties by choosing the most accurately inserted species and stoichiometry. Of course, one of the most exciting properties is the anisotropic conductivity and related to this a most important question has been: what is the charge transfer between the graphite lattice and the inserted species? However, as progressively more results and reflexions came out, this question did not longer appear the right one. Indeed, G.I.C. are not ionic compounds and the problem of their electronic structure may now be formulated differently: what is the space-localization of the electrons and what is their orbital character? About such a question, N.M.R. and E.P.R. techniques may bring a lot of informations. But before going further in a description of their use in G.I.C., we need some informations about the G.I.C. structures.

## 2. Structural Features of G.I.C.

As we saw above, G.I.C. in  $\vec{c}$ -direction are well-organized and their stage well defined. Daumas-Herold model of folded graphite-planes (Fig. 3) explains almost all the experimental results concerning the intercalation-desintercalation processes, coherence-domain limitation in the planes, stage evolution possibility. The carbon planes keep their identity but their stacking changes through intercalation: in pure graphite, two neighbouring C-planes are stacking in A-B configuration (the C-hexagons do not superimpose in two neighbouring planes) whereas two C-planes, adjacent to an inserted plane stack in A-A configuration. In higher stages, if two C-planes are neighbouring, they also stack in the A-B stacking (Fig. 3-4).

Let us now look inside the inserted planes. A rough description has been admitted for many years: donor-compounds are well organized  $MC_8$  (1st stage, octal lattice),  $MC_{12n}$  ( $n^{\text{th}}$ -stage, dodecal lattice) and for Li,  $LiC_{6n}$  with hexal lattice for all  $n^{\text{th}}$  stages; acceptor compounds are completely in-plane disordered. However numerous precise cristallographic measurements show the reality to be a bit more complex.

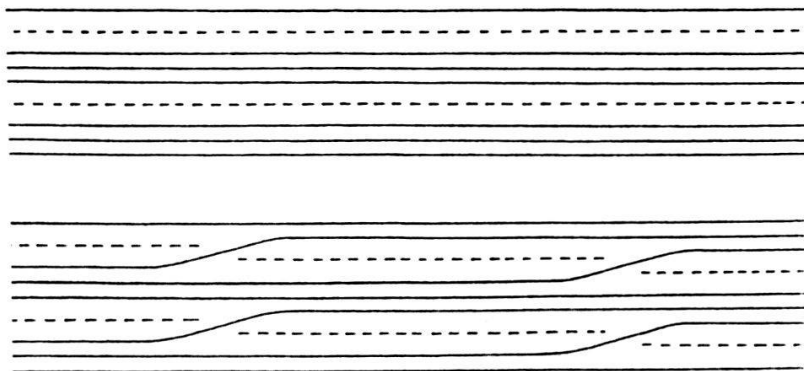


Fig. 3. Third stage compound in the classical and in the Daumas-Herold pleated layer model.

In donor compounds, the first stages  $MC_8$  and  $LiC_6$  use to be stoichiometrically defined and their structure too; but higher stages are often more or less lacunar; this lacunarity allows atomic diffusion from site to site and the crystallographic structure will depend on all physical conditions (temperature, pressure, stoichiometry...) and transitions will occur: the inserted lattice may change from ordered and commensurate to the graphite one to ordered and incommensurate, or from ordered to disordered. Recent studies show similar transitions to take place in acceptor-G.I.C. At last in ternary compounds, graphite-alkali-organic molecules, few structural informations have been yet obtained except the identity period showing the organic molecules to surround the alkali atoms, forming or not a compact complex. In graphite-alkali-hydrogen or graphite-alkali-X (X = mercury or tantalum) it seems that in the inserted space, two alkali planes are jamming an H or X plane, the interatomic distances being then similar to those measured in the respective hydrides or in X-alkali amalgams.

And now let us look on informations got first from E.P.R. techniques and then from N.M.R.

### 3. E.P.R. in Graphite Intercalation Compounds

Most of the E.P.R. measurements on G.I.C. have been performed on

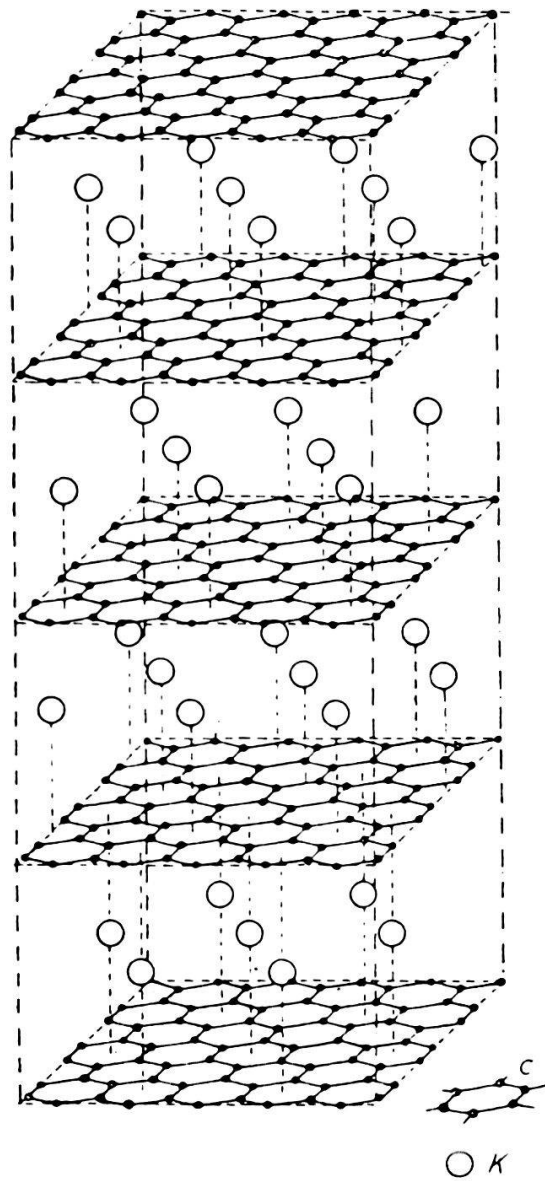


Fig. 4. Potassium graphite, C<sub>8</sub>K.

either single crystals (obtained from natural graphite flakes) or oriented samples (from H.O.P.G.: high orientation pyrographite and more recently from oriented fibers). With the usual configuration in the microwave cavity, the H.F. field  $H_1$  is parallel to the a,b plane and the wave penetration parallel to the c-axis is limited by the  $\sigma_{a,b}$  conductivity, whatever the angle between  $\vec{c}$  and  $H_0$  is.

In all the G.I.C. so studied, the E.P.R. spectra have the typical dissymmetric shape of conductors as described by Dyson [8] or Feher and Kip [9]. Due to the conductive character of the material, the H.F. wave is greatly attenuated and phase-shifted when penetrating into the sample. However, the polarization of the conduction carriers directly irradiated in the skin depth may be transmitted much deeper through spin-diffusion. Both phenomena, give the line its peculiar shape (Fig. 5) the characteristics of which (asymmetry factor  $A/B$ , line-width  $\Delta H$  and line-position) may be used to determine the transport properties of the sample, through three parameters  $T_D$ ,  $T_2$  and  $g$ -factor.

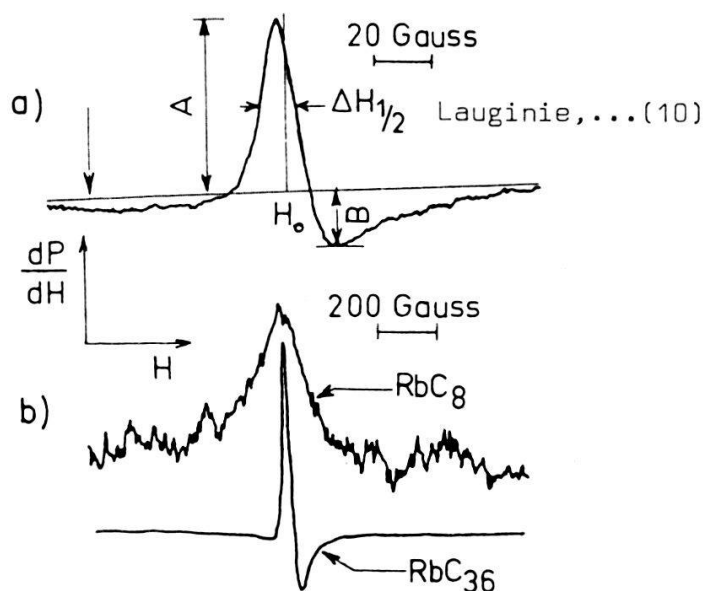


Fig. 5. EPR line shape in conductors.  $H_0$  is the resonant field. (a) The line recorded here is from the stage IX K-compound (from HOPG,  $H \parallel c$ ). The graphite line, if present, should have appeared under the arrow. (b) Stages I and III Rb-compounds EPR line (powders), from Laugnie, ... [10].

#### A) Diffusion Time $T_D$

$T_D$  is defined as the time necessary for an electron to diffuse through the skin depth  $\delta_a$ . In simple metals,  $T_D$  may be related to the density of states of the Fermi level  $N(E_F)$  through the formula  $T_D \sim N(E_F) / \sigma_a \sigma_c$  in which



$\sigma_a$  and  $\sigma_c$  are the conductivities respectively perpendicular and parallel to the  $\vec{c}$ -axis. If  $\sigma_a$  and  $\sigma_c$  are known from other measurements,  $N(E_F)$  may be estimated. This has been done for a lot of G.I.C.: they all have a Fermi density of states greater than that of graphite. For the donor-G.I.C., it is even greater than the metallic one but it remains small in acceptor-G.I.C. [10,11]. Those results are in qualitative agreement with the  $N(E_F)$  values deduced from low temperature specific heat measurements  $\gamma(T)$ .

From another point of view,  $T_D$  may be related to the carrier mean free path  $\Lambda_c$  along the c-direction:  $T_D = \frac{3}{2} \delta_a^2 \tau \Lambda_c^{-2}$  where  $\tau$  is the conductivity relaxation time (related to  $T_2$ ). Knowing  $\sigma_a$  (and then  $\delta_a$ ) and  $\tau$ ,  $\Lambda_c$  may be estimated. One obtains in this way reasonable  $\Lambda_c$  for the donor-G.I.C. (for instance  $\sim 20 \text{ \AA}$  for the Li-compounds known to be the most tridimensional ones, some  $\text{\AA}$  for the other alkali-compounds) while for the acceptor-compounds which present the highest known anisotropy ( $\sim \sigma_a/\sigma_c \sim 10^6$ ), the estimated  $\Lambda_c$  is senseless small ( $\sim 10^{-2} \text{ \AA}$ ) but in "qualitative" agreement with their nearly insulator character perpendicular to the layer-planes.

### B) Relaxation Time $T_2$

Following Elliott's theory of metals,  $T_2$  is directly proportional to the conductivity relaxation time  $\tau$  and then to the conductivity itself (at least when the g-factor anisotropy is small, which is the case in G.I.C. as we will see). So the temperature dependence of  $T_2 = (\gamma\Delta H)^{-1}$  would be a good test for the metallic character of the samples. A linear variation against T for  $\Delta H$  has been found for  $T > 100 \text{ K}$  in most of the K-compounds [10,12] but not at all in the Li-ones, in which the linewidth is temperature independent (Fig. 6a). Moreover at low temperature, some K-G.I.C. show an increase of the linewidth and even more remarkably some exhibit an unexpected and unexplained maximum around 15-17 K (stages 3 and 5) or 40 K (stages 2 and 4). So at low temperature the classical theory for metals does not apply. (Fig. 6b).

However another feature of the metallic character may be observed in donor G.I.C., that is the spin-orbit coupling between the conduction electron and the inserted nucleus. Indeed the linewidth is very sensitive to the stage (that is to say to the alkali-nuclei concentration) and to the atomic number of the inserted species (Fig. 7) [10,13,14]. This fact is important in G.I.C.: indeed, as the line is unique even in higher stages, it proves the electrons

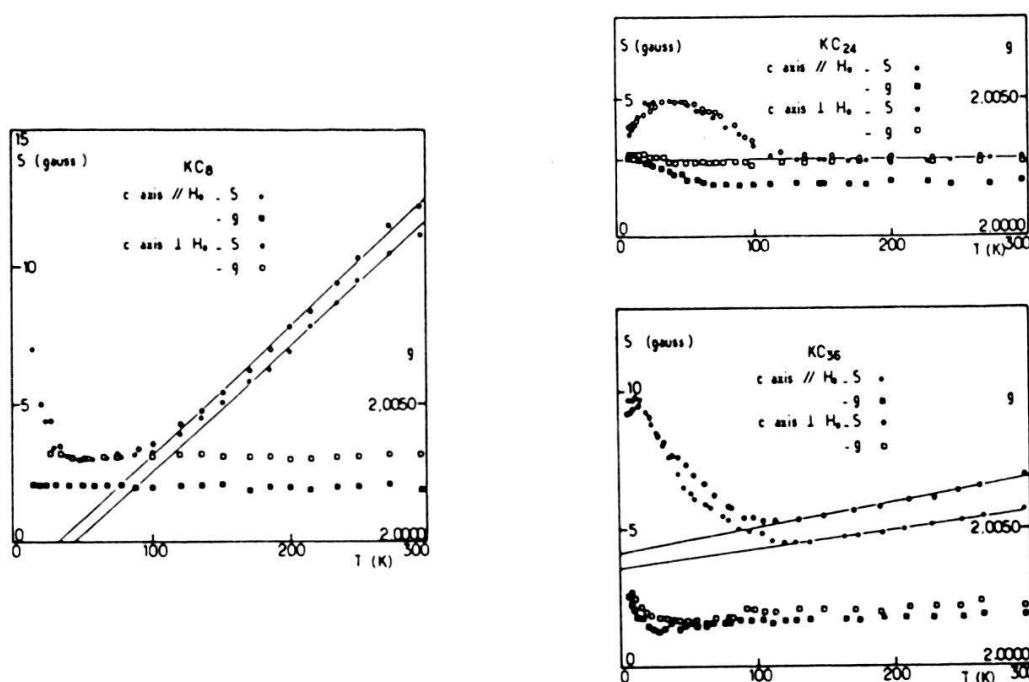


Fig. 6a). Lamellar compounds of pyrographite with potassium (stages 1-3). The temperature dependences of linewidth ( $S$ ) and  $g$ -factor are given for the two standard positions, the C-axis sample parallel or perpendicular to the magnetic axis, from Delhaes,...[12].

to experience the whole material, and their localization not to be restricted in the graphitic  $\pi$ -orbitals as they also interact with the inserted nuclei. As we will see later, the  $s$ -wave function on those nuclei is not completely zero. Such a delocalization of the electrons on the inserted species has also been observed in graphite-fluoride compounds [14,15].

In ternary compounds graphite-alkali-organic molecule, the linewidth is reduced by a factor of 2 to 6 depending on the stoichiometry and stage [16,17]: the organic molecules surrounding the alkaline atoms decouple them from the conduction electrons system and reduce thereby the spin-orbit coupling.

### C) $g$ -factor Anisotropy

Graphite is a semi-metal in which two bands are degenerate near the Brillouin zone edge. This fact induces a great orbital susceptibility and a great  $g$ -factor shift for the direction  $H_0 \parallel c$  whereas  $g_{\perp c}$  remains very close to the free electron  $g$ -factor value. A small doping, changing even very little the Fermi level, lifts the band degeneracy and modifies drastically those pro-

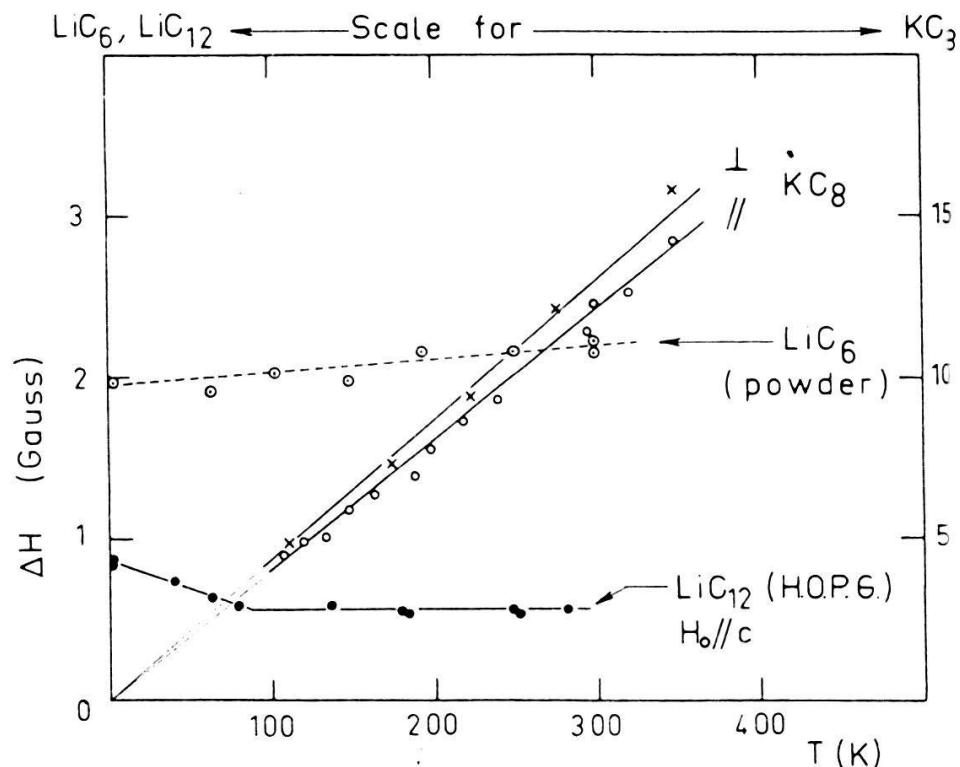


Fig. 6b). Li and K-compounds: linewidth temperature dependence. For  $KC_8$ :  $\circ H_0 \parallel c$ ;  $\times H_0 \perp c$ . From Lauginie, ... [10].

erties, reducing both the orbital susceptibility and the  $\delta g = g_{\parallel c} - g_{\perp c}$ . This is the case in all the G.I.C. where the observed  $\delta g$  lies around  $10^{-3} - 10^{-4}$  and is opposite to that of graphite, equal to  $47 \cdot 10^{-3}$ . Even the highest well defined (9th) observed stage does not seem to come back to the graphite situation [10]. Moreover, even in this highest stage, the E.P.R. line is unique, all the graphitic planes are charged enough to see their  $\delta g$  reduced: the resulting electrostatic forces are probably responsible for stable staging and long range periodicity.

#### 4. N.M.R. in G.I.C.

Before describing the informations about the G.I.C. from N.M.R. we have to recall that all the interactions revealed by this technique are essentially short ranged and for this reason, only local informations will be

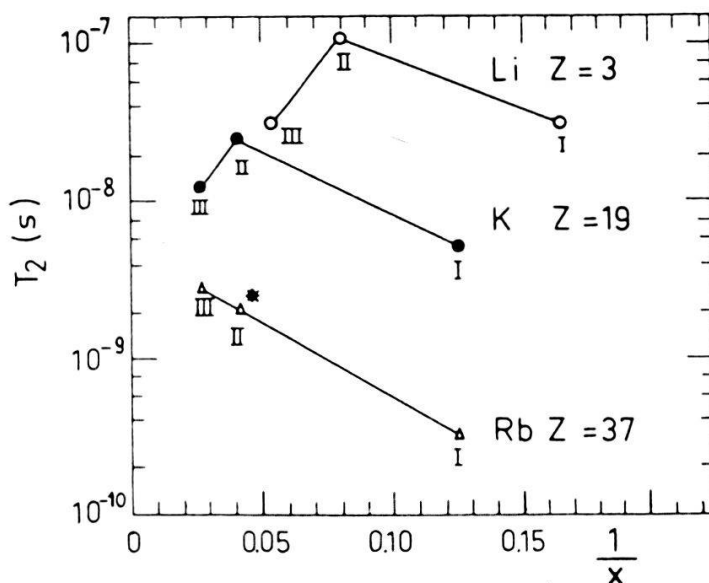


Fig. 7. Spin relaxation time  $T_2$  in  $MC_x$  alkaline compounds versus metal concentration (room temperature), from Lauginie, ... [10].

obtained. The ones studied till now in G.I.C. concern A) the interaction with the conduction electrons, B) the mobility of the inserted species, C) the site symmetry and the local electric field gradient at the insertion site. B) and C) are observed through the N.M.R. of the inserted species, whereas A) through both the inserted species and the  $^{13}\text{C}$  of the graphitic planes. Indeed this last nucleus is a very suitable probe to observe the charge distribution in the C-planes. Its natural abundance (1%) is not very favourable for the signal intensity but this rareness prevents from dipolar broadening and lets then the line be resolved. N.M.R. has been performed both on powdered and on oriented G.I.C.

#### A) Interaction with the Conduction Electrons

The classical contact interaction between the nuclei and the conduction electrons produces a line shift from which we may deduce the local charge. Indeed this Knight shift may be written:

$$\begin{aligned}
 K &= \frac{\Delta\nu}{\nu} = \frac{8\pi}{3} \chi_p |U_F(o)|^2 \\
 &= \frac{8\pi}{3} \mu_B^2 N(E_F) |U_F(o)|^2
 \end{aligned}$$

where  $\chi_p = \mu_B^2 N(E_F)$  is the Pauli susceptibility proportional to the density of states at the Fermi level.  $|U_F(o)|^2$  is the probability to find an electron at the nucleus site averaged on the Fermi surface.

In the case of alkali nuclei, this interaction with the s-electrons is dominant, isotropic and results in a low field shift of the line. It may be considered as a measure of the s-character of the electrons around the nucleus at the Fermi level. In the case of  $^{13}\text{C}$ , the conduction electrons are of  $\pi$ -type and their probability to be found at the nucleus site is zero. Moreover they are polarized in the magnetic field and this polarization is indirectly transmitted to the inner-s-electrons: the whole mechanism results in an indirect Knight shift which is upfield and, as well as the direct one, proportional to  $N(E_F)$ . The conduction electrons interact also through their dipolar moment with the one of the nucleus. This dipolar interaction may be anisotropic in a non-cubic site but is traceless, that is to say it will not affect the center of mass of the line. It is also proportional to  $N(E_F)$ . In the case of s-electrons, this dipolar interaction is zero.

The interaction between the nucleus and the orbital moment of the electrons is also zero for the s-electrons but very important in the case of  $^{13}\text{C}$ . It is anisotropic but not traceless. In the case of G.I.C., this orbital term will be maximum when  $H_o$  is  $\parallel \vec{c}$  (large orbits and conductivity in the C-planes, large orbital susceptibility of same origin) and small or even zero when  $H_o$  is  $\perp \vec{c}$ . This orbital interaction is of course greatest in pure graphite. If we include in it the susceptibility effect of same origin, we may obtain 600 ppm anisotropy, depending on the shape of the sample both in sign and in magnitude. In G.I.C. this term may be reduced but is not negligible.

Now we have to define a reference for the line shift. For alkaline atoms, the ionic species in dilute solution is the ideal reference both theoretical (no Knight shift) and experimental (easy to obtain!). For  $^{13}\text{C}$ , the problem is more complex as the ionic species does not exist. It would be necessary to find a carbon in which the density of states at the Fermi level

would be zero and zero also its orbital shift. As we saw in part 3- C (E.P.R. g-anisotropy) a very slight doping reduces strongly the susceptibility by moving even slightly the Fermi level, whereas density of states remains very low. Indeed a boron doped graphite (B.G.) (0.5% of boron in substitution) gives a narrow isotropic  $^{13}\text{C}$  N.M.R. line which has been taken as a reference for all the measured shifts. The experimental reference is liquid benzene (50 ppm upfield shifted/B.G.). In fact all the  $^{13}\text{C}$  lines need long time accumulations: their relaxation times lie between 1 and 100s and the scan number necessary to observe the line with reasonable signal to noise-ratio is about 1000 at 300 K.

Let us now look at the experimental results.

a) Alkali-N.M.R. in G.I.C. The N.M.R. of the inserted alkaline nuclei show a general feature: in the 1st stage, the lines are low field shifted like in the metal but the Knight shift is now reduced by a factor 6-7 ( $^7\text{Li}$ : [18,19],  $^{89}\text{Rb}$ : [20],  $^{133}\text{Cs}$ : [21,22,23]). This means that the s-wave function around the alkali nucleus is not completely zero but strongly reduced. A complete quantitative interpretation is complicated as the Knight shift is proportional both to  $N(E_F)$  and to the s-character at the Fermi-level. Two band structure calculations of  $\text{LiC}_6$  [24] gave a very good agreement with the experimental result.

In this same sample, the contact interaction with conduction electrons has been confirmed through the Korringa relation between the Knight shift, the relaxation times  $T_1$  and the temperature for  $T < 150$  K both with  $^7\text{Li}$  and  $^6\text{Li}$  isotopes [18]. In the second stage Li-compounds, the K.S. is equal to that in stage I but in higher stage, the line is not shifted relatively to  $\text{Li}^+$  position or even little up field shifted. This is also the case in higher stage Cs-G.I.C.: the s-character has almost disappeared and the lines are up field shifted - the shift direction imposed by the chemical shift which is no longer negligible [22]. This result is in good agreement with the idea, usually admitted by the chemists of the ionic character of the alkaline atoms in stage  $> 2$ .

Interesting results have been obtained on the thermal dependence of the line position in  $\text{RbC}_8$  and  $\text{CsC}_{24}$ . In both cases, the K.S. increases with increasing temperature in  $\text{RbC}_8$  at  $T \sim 580$  K [25] and in  $\text{CsC}_{24}$  for  $T > 200$  K [22,26]. In the first case, this K.S. increasing, that is to say the increase

of the s-character, corresponds to a change from Rb rigid lattice to lattice gas situation: Rb is then more loosely coupled with the graphite lattice (Fig. 8). Same thing occurs in  $\text{CsC}_{24}$  when the Cs lattice seems to change its correlation with the graphitic one (Fig. 9). So in both cases, the alkali atom

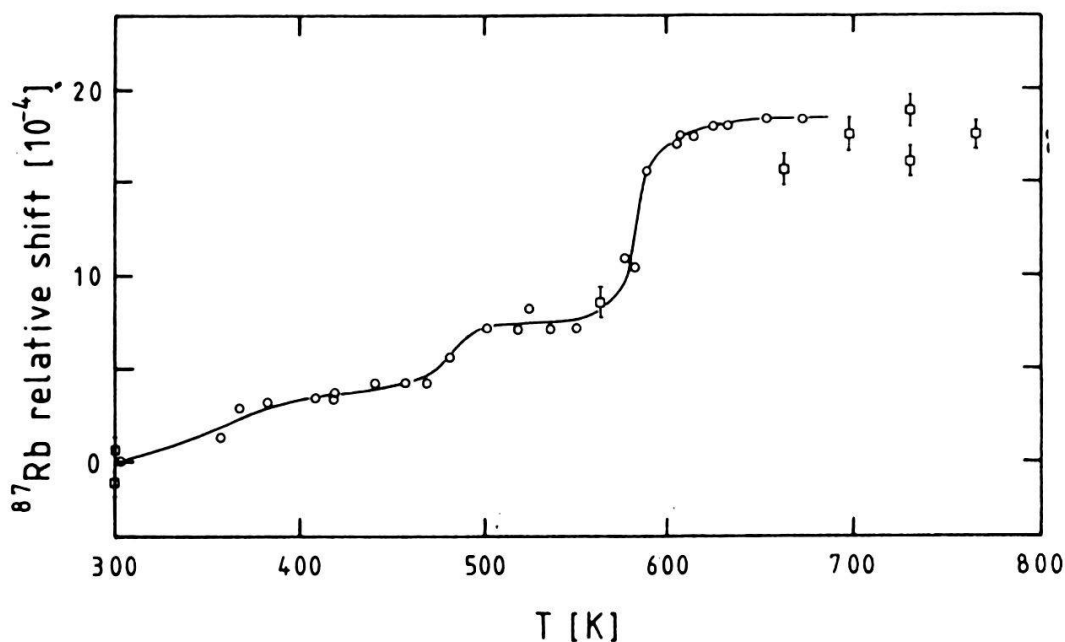


Fig. 8. Temperature dependence of the  $^{87}\text{Rb}$  shift relative to the 300 K position of the line at 57.3 MHz in an  $\text{RbC}_{8+\delta}$  HOPG sample with  $\text{H}_2 \parallel c(o)$ . Preliminary measurements at 59.2 MHz with  $\text{H}_2 \parallel c$  are also reported ( $\square$ ). From Chabre, ... [25].

recovers at least part of its s-electron when loosing part of its bonding to the graphitic layers.

At last, in Li-T.H.F.-G.I.C the  $^7\text{Li}$  line position is very close to the  $\text{Li}^+$  one [17] whatever the stage of the pristine binary compound was: the complexations of the Li by the T.H.F. molecules removes completely the s-electron. A similar conclusion has been drawn from EXAFS threshold experiment in  $\text{RbC}_{24}(\text{T.H.F.})_x$ .

In this paragraph, we can also speak about  $^{19}\text{F}$  N.M.R. on  $\text{AsF}_5^-$  and  $\text{SbF}_5^-$  G.I.C., although the results do not show real interaction with conduction electrons. The problem is the determination of the nature of the inserted

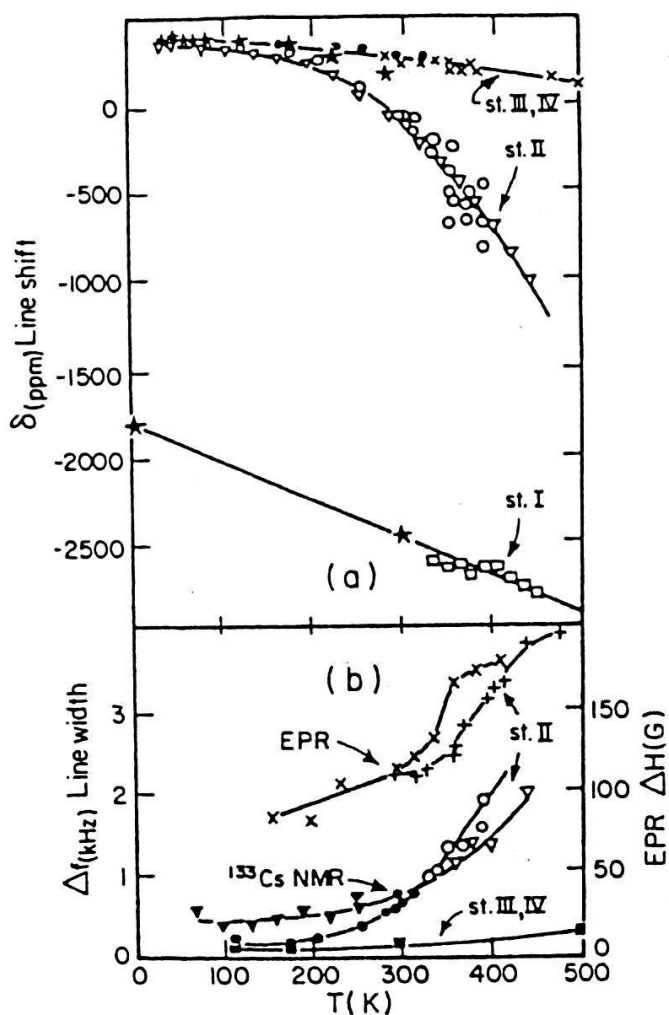


Fig. 9.  $^{133}\text{Cs}$  NMR line position a) and NMR and EPR linewidth b) vs  $T$ . ●  $\text{CsC}_{48}$  x  $\text{CsC}_{36}$  □  $\text{CsC}_8$  ○  $\text{CsC}_{24}$  at 11.8 MHz  
 ▽  $\text{CsC}_{24}$  at 44 MHz, from Estrade, ... [26].

species. Do the fluorides decompose? How many fluorine species are present? Which ones?  $^{19}\text{F}$  N.M.R. gave some answers; we can find  $\text{AsF}_6^-$ ,  $\text{AsF}_5$ ,  $\text{AsF}_3$  or similar species with Sb [27,28]. They have been characterized by their position and relaxation time  $T_1$ . Their proportions depend on stage but not on temperature. As EXAFS  $\text{K}^+$  threshold experiments confirm those results.

b)  $^{13}\text{C}$  N.M.R. in G.I.C. All the  $^{13}\text{C}$  N.M.R. spectra in powdered G.I.C. show the classical shape of anisotropic shift [29] (Fig. 10a). In those spectra,



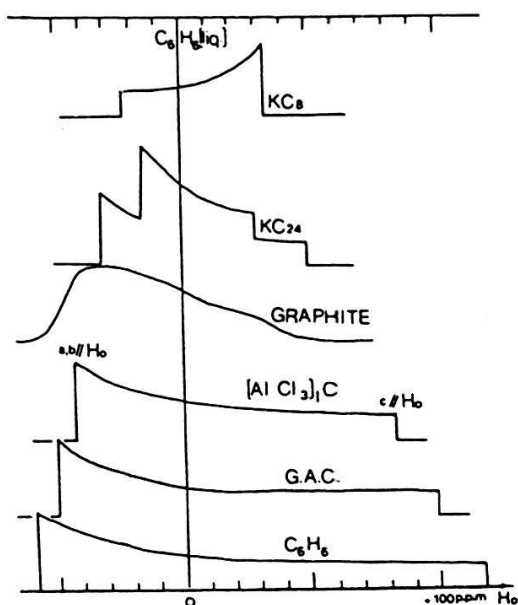


Fig. 10a).  $^{13}C$  N.M.R. schematic lineshapes in powdered samples from Conard, ... [18].

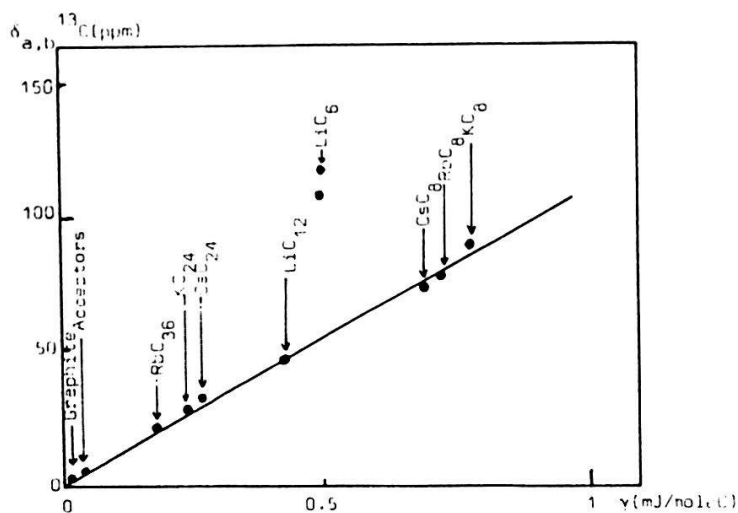


Fig. 10b).  $^{13}C$   $\delta_{a,b}$  shifts vs. specific heat. Good proportionality (except  $LiC_6$ ) from Conard, ... [18].

it is possible to point out the  $H_0 // a.b$  peak position. Its shift relative to the B.G. reference gives a very good linear variation against the specific heat measurements: in this  $H_0 // a.b$  direction, the only contributions to shift (contact and dipolar) are proportional to  $N(E_F)$  as the orbital term is negligible (exception:  $LiC_6$ ). No correlation can be observed on the  $H_0 // \vec{c}$  peak (Fig. 10b). However the first stage donor-G.I.C. have an anisotropy opposite to that of graphite, solid benzene, higher stage donor-G.I.C. or all stage acceptor ones: in those  $LiC_6$ ,  $RbC_8$ ,  $KC_8$  or  $CsC_8$ , the density of stages at  $E_F$  is great and the dipolar interaction imposes its anisotropy direction to the shift.

In all the other compounds,  $N(E_F)$  is much smaller and the orbital term is dominant.

Moreover in higher stage  $n \geq 3$ , a peak appears at the (a-b) graphite position [29]. This peak is relative to the inner graphitic layers, not directly in contact with the inserted species. On oriented  $KC_{12n}$  samples, very beautiful spectra have been obtained [30]. They are remarkably resolved and reveal different C-sites, first and second neighbours relative to the inserted K atoms in the adjacent planes and also in the further ones (Fig. 11). The relaxation times  $T_1$  of the  $^{13}C$  nuclei at all those sites are different and shorter than that of pure graphite and they may be used, through the Korringa relation to determine the local density of states on C-atoms. They confirm the model proposed by J. Conard [29] of a density of states for each C-planes, first, second, third... neighbour to the inserted planes, but show and precise the charge distribution in each of these planes.

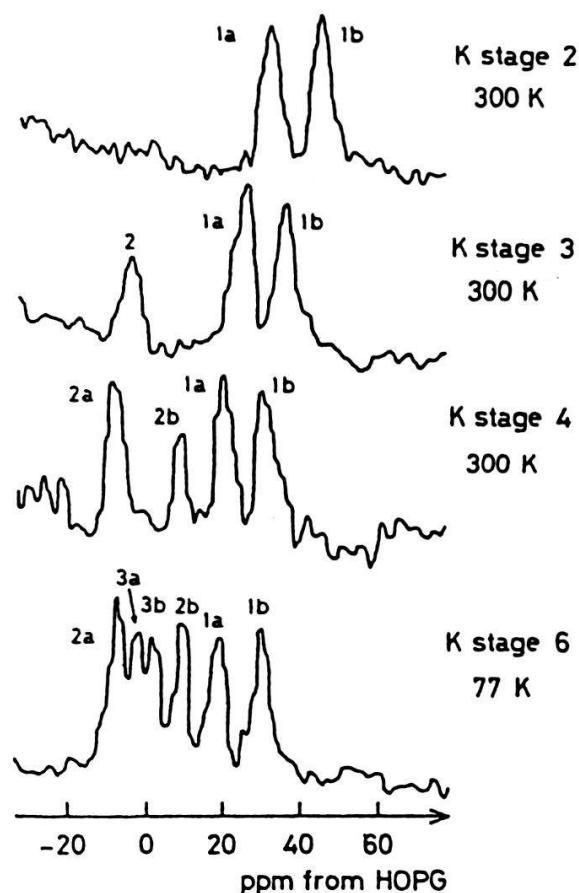


Fig. 11.  $^{13}C$  N.M.R. spectra of K-G.I.C., from Kume, ... [30].

New results in  $\text{AsF}_5$ -GIC 1<sup>st</sup> stage allow the C-C distance determination using the high resolution situation (mobility of  $\text{AsF}_5$ ) and  $^{13}\text{C}$  isotope concentration.[31]

### B) Mobility of the Inserted Species

Several of the inserted species show thermal transitions of their line width due to increasing mobility. This has been the case in  $\text{LiC}_6$  and  $\text{LiC}_{12}$  near 280 K: at this temperature, the  $^7\text{Li}$  line narrows, whereas the first order quadrupolar structure remains unchanged [19]. Atomic diffusion takes place between equivalent axially symmetric sites as it does at almost the same temperature in metallic Li, averaging to zero the dipolar broadening of the line. From the slope of the transition, we may estimate the activation energy of this motion: it is lower in  $\text{LiC}_{12}$ , known to be lacunar, than in  $\text{LiC}_6$  more stoichiometric. In  $\text{HNO}_3$ -G.I.C.,  $^1\text{H}$  N.M.R. and E.P.R. [32,33] spectra show similar narrowing at 220 and 250 K where the inserted acid begins to be mobile. Cristallographic studies confirm these transitions.

In graphite-alkali-organic molecule ternary compounds, a lot of work has been done on the mobility of the organic molecules and the structure of the cation-organic molecules complexe (benzene or T.H.F.) [34,35].  $^1\text{H}$  N.M.R. and X-rays studies show that, depending on the stoichiometry and on the stage, the complexes are either flat or tridimensional in the inserted space. When temperature increases, the flat complex does not change, whereas in the tridimensional complex several motions take place successively. Theoretical calculations determine the line narrowing expected for different possible motions (oscillation, rotation, torsion...) and the comparison with experimental results allows the attribution of the different observed transitions (Fig. 12).

The mobility of the inserted species has been observed not only through the linewidth but also as we saw above, on the line positions [25,26] characterizing the coupling between graphitic and inserted lattices, or on  $T_1$  thermal dependence when the Korringa law ( $T_1^{-1}$  proportional to  $T$ ) is no longer valid [18]

### C) Site Symmetry and Electric Field Gradient (E.F.G.)

All the alkaline nuclear spins studied have spin  $\geq \frac{3}{2}$  and are able to give informations about their site symmetry and the E.F.G. to which they are submitted. In all the binary G.I.C. of Li, Rb or Cs, the alkali site is axially

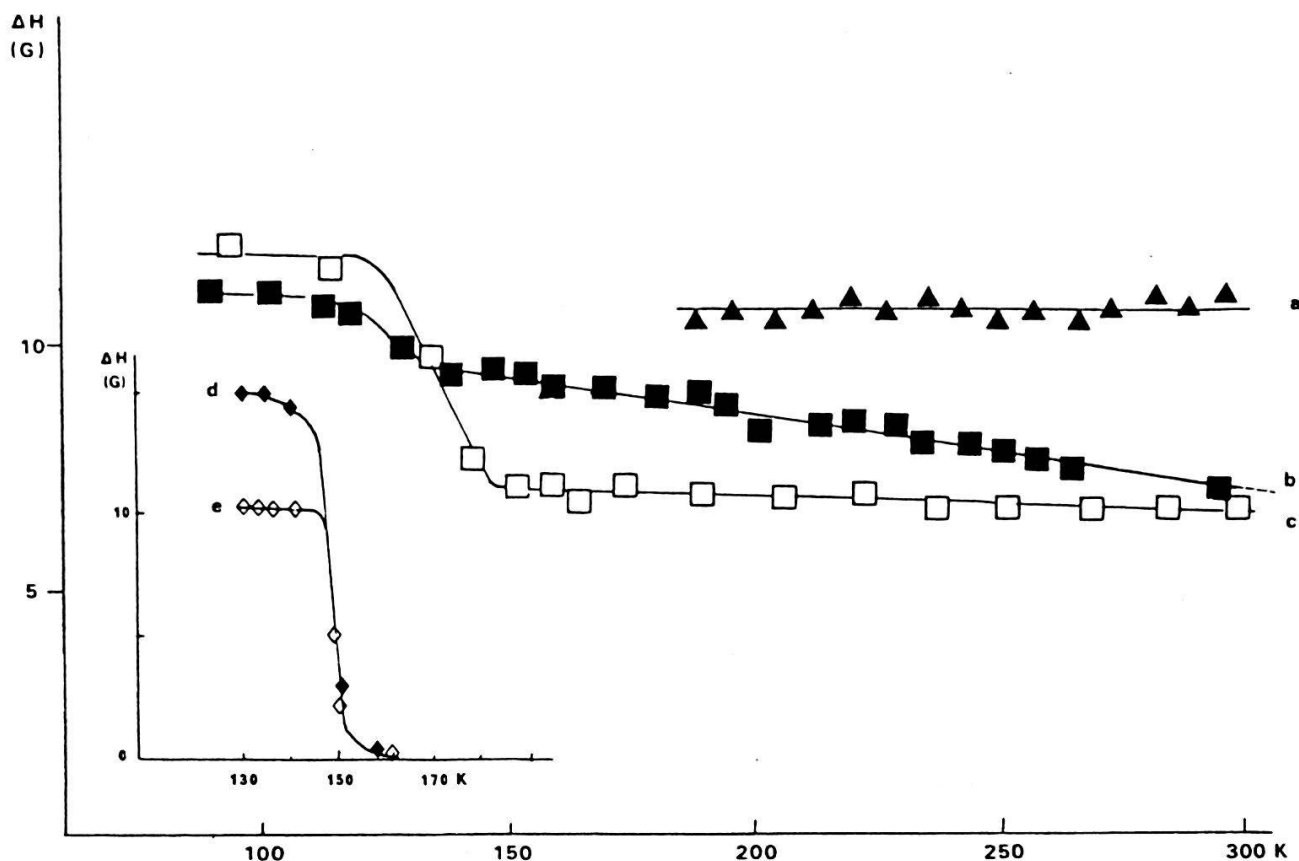


Fig. 12.  $^1\text{H}$  NMR of various compounds, as a function of temperature: (a)  $\text{KC}_{24}(\text{THF})_1$  (st.II); (b)  $\text{KC}_{24}(\text{THF})_2$  (III) or (I); (c)  $\text{KC}_{24}(\text{THF})_2$  (IV); (d) pure THF; (e) THF in  $\text{CDCl}_3$ , from Quinton,... [35].

symmetric and the first order quadrupolar structure has been observed [18,20-22]. In several cases described here above, this axial symmetry and the  $\nu_Q$ -values do not change when atomic diffusion takes place [18,25,26]: inserted atoms are in a lattice gas configuration. In Cs-higher stages ( $n \geq 2$ ) the second-order quadrupolar splitting (proportional to  $H_0^{-1}$ ) is well resolved at low field (2.1 T) and disappears at 8 T. In  $\text{RbC}_8$ , the Rb central line is so broadened by this second order quadrupolar interaction that it is not observable in powdered samples.

Using the quadrupolar constant  $Q$  from the literature (for Li and Cs, the values vary a lot from one author to the other!) we can deduce the electric

field gradient from the experimental  $\nu_Q$  values. (Table I). Surprisingly, the so calculated E.F.G. are almost stage and alkali-nature independent: the E.F.G. cannot result from the sole alkali-neighbour charge (it would be strongly stage dependent) but it is essentially due to the surrounding  $\pi$ -functions. A complete calculation from the total band structure results in a relatively close value in  $\text{LiC}_6$ . From dependence of  $\nu_Q$  in the same  $\text{LiC}_6$  [36], compressibility coefficient was deduced but did not account for the thermal dependence of  $\nu_Q$  related to dilatation coefficients.

In ternary Li-T.H.F.-G.I.C. [37] the observed  $\nu_Q$  is 6-7 times smaller than in the binary ones: this result is a supplementary argument for a tetrahedric complex  $[\text{Li}, 4 \text{ T.H.F}]$  deduced from stoichiometry and X-rays studies. In such a highly symmetric situation, the E.F.G. must be strongly reduced.

Nucleus	G.I.C.	I	Q(barns)	$1-\gamma_\infty$	$\nu_Q$ (Hz)
$^7\text{Li}$		3/2	$1-4.3 \cdot 10^{-2}$	0.75	
	$\text{LiC}_6$				$22.5 \cdot 10^3$ (300K)
	$\text{LiC}_{12}$				$19.4 \cdot 10^3$ "
	$\text{LiC}_{18}$				$18.5 \cdot 10^3$ "
$^{87}\text{Rb}$		3/2	0.12-0.15	49	
	$\text{RbC}_8$				$11.1 \cdot 10^6$
$^{133}\text{Cs}$		7/2	$2-4 \cdot 10^{-3}$	106	
	$\text{CsC}_8$				$84 \cdot 10^3$ (4K)
	$\text{CsC}_{24}$				$78 \cdot 10^3$ (300K)
	$\text{CsC}_{36}$				$86 \cdot 10^3$ (100-500K)
	$\text{CsC}_{48}$				$85 \cdot 10^3$ ( " " )

Table I. Quadrupolar interaction constants and frequencies. The experimental  $\nu_Q$ -values may be calculated through the formula:  $\nu_Q = 3eQ(1-\gamma_\infty)eq/2I(2I-1)h$  in which Q and  $\gamma_\infty$  are respectively the quadrupolar constant and the antishielding factor of the I-spin observed nucleus, whereas eq is a measure of the electric field gradient at the nuclear site.

### 5. Discussion and Conclusion

Not all relevant questions have been mentioned in this brief review. For example the beautiful E.P.R. - N.M.R. Schumacher-Slichter technique for determination of the Pauli susceptibility, scaling the E.P.R. signal through the N.M.R. one, has been performed both on some acceptor- and donor-G.I.C. [38-40].

Several fundamental problems have not been invoked here: for instance is the electronic relaxation anisotropic in an anisotropic conductor and which conductivity  $\sigma_a$  or  $\sigma_c$  does govern the electronic spin relaxation?

Several other problems have been invoked but not solved: how is it possible to separate the dipolar from the orbital contribution in  $^{13}\text{C}$  N.M.R. (they have both the same angular variation and crystalline samples give only higher resolution but not greater information)? In the Knight shift itself, how is it possible to separate the local information (probability of presence of an electron at the nucleus site) from the collective one ( $N(E_F)$ )?...

However in spite of those restrictions, both magnetic resonances have been very useful in the description of the electronic structure of the G.I.C. Particularly, they allowed the construction of the band structure-per-layer model. But of course as all the characterization methods in physics, their efficiency is highly increased when used together with other techniques. For example, the phase transitions observed by N.M.R. have to be supported and explained by structure studies.

In G.I.C., like in other compounds, N.M.R. and E.P.R. remain relatively simple and powerful tools... among all the necessary other ones.

### Acknowledgments

Here above is written that any single technique cannot give the highest efficiency. Same thing occurs with single thought: most concepts and progress described in this paper result from several thoughts and numerous collective discussions, especially in our group in Orléans. My colleagues J. Conard and P. Lauginie are sincerely acknowledged for all those years working together.

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