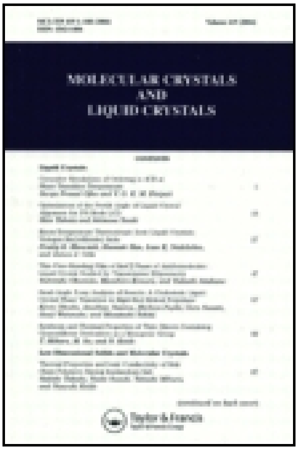

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Puzzling Facts in Alkali Gic

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Version of record first published: 23 Oct 2006.

To cite this article: P. Lauginie & J. Conard (1994): Puzzling Facts in Alkali Gic, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 245:1, 19-24

To link to this article: http://dx.doi.org/10.1080/10587259408051660

Mol. Cryst. Liq. Cryst. 1994, Vol. 245, pp. 19–24
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Printed in the United States of America

PUZZLING FACTS IN ALKALI GIC

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Abstract Some Alkali-GIC puzzling features, which may be of more general interest (specially to fullerides and conducting polymers) are discussed, namely : the validity of charge transfer heterogeneity deduced from NMR shifts ; carbon-alkali hybridization in stage 1 viewed from 13-C shifts and relaxation rate ; evidence of carbon σ-π hybridization in G.I.C. ; possible long-range effects of inserted alkali atoms.

INTRODUCTION

In spite of a considerable amount of work and literature on alkali-G.I.C., a number of problems have remained unsolved, or incompletely understood, or demand some clarification. For four among them related to the interpretation of NMR and EPR, which are selected below, solutions or routes for solutions are proposed, namely :

1) Is the similarity between the total transferred charge distribution among the graphene planes and the respective Fermi-level populations general or fortuitous ? A very simple model for charge transfer heterogeneity will put forward the particular role of the in-plane interaction parameter γ_0 in graphite.

2) A non-diagonal contribution of alkali s-states in stage 1 GIC can reconcile ^{13}C-T_1 values with alkali-NMR results.

3) Carbon σ-π hybridization (claimed in fullerenes and fullerides) was already present in GIC : literature results are reinterpreted in the light of theoretical models.

4) ^{13}C-NMR and EPR give evidence of interaction between carbon atoms in graphene planes and inserted alkali atoms well beyond the sole alkali-adjacent planes.

CHARGE TRANSFER HETEROGENEITY AND FERMI LEVEL POPULATIONS

The observed similarity between the stage behaviour of these properties bound to the total charge transfer (in-plane C-C bond length)[1] and those only related to the Fermi-level populations (low temp. specific heat, NMR metallic shifts)[2,3,6] has remained a quite puzzling fact.

The Fermi level population for a carbon plane or site is a local property in reciprocal space : it is the ratio of the local π–D.O.S. to the total D.O.S. at E_F. On the other hand, the charge transferred in this plane or site is a different quantity obtained through integration of the local D.O.S. over all occupied states in the conduction band.

Kume et al[4,5] gave the most accurate ^{13}C-shift results in various stages K-G.I.C.. However, in our opinion, their determination of charge transfer heterogeneity suffers from the general use made of the rigid band model, the validity of which having been shown to be restricted to little charged (i.e. non alkali-adjacent) planes[7,8].

Hence, starting with C-planes local Fermi D.O.S., the following strategy is proposed for stages >1 :

- for alkali non-adjacent (or "remote") planes, the rigid band model is used. An acceptable choice of the graphite γ_o parameter (2,77 eV) for a gross description of the 0-1,5 eV range leads to a n(E) slope of 0.048 eV^{-2} per C-atom[8]. The charge of each "remote" plane can then be easily deduced (area of a triangle).

- for the adjacent planes, avoiding any hypothesis about the true bandshape, the charge transferred to these planes is the complement to 1 of the charge transferred to the "remote" planes.

Surprisingly, this distribution is almost the same (within 1%) as the distribution of Fermi level populations (43% in each adjacent plane and 14% in the remote plane for a stage-3 K-G.I.C. ; 45% and 10% resp. for the Rb and Cs derivatives).

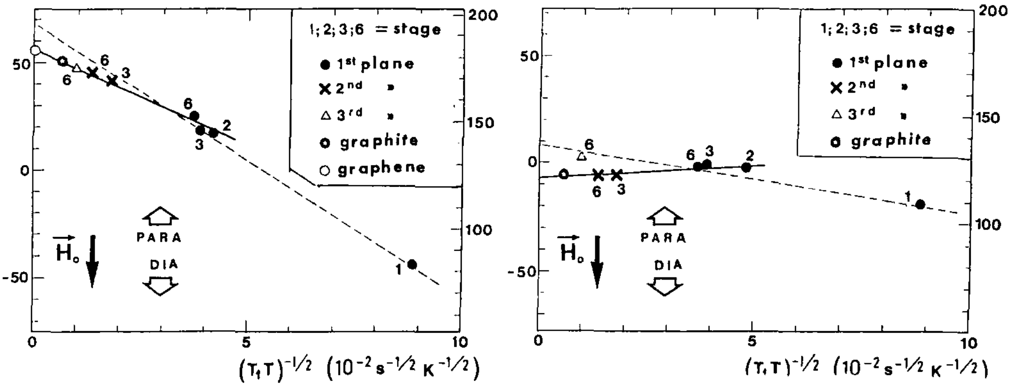
Nevertheless, according to the above discussion, this agreement follows directly from the particular value of the graphite γ_o parameter. This near coincidence also explains why NMR shifts or Fermi D.O.S. yield good estimates of the total charge transfers in alkali G.I.C., thus adding self-consistency to our choice of γ_o.

This lucky opportunity is peculiar to graphite and the G.I.C. (but maybe are there more fundamental causes ?); it cannot be generalized to other systems. Beyond the trivial case (not realized in G.I.C.) of constant populations along the conduction band, a detailed examination of each situation is required.

STAGE-1 ALKALI-CARBON HYBRIDIZATION AND ^{13}C-RELAXATION RATE

From comparison of their ^{13}C- T_1 data with Fermi D.O.S. deduced from specific heat data, Maniwa et al[4] concluded that the alkali s-state Fermi level population reached 54%, in disagreement with the roughly 10% deduced from alkali Knight shifts[7,10].

We show in Fig.1-a the **(a,b)** component of the ^{13}C-shift tensor versus $T_1^{-1/2}$. Data are not taken from the published curves but directly from the authors tables[4,5,9]. Clearly the stage-1 point does not fit the linear law followed by higher stages, (contrary to the published curve[4]). More, except the stage 1 point, the extrapolated full line now intersects the zero-D.O.S. axis *exactly* at the graphene position (55 ppm from liquid C_6H_6[11]), as it should! We shall now try to interpret the deviation observed for stage 1.



a) b)

FIGURE 1 ^{13}C shift tensor versus relaxation rate from the literature data[4,5].

a) In-plane component $\delta_{a,b}$ b) Isotropic component δ_{iso}

The abscissa is proportional to the local Fermi D.O.S.
Left scale : ppm / C_6H_6. Right scale : ppm / T.M.S.. The broken lines correspond to the curves reported by the authors (close to the linear regression lines of the whole set of points). Full line : our proposed interpretation.

Suppose, in an oversimplified model, the Fermi wavefunction to be an admixture of s-alkali and π-carbon states (denoted s and π resp.). The shift $\delta_{a,b}$ (here denoted δ) *refered to graphene* is mainly of dipolar origin[6,8] . Neglecting the overlap for a crude estimate, we write :

$$\delta = \delta_s + \delta_\pi \qquad (1)$$

Assuming further the s and π states not to be correlated, the dipolar rate will be the sum of both contributions (contrary to Maniwa et al[4], the s-term is not neglected a priori) :

$$T_1^{-1} = (T_1^{-1})_s + (T_1^{-1})_\pi \qquad (2)$$

Since Korringa-type laws have been observed[4], we attribute the same constant C to the Korringa product of both contributions, the same ^{13}C nucleus being involved :

$$(T_1T)_i\,\delta_i^2 = C \qquad (\, i = s \text{ or } \pi\,) \qquad (3)$$

Then, squaring Eq. (1) and substituting into (3), we get in a 1st order approximation :

$$-\,\delta = C\,(T_1T)^{-1/2}\,(\,1 + C^{-1}\,\delta_s\delta_\pi\,T_1T\,) \qquad (4)$$

The second term in brackets in Eq. (4) represents the relative excess shift over the extrapolated full line in Fig. 1-a and the slope of this line yields the constant C, from which the $\delta_s\delta_\pi$ product is deduced. Knowing their sum δ, we get finally :

$$\delta_s \approx -\,20\text{ ppm} \qquad \delta_\pi \approx -\,80\text{ ppm}$$

This would mean a Fermi level population of the alkali s-state about 20% (*not* 54%!). Since other carbon or alkali orbitals may eventually contribute to the dipolar interaction, this value should represent an upper bound for the alkali-s population. On the other hand, in agreement with the strong electron-phonon coupling suggested by Pauli susceptibility direct measurements[13], the above-mentionned estimates from the alkali Knight-shifts (≈ 10%) might be increased by a factor lying between 1 and 2, thus getting closer to the present estimate.

CARBON σ–π HYBRIDIZATION

Carbon σ–π hybridization has been claimed to occur in fullerenes and fullerides as a result of curvature. In fact, such an admixture was already predicted in alkali-G.I.C. by Saito et al[9] in their attempt to calculate ^{13}C-shifts : a small σ-π hybridization was invoked, yielding a direct or *paramagnetic-like* contact interaction (also mainly responsible for the ^{13}C doublets). This seemed at first contradictory with the as-reported results which seemed in favor of an indirect, or *diamagnetic-like* interaction (broken line in Fig. 1-b), quite in accordance with the idea that π-orbitals have no density on the C- nucleus.

Reinterpreting the published experimental ^{13}C-shifts, we claim, on the contrary, that they strongly support Saito's theory.

As shown in Fig. 1-b (on which authors data are shown), and excluding 2 anomalous points (stage 1 and 3rd plane in stage 6), the points fit, with much higher accuracy, a straight line of *opposite* slope, thus revealing a *paramagnetic-like* interaction. From this slope we deduce the isotropic part of the hyperfine field to be ≈ +8000 Gauss (or more if a strong electron-phonons enhancement is taken into account), characteristing a predominating *direct* interaction. If we accept the negative core polarization contribution estimated by Maniwa et al[4], then the direct polarization would reach ≈ 18000 Gauss (or more).

There are reasons for the stage-1 point on Fig. 1-b not to lie on the same line as the higher stages, due to incomplete charge transfer : the alkali s-state cannot contribute significantly to the carbon contact shift ; more, the diamagnetic-like shift resulting from the decrease in paramagnetic Van-Vleck interaction due to charge transfer[6,8] is more important in stage 1 because of the larger charge tranferred per carbon atom. The case of the 3rd plane in stage 6 G.I.C. (the deviation of which being due to the sole c-component) is more complicated. An explanation in terms of orbital effects (not traceless) has been suggested[8].

LONG RANGE INTERACTION WITH INSERTED ALKALI PLANES ?

Facts from ^{13}C-NMR :

The ^{13}C doublet splittings reported in table 1 were attributed by Maniwa et al[4] to different C-positions relative to the alkali site for the adjacent plane, and to the recovering of graphite A-B stacking for the remote planes.

TABLE 1 ^{13}C-Doublets splittings (ppm) in stage-6 K-G.I.C.[4,5] and in graphite[11,12] for (**a**,**b**) and **c** field orientations

Field orientation	// **a**,**b**	// **c**
Plane 1	11	12
" 2	16	7
" 3	3	3
Graphite	0	37

However, the lack of any tendency towards the graphite value for the **c**-component decreasing series seems rather in favor of a decreasing differentiation of the carbon sites in remote planes along their position *relatively to the alkali atoms* .

Facts from EPR

The most striking fact is the near - Z^{-4} dependence of the relaxation time T_2 (prop. to the reciprocal linewidth) for a given stage K-Rb-Cs series (Fig.2).

This proves that the linewidths are dominated by spin-orbit interaction with the alkali. Since this interaction is extremely effective with heavy alkalis, a very small admixture of alkali states (too low to yield an appreciable alkali Knight-shift) in the Fermi wavefunction is sufficient to account for the broadening observed . It is important to notice that alkali-doped fullerenes yield practically the same values as stage-2 alkali-G.I.C.[6].

The second fact is an increasing linewidth with increasing stage beyond stage 2, for a given alkali. This increase was interpreted by Sugihara[14] in the frame of exchange interaction between slightly splitted π-bands (the number of which is equal to the stage). Such a theory however does not account for the Z-dependence which quantitatively dominates the linewidth.

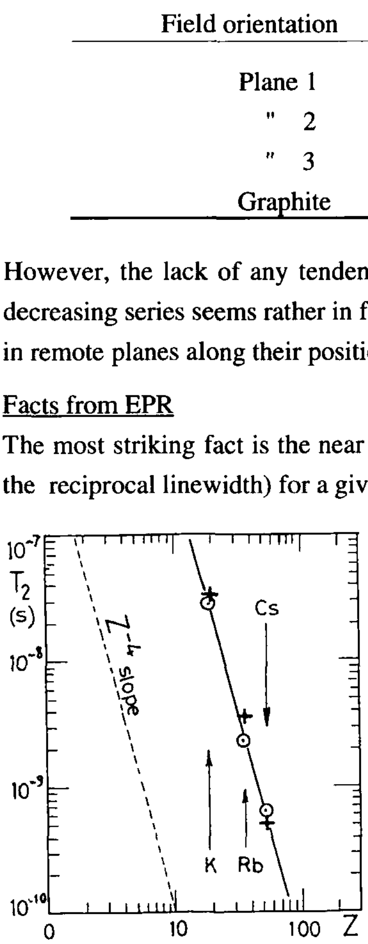


FIGURE 2 EPR relaxation time T_2 versus alkali atomic number Z.
⊖ 2nd stage G.I.C. + M_3C_{60}

Thus, both the above EPR and ^{13}C-NMR features have, we believe, a simple meaning : a 3rd-neighbour plane is *not* a graphite plane! Nor is a 4th or 5th plane.In fact, our EPR study[8] on a series of high ($\leq$ 10) and very high stage (more or less mixtures) K-G.I.C. has shown the graphite properties (linewidth and axial g-shift) to be progressively recovered as from a $\approx$ 7th plane. Only in such remote and very low-charged planes does the Fermi level return to band-degeneracy, a necessary conditon for recovering the graphite properties.We guess in such planes the splitting of the ^{13}C doublets- **c**-component to increase again towards the graphite value. Note that the occurrence of a single (**a**,**b**) line in graphite has never been accounted for.

CONCLUSION

Though apparently disparate, the above topics are strongly related to the status of the conduction electrons. The benefit of our charge-transfer-heterogeneity model resides mainly in the statement of principles for connecting Fermi D.O.S. to charges.

The literature data on ^{13}C NMR shifts and relaxation rate was carefully re-examined . Though quite conscious of the crudeness of our assumptions, we believe that it is possible, as shown, to reconcile ^{13}C and alkali NMR for stage 1. The small carbon σ-π hybridization theoretically forecast is shown to agree fairly with the data. The present interpretations of ^{13}C-doublets and EPR linewidths seem incomplete and appear to underestimate the effects connected with the intercalated planes of alkali .

Finally, through σ-π hybridization and EPR, a continuity has been established between respectively graphite and fullerenes, G.I.C. and fullerides.

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