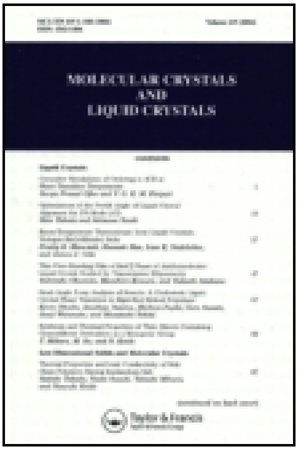

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^{13}C NMR Orbital Shift Calculation in Graphite Intercalation Compounds

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^{13}C NMR ORBITAL SHIFT CALCULATION IN GRAPHITE INTERCALATION COMPOUNDS

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Abstract As suggested by previous results, we show that the conventional analysis of the results of ^{13}C NMR line shifts used for metals do not apply in GICs: an orbital contribution to the shift must be taken into account. To evaluate quantitatively this contribution, we apply a recently developed formalism for orbital shifts in crystals to the case of first and second stage GICs (for **B** // **c**), in the independent subsystem approximation. It is shown that the sign of the orbital contribution is different for donor and acceptor compounds but its magnitude is almost independent of the charge transfer amplitude. For second stages, the calculation predicts a splitting of the lines though dipolar contribution does not. These results explain the experimental data.

INTRODUCTION

In Nuclear Magnetic Resonance experiments the characteristics of spectra (shape and shift) are related to both nuclear and electronic surroundings of each nucleus. In particular the behaviour of the electrons in the external magnetic field induces around each nucleus a local magnetic field which is responsible for a deviation of the resonance line position. In return, from a detailed analysis of these shifts it is possible to obtain useful informations on the electronic states around the nucleus. The shift has two origins : one corresponds to the coupling of the nuclear moment with the electron spins (dipolar and contact terms) and the other with the electron current (orbital term)[1]. In metals, this last term is often neglected.

This powerful technique has been extensively applied to Graphite Intercalation Compounds (GICs) to study the electronic properties of these anisotropic conductors. Nevertheless, no satisfying interpretation of the experimental ^{13}C data based solely on the dipolar shift has been done up to now[2]. In particular this contribution alone fails to interpret the differences observed between the results on compounds intercalated by donor and acceptor species and cannot completely explain the splitting observed in the second stage. Indeed, since the dipolar contribution is proportional to the density of states at the Fermi level, if we compare acceptor and donor compounds with equivalent magnitude of charge transfer, due to the nearly symmetrical shape of the 2D graphite density of states, we can expect equivalent dipolar shifts. But the experimental results in GICs reveal the existence of an other contribution: for instance, the acceptor 1st stage AsF_5-GIC and donor 1st stage $M(THF)_{\approx 2}C_{24}$ (M = K, Rb, Cs), both well described by the independent subsystem model and expected to exhibit the same Fermi level density of states, give rise to about 20 ppm difference when the magnetic field is along the c axis[3]. Moreover, the acceptor compounds of stage 2 display a splitting at **B** // **c**, though a single line is observed when the magnetic field is along the layer plane (Fig. 1)[3, 4]. This behaviour cannot be explained neither by the contact term nor by the dipolar one, both of them should give a splitting in both directions.

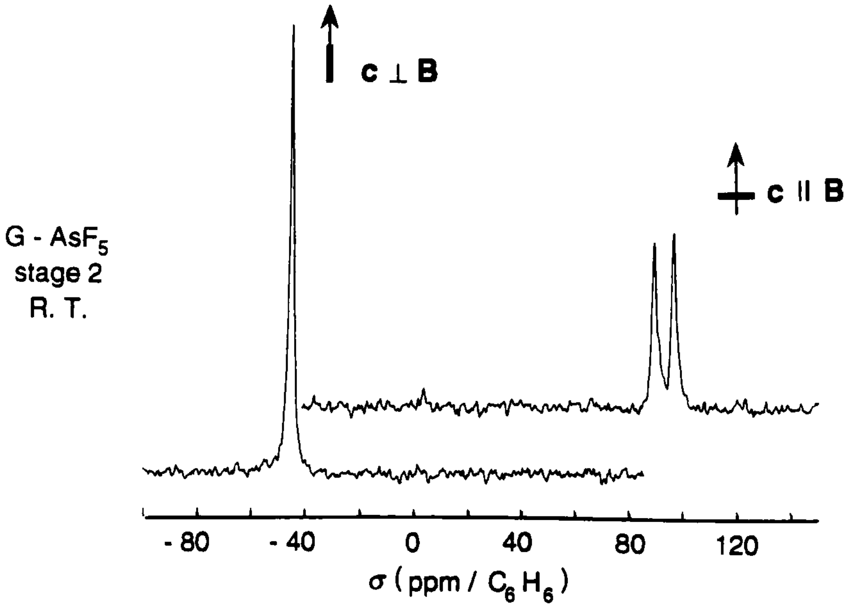

FIGURE 1: ^{13}C NMR spectra of AsF_5 - GICs, stage 2. There is no splitting at the sample orientation $c \perp B_0$ for the second stage compound.

To evaluate the effect of the orbital contribution to the shifts quantitatively, we used a recently developed formalism for the crystals[5] in the independent subsystem approximation of Blinowski and Rigaux[6]. This model permits an analytical derivation of the orbital contribution and allows a discussion of the effect of the charge transfer.

CALCULATION OF THE ORBITAL SHIFT

For a nuclear moment $\boldsymbol{\mu}$ in an external magnetic field $\boldsymbol{B}_0$, the Zeeman splitting of the nuclear level is:

$$E_0 + \Delta E = -\boldsymbol{\mu}\cdot(1-\boldsymbol{\sigma})\cdot\boldsymbol{B}$$

where - $[\sigma]\,\boldsymbol{B}$ is the field at the nucleus position originated by the electrons, $[\sigma]$ being a symmetric second-rank tensor. Kobayashi and Tsukada proposed a rigorous derivation of $[\sigma]$ in crystals which avoids the questionable approximations made in the usually employed Ramsey treatment[5].

Restricted to the case $\boldsymbol{B} \parallel \boldsymbol{c}$, the Kobayashi-Tsukada formula of the shielding term $\boldsymbol{\sigma}$ is reduced to:

$$\sigma_{zz} = -(4\pi - D)\chi_{zz} + \frac{ie^2}{m^3c^2\beta}\sum_n \int d^3k\; Tr\left(l_z\, \mathcal{G}\gamma_\mu\, \mathcal{G}\gamma_\nu\right)\varepsilon_{\mu\nu z}$$

where D is the demagnetising factor, χ the bulk susceptibility, $\mathcal{G}$ is the thermal Green's function. The current operator $\boldsymbol{\gamma}$ is proportional to the momentum operator and l_z is the z component of $\frac{\boldsymbol{L}}{r^3}$ where $\boldsymbol{L}$ is the angular moment, centred on the atom at the origin of the system. The other symbols have their usual meaning. In the basis (conduction, valence), the thermal Green function is :

$$\mathcal{G} = \left[\varepsilon_n - H(k)\right]^{-1}$$

where

$$\varepsilon_n = (2n+1)i\pi k_B T + E_F$$

and $H(k)$ is the Hamiltonian of the system.

In this expression, the first term is the demagnetising field contribution and the second one comes from the microscopic current which has the lattice periodicity and is free from the ambiguity which occurs in applying the Ramsey's expression to a crystal. We have used this formula to derive the orbital shift in the case of first and second stages compounds.

The thermal Green functions and the current operators have been calculated with the electronic states of the independent subsystems model of Blinowski et al.[6] For first stage, interactions up to the second neighbours are taken into account since a calculation of the magnetic susceptibility using the Fukuyama formula reveals that the second neighbour interactions are responsible for the differences between donor and acceptor compounds[7]. In contrast, our results show that it does not qualitatively affect very much the NMR shifts. So we neglected it for the second stage for which we are mainly interested in the splitting between the two resonance lines. In this frame, the orbital shift can be completely obtained analytically, the details will be published elsewhere. The results show that the effect of the temperature is negligible for usual charge transfer values and that the second neighbour interactions do not introduce important corrections. We present here the results, with T = 0 K and in the first neighbour approximation.

RESULT AND DISCUSSION

First stage

For first stage, the final expression of the orbital shift is :

$$(\sigma_{DA})_{zz} = \mp A\, h(|E_F|/\gamma_0)$$

where

$$A = \frac{e^2}{\hbar^2 mc^2}\frac{\gamma_0}{(2\pi)^2} b^2\sqrt{3}\,(2\lambda_A + \lambda_B)$$

$h(\varepsilon)$ is a function of elliptic integrals of first and second order, λ_A and λ_B are the matrix elements of $\frac{L}{r^3}$ operator between the p_z atomic orbitals of respectively A A and B B first neighbour atoms (the origin is taken on a A atom), A and B are the two atoms of the unit cell, b is the distance between them, E_F is the Fermi energy and γ_0 the first neighbour interaction.

From this expression, we can deduce that the orbital shift is an odd function of E_F. Moreover, the numerical calculation of $h(\varepsilon)$ shows that, for realistic values of E_F ($|E_F| \leq 0.8\,\gamma_0$), $h(|E_F|/\gamma_0)$ does not depend very much on the Fermi energy.

From these results, we can conclude that the orbital shift is independent of the charge transfer in each group (donor and acceptor). This fact can explain that early explanations of the ^{13}C NMR shift of donor compounds interpreted them as dipolar, or Knight interactions, proportional to the Fermi level density of states[8,9]. Only a comparison of the shifts of donor or acceptor compounds could evidence the additional contribution.

An order of magnitude for this contribution can be estimated from first stage compounds with opposite sign charge transfer: $M(THF)_{\sim 2}C_{24}$ (M = K, Rb, Cs) and C_8AsF_5. From the chemical formula of these compounds, it can be seen that the charge transfer per C atom is almost the same in the donor ternary compounds, where the alkali atom fully ionised is shared out between 24 atoms, and in C_8AsF_5 where the charge transfer per AsF_5 molecule is about 1/3 [6]. If we consider that the Fermi level density of states is almost the same for both compounds, the difference between the line shifts has to be attributed to the orbital contribution. This difference is about 20 ppm, and this value is too large to be attributed to the effect of the magnetic susceptibility alone. Using $\psi_{p_z} = z\exp(-1{,}59\ r/a_B)$ [7] to evaluate the λ_A and λ_B matrix elements, we obtain a difference of about 7 ppm. The calculation gives the correct sign for this contribution. The agreement with the experiment should be improved by doing a more precise evaluation of the L_z matrix elements.

It is worthwhile to notice that the pure graphene line shift, when corrected for the magnetic susceptibility, falls in between donor and acceptor positions, as predicted by the model.

Second stage.

For the second stage, similar results are obtained. The results show that the two C sites give rise to different shifts. It is important to notice that this effect is purely "orbital" since the local density of states at the Fermi level at each site is identical in the Blinowski-Rigaux model. Moreover, we can expect that this orbital contribution is strongly reduced when the magnetic field is perpendicular to the c-axis. This explains the splitting of the line for **B//c** for acceptor compounds. In case of donors, the interpretation is more difficult due to the 3D character of these compounds [6]. The average orbital shift of the two lines follows qualitatively the results obtained for the first stage.

CONCLUSION

To conclude, the orbital contribution to the N.M.R. ^{13}C shift, suggested by the experimental results [3], is calculated. Two features of experimental data prescribe to take into account this contribution: the large difference between the shift values for acceptor and donor ternary 1st stage compounds even though the spin contribution is expected to be almost the same, and the absence of AB splitting at $\boldsymbol{c} \perp \boldsymbol{B}_0$ for acceptor GICs of stage two or higher. The calculated results explain the order of magnitude of the difference between donor and acceptor compounds and the splitting for the second stages and reproduce the sign.

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