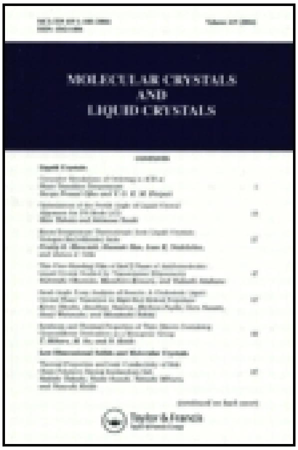

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ELECTRONIC SPIN DIFFUSION IN THE METALLIC STATE OF FLUORANTHENYL RADICAL CATION SALTS $(FA)_2X$: ^{13}C KNIGHT SHIFT AND FIELDGRADIENT ESR MEASUREMENTS

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Abstract We have observed ^{13}C Knight- and anti-Knight shifts in the metallic state of $(FA)_2SbF_6$. The observed shifts range around 50 ppm. The corresponding spin lattice relaxation times T_1 are on the order of 100 ms and obey a modified Korringa law. We also measured the longitudinal electron spin diffusion constant $D_\parallel = 1.5\ cm^2/s$ directly by applying a magnetic field gradient.

INTRODUCTION

In this communication we want to present two different techniques, namely ^{13}C NMR Knight shift measurements and electron spin echo field gradient experiments, which allow one to determine the spin distribution of the conduction band molecular orbital and the anisotropic diffusion constant of conduction electrons in organic conductors. We will be concerned with an interesting sub-class of organic conductors, namely $(fluoranthenyl)_2SbF_6$ abbreviated in the following by $(FA)_2SbF_6$, a radical cation salt, consisting of a pure hydrocarbon as organic constituent.[1,2] We have also investigated other systems like $(FA)_2X$ where X = AsF_6 and PF_6 which show similar results. Above $T_c \simeq 180$ K these solids show a high anisotropic conductivity, whereas below T_c semiconducting behavior is observed.[2] The crystal structure has been analyzed above and below T_c by Enkelmann et al.[3] Figure 1a shows a schematic drawing of the fluoranthene molecule. The molecules are arranged to form a collumnar crystal structure with the average intermolecular distance along the stack axis being 3.3 Å. The large dc conductivity is believed to occur along the molecular stacks. One of the most interesting aspects of these crystals are their unique ESR properties.[4-8] Among these the extremely narrow linewidth and corresponding long relaxation times are characteristic features which are quite unusual even for an organic "metal".

^{13}C KNIGHT SHIFT AND ^{13}C SPIN LATTICE RELAXATION

In ordinary metals it is well understood that the electrons near the Fermi surface cause rapid field fluctuations at the nuclear sites, leading to an average shift in resonance frequency (known as Knight-shift[9]) and causing short spin lattice relaxation times T_1.[10] Since shift (K) and relaxation (T_1) are caused by the same fluctuating fields they should be related and can be combined into the so-called Korringa relation

$$K^2 T_1 T = \frac{\hbar}{4\pi k}\left(\frac{\gamma e}{\gamma n}\right)^2 S_1 \qquad (1)$$

where γ_e and γ_n are the magnetogyric ratio of the electrons and the nuclear spins, respectively and the other symbols have their usual meaning. S_1 is a scaling parameter, which takes account of the deviation from the three-dimensional free electron gas, to be discussed later. In order to observe this typical metallic behavior we have performed ^{13}C high resolution NMR experiments[11] including magic angle spinning (MAS, at different spinning rates 1-3 kHz) at 45 MHz ^{13}C Larmor frequency at room temperature. Different techniques have to be applied to obtain isotropic as well as anisotropic shifts in the solid state.[12] Note, that ^{13}C in natural abundance (1.1 %) is observed leading to narrow lines under MAS and spin decoupling even in a solid.[12] Figure 1b shows different examples. At the top the isotropic ^{13}C chemical shifts in liquid solution of fluoranthene (artificially broadened) compare fairly well with the isotropic shifts in solid fluoranthene (Fig. 1b middle). All lines have been identified and correspond to different positions in the molecule. In the radical cation salt, however, the isotropic part of the spectrum is spread over a much wider range (Fig. 1b bottom).

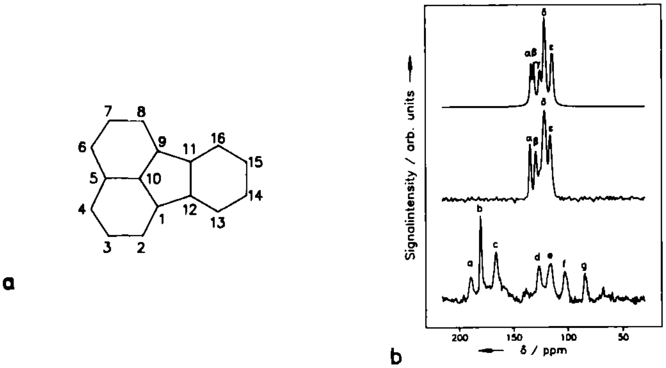

FIGURE 1 (a) Fluoranthene (FA) molecule with spin densities of the conduction band molecular orbitals as explained in the text. (b) ^{13}C spectra of FA in liquid (top) and solid state (middle). Bottom: $(FA)_2SbF_6$.

The position of the Knight shifted lines (a,b,c,g) together with the corresponding relaxation times T_1 to be discussed below are summarized in Table I. Clearly three different areas can be distinguished: (i) Three lines (a,b,c) are shifted to the left (paramagnetic shift) (ii) at least one line (g and maybe f) is shifted to the right (antiparamagnetic shift) whereas (iii) lines d,e are unshifted with respect to the average chemical shift of liquid and solid fluoranthene. The observed paramagnetic shifts (Knight shift) are on the order of 40-60 ppm (typical metal values are[9]: 249 ppm (^{7}Li); 2320 ppm (^{63}Cu)). The Knight shifts have to be determined with respect to some reference as given by the lines α - ε. Therefore an assignment of the lines is needed. Although a unique assignment can only be achieved by separate isot-opic ^{13}C labelling, we have made a tentative assignment, based on gated decoupling experiments.[12] This allows us to determine which carbon is connected to a proton and which is not. Based on these arguments we have tentatively assigned the lines and the corresponding Knight shifts to specific sites of the molecule.

TABLE I ^{13}C Knight shift K (in ppm) and spin lattice relaxation times T_1 for the lines a, b, c and g.

Line	K/ppm	T_1/ms	$K^2T_1T/10^{-6}$ sK	Position
a	61	75	0.084	(3,4)
b	42	100	0.053	(1,9); (11,12)
c	34	115	0.040	(2,8)
g	- 45	580	0.350	(5,10)
^{7}Li	249	150	2,8	
^{63}Cu	2320	3	4,8	

As was evident already from Table I the relaxation times T_1 for the Knight shifted lines a,b,c get shorter with increasing Knight shift in accord with the Korringa relation Eq.(1). In order to compare the ^{13}C data in the organic metal $(FA)_2X$ with "real" metals we have listed also the expression K^2T_1T. Note, that this quantity is smaller by a factor of about 100 than in ordinary metals. This scaling of the Korringa relation is typical for one-dimensional metals and will be discussed below. The isotropic paramagnetic shift K_j of the NMR line of nucleus j in the fluoranthene molecule may be expressed as

$$K_j = \chi_p \frac{a}{\hbar\gamma_e\gamma_n} \rho_j \quad \text{with } \chi_p = n_e\hbar^2\gamma_e^{\,2}/4kT \qquad (2)$$

where χ_p is the Pauli susceptibility per molecule, a is the isotropic part of the hyperfine tensor and ρ_j is the spin density at carbon position j normalized to unity over the molecule. The Pauli susceptibility may be expressed by the effective electron density n_e per molecule. Values of n_e were measured in $(FA)_2X$ crystals by proton NMR and ESR investigations.[5,6] We use $n_e = 3 \cdot 10^{-2}$ as an estimated value for our crystal. As a typical value for a in sp^2 radicals we take 72 MHz.[13] Using $\gamma_e/\gamma_n = 2618$ for ^{13}C nuclei and T = 300 K we obtain by combining Eqs. (2) and (3) $K_j = 2.26 \cdot 10^{-4}\ \rho_j$. With the Knight shifts ranging around 40-60 ppm according to table I we arrive at $\rho_j = 0.177$-0.265. Together with the tentative assignment of the lines we derive a spin density map of the conduction band molecular orbital in $(FA)_2X$ as shown in Figure 1a. Note that the numbers presented here depend on several only roughly known parameters and can therefore be considered only as guide lines. However, suppose the electronic spin density would be equally distributed among the six carbon atoms leading to conduction. In this case $\rho_j = 1/6$ for $j = 1, \ldots 6$ and $\rho = 0$ for the residual carbons. Due to electron-electron correlation it is known that carbon atoms at nodes of the wavefunction acquire negative spin density, leading to higher spin density at the other positions. Moreover the negative spin density leads to anti-Knight shift as is observed here (line g in Figure 1b). The same fluctuating field which leads to the Knight shift causes relaxation of the nuclear spins. The relaxation rate may be expressed as

$$T_{1j}^{-1} = n_e \rho_j^2 \left[\frac{3}{20} d^2 J(\omega_{on}) + \left(\frac{1}{4} a^2 + \frac{1}{20} d^2\right) J(\omega_{oe}) \right] \qquad (3)$$

where $J(\omega_{on})$ is the spectral density of the fluctuating fields caused by the conduction electrons at the Larmor frequency ω_{on} of the nuclei and $J(\omega_{oe})$ is the spectral density at the electron spin Larmor frequency $\omega_{oe} = (\gamma_e/\gamma_n)\omega_{on}$. The parameters a and d are the isotropic (a) and anisotropic (d) part of the hyperfine tensor, respectively. The spectral density $J(\omega)$ in the case of interrupted one-dimensional diffusion may be expressed as[4,7]

$$J(\omega_{on}) = \Delta a \left(\frac{\tau^*}{D_\parallel}\right)^{1/2} \quad \text{with } \omega_{on}\tau^* \ll 1 \qquad (4a)$$

$$J(\omega_{oe}) = \Delta a \; (2D_\parallel \omega_{oe})^{1/2} \quad \text{with } \omega_{oe}\tau^* \gg 1 \qquad (4b)$$

where $\Delta a = 3.3$ A is the lattice spacing, $D_\parallel = 1{,}3\ \mathrm{cm}^2\mathrm{s}^{-1}$ is the 1D diffusion constant and $\tau^* = 1{,}6\cdot 10^{-11}$s is the 1D cut off time. The parameters which contribute to the spectral density $J(\omega)$ have been determined by pulsed ESR recently.[5,7] For the isotropic hyperfine interaction constant a we use the same value as above and assume for the anisotropic part $a \simeq 2d$. In this case we arrive at a value of $T_1 = 166$ ms for $\rho_j = 0.25$ in fair agreement with the values measured e.g. for lines a-c. This demonstrates that the one-dimensional motion enhances the relaxation rates and the scaling factor S_1 in the Korringa relation Eq. (1) can be expressed as

$$S_1 = n_e \frac{\pi\hbar}{kT} \left(\frac{D_\parallel}{\Delta a^2 \tau^*}\right)^{1/2} \left[\frac{3}{5}\,\varepsilon + \left(1 + \frac{7}{5}\,\varepsilon\right)(2\omega_{oe}\tau^*)^{-1/2}\right]^{-1} \qquad (5)$$

where $\varepsilon = d^2/a^2$, $S_1 \ll 1$ in highly one-dimensional solids and $S_1 \simeq 1$ for three-dimensional solids. In our case we obtain from the experimental data $S_1 \simeq 10^{-2}$ and by using Eq. (5) together with the different parameters as given in the text $S_1 = 3.8\cdot 10^{-2}$.

A similar analysis has to be invoked in the hyperfine interaction with the proton spins in the sample. Experiments along those lines have been reported recently.[15,16] Note also poster session 1 by Denninger et al. (P74) at this conference.

DIFFUSION IN MAGNETIC FIELD GRADIENTS

We have performed electron spin echo experiments in $(FA)_2X$ at 9.6 GHz by applying two microwave pulses with separation τ which lead to a spin echo at time 2τ. When a magnetic field gradient G is applied parallel to the homogeneous external magnetic field B_o, the spin echo decays according to the spin-spin relaxation time T_2

$$M(t_E) = M_o \exp\,(-\,t_E/T_2)\,\exp\left[-\,\frac{1}{12}\,\gamma_e^2 G^2 D t_E^3\right] \qquad (6)$$

where $D = D_\parallel \cos^2\beta + D_\perp \sin^2\beta$ and $t_E = 2\tau$, with β being the angle between the field gradient and the main axis of the diffusion tensor ($D_\parallel$; $D_\perp$). If the diffusion parallel ($D_\parallel$) to the unique axis, which is the stacking direction in $(FA_2)X$, is much larger than in the perpendicular direction ($D_\perp$), a strong orientation dependence of the echo decay is expected. Fig. 2a demonstrates this behaviour for a gradient $G = 190$ mT m^{-1}. The one-dimensional character of the diffusion process is clearly visible. We obtain $D_\parallel = 1.5$ cm^2 and $D_\perp < 0.1$ cm^2 s^{-1}. *In principle it is possible to determine the anisotropy* of electron transport this way. However, the value for $D_\perp$ is fairly unreliable since non-linear gradients, sample shape etc. can obscure the determination of $D_\perp$ especially when $D_\parallel \gg D_\perp$. We do know, however, the transverse hopping rate $\tau_\perp^{-1}$ ($\tau_\perp \simeq 10^{-11}$ s) from earlier electron spin lattice relaxation measurements.[7] Using the definition $D_\parallel = v_F^2 \tau_s$ leads to a phonon scattering time $\tau_s = 1.7\cdot 10^{-15}$ s, when $E_F \simeq 0.22$ eV and a mean free path length $\lambda = v_F \tau_s$ of $\lambda = 4.8$ Å which corresponds to about a lattice spacing Δa. The transverse tunneling integral $t_\perp$ may be estimated from $t_\perp = \hbar(\tau_s \tau_\perp)^{-1/2}$ which leads to $t_\perp = 4$meV.

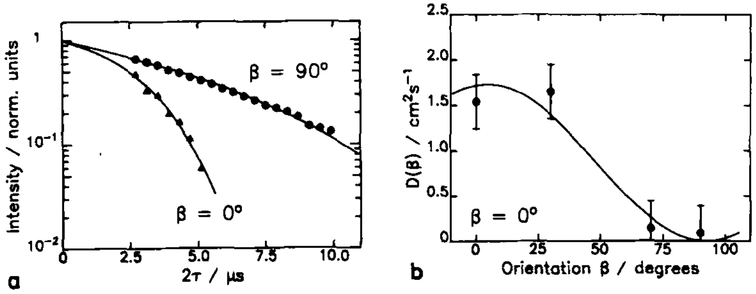

FIGURE 2 (a) Electron spin echo decay curves for $\beta = 0$ and $\beta = 90^\circ$.
(b) Orientation dependence of D.

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