^{13}C NMR and Charge Transfer in Graphite Intercalation Compounds

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Abstract. Three main contributions have been considered for the carbon-13 NMR chemical shift: (a) paramagnetic shift which is insensitive toward intercalation, (b) spin polarization term which is proportional to the electronic specific heat, (c) interband susceptibility term. The data agree well with the theoretical results and may also be used to infer the charge transfer in these systems.

For the highly oriented pyrolytic graphite (HOPG) and its intercalates, the ^{13}C nuclear magnetic resonance (NMR) spectra have been obtained experimentally. The NMR chemical shifts (CS) may be used as microscopic probes for electronic structures of graphite intercalation compounds of both the acceptor (GICA) and donor (GICD) types. The CS-tensor is characterized by the two principal values, $\delta_{\parallel}$ and $\delta_{\perp}$ in ppm (with respect to tetra-methylsilane as standard) for magnetic field B parallel and perpendicular to the c-axis of HOPG. The isotropic and anisotropic CS are $\delta_i = (\delta_{\parallel} + 2\delta_{\perp})/3$ and $\delta_a = \delta_{\parallel} - \delta_{\perp}$. Three main contributions have been considered:

(a) The paramagnetic (Ramsey) intra-atomic term is due to the deviation of the electronic charge distribution from spherical symmetry and may be calculated from the interaction between the occupied (valence band v) and empty (conduction band c) electronic orbitals:

$$\delta_{\parallel} = (2e^2\hbar^2/m^2c^2)\langle r^{-3}\rangle_{2p}\sum_v\sum_c\left[(E_c-E_v)^{-1}\right.$$
$$\left.|\langle\psi_v|L_z|\psi_c\rangle|^2\right]$$

where c is the light velocity, $\hbar$ is Planck's constant divided by 2π, e and m are electronic charge and mass, L_z is the z-component of angular momentum operator, ψ and E are the wave functions and their energies, $\langle r^{-3}\rangle_{2p}$ is the

expectation value of the inverse cube distance of the carbon 2p orbitals. The expression for $\delta_{\perp}$ is similar except that L_z is replaced by L_x.

Usually, the electronic states of graphite are arranged from the lower to higher energies in the order of $2p\sigma$, $2p\pi$, $2p\pi'$ and $2p\sigma'$, where the unprimed denotes valence orbitals and the primed denotes conduction orbitals. The selection rules are $\sigma\pi'$ and $\pi\sigma'$ for $\delta_{\perp}$, and $\sigma\sigma'$ for $\delta_{\parallel}$. Thus the denominator E_c-E_v is smaller in the former case. It follows that $\delta_{\perp} > \delta_{\parallel}$ or $\delta_a < 0$. Our calculation gives $\delta_a = -140$. If we arbitrarily choose $\delta_{\perp} = 180$, then we get $\delta_{\parallel} = 40$, and $\delta_i = 133$.

This paramagnetic term comes from the entire band structure and is insensitive toward intercalation. Thus this term is universal (with the same value) for all types of GICD and GICA.

(b) For GICD such as C_xK or C_xCs, there is considerable mixing between the metal conduction electrons and carbon $2p\pi$ orbitals. In the presence of the external magnetic field B, there is additional contribution to CS from the dipole magnetic fields at the nuclear site due to the spin-polarized carbon $2p\pi$-orbitals. This spin-polarization CS-term may be related to the

experimental electronic specific heat term γT where the constant γ is in units of $(mJ)(mole)^{-1}(°K)^{-2}$. The CS is given by:

$$\delta_a = 333\,\gamma\eta \qquad\qquad \delta_i = 0$$

where $\eta = x/(x+1)$ is the mole fraction of carbon atoms in the GICD.

(c) When the external magnetic field B is parallel to the c-axis, it is well known that pristine graphite and also the higher stage (low intercalant concentration) GICA are diamagnetic. There is a large interband contribution to the diamagnetic susceptibility $\chi_{\parallel}$.

A similar mechanism is also present for the CS. For the interband contribution, we have $\delta_{\perp} = 0$ and $\delta_{\parallel}$ is proportional to $\chi_{\parallel}$.

The theoretical values of CS may be compared with the experimental data. For low stage (high intercalant concentration) compounds, the CS would come from (a) alone for GICA and from (a)+(b) for GICD. For pristine graphite as well as the higher stage GICA, the CS would come from (a)+(c), hence the CS data may be used to infer the charge transfer for individual carbon layers. For example, three distinct carbon-13 NMR spectral lines have been observed for the fifth stage compound intercalated with HNO_3. From the experimental CS, we have obtained the charge transfer for each of the individual carbon layers.