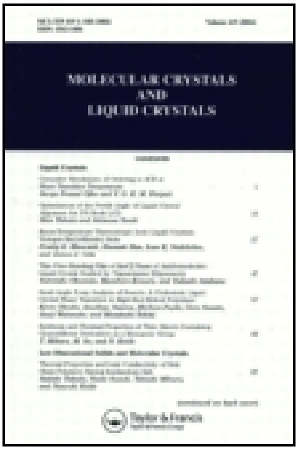

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The Correlation of Proton-NMR, Fluorine-MMR and ESR-Experiments on Some $(\text{Fluoranthenyl})_2{}^{+} XF_6{}^{-}$ Salts

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THE CORRELATION OF PROTON-NMR, FLUORINE-NMR AND ESR-EXPERIMENTS ON SOME $(\text{FLUORANTHENYL})_2^+XF_6^-$ SALTS.

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In $(\text{fluoranthenyl})_2^+XF_6^-$ salts (X = P,As,Sb) the temperature dependent proton relaxation rates are due to three processes, namely the interaction with (i) mobile paramagnetic species (above 160 K), with (ii) fluorine nuclei linked to the anions (between 160 and 40 K) and with (iii) fixed paramagnetic centers (below 40 K). Inserting As or Sb for P, the center atom of the anion, leaves the high temperature properties of the crystals unchanged but results in higher hindering potentials for the reorientational motion of the anions and in a shift of the phase transitions to lower temperatures.

INTRODUCTION

Open questions on the highly conductive radical-cation salts are, among others, concerned with the dimensionality of the conduction and the kind of stack in which the carriers migrate[1,2]. We have addressed the latter question via nuclear-magnetic-resonance studies of the protons (linked to the fluoranthene cations) and of the fluorine nuclei of the XF_6 anions (X=P,As,Sb). These ^1H and ^{19}F nuclei both "see" - but probably in a different manner - the spins of the localized and mobile electrons via hfs-interaction. Some of their dynamical properties should therefore be reflected in the temperature dependence of the longitudinal relaxation rates. These can be compared with the ESR-intensity in the same temperature range in order to distinguish different relaxation processes. An outstanding feature is the width of the ESR-line which is the smallest ever found, so far in solids [3,4]. T_2-values of about 10 μsec are accessible easily by means of a pulsed NMR apparatus (applying very low B_o-fields) which on the other hand allows monitoring the nuclei as well.

In a previous paper we have discussed the results of NMR and ESR on $(\text{fluoranthenyl})_2^+PF_6^-$ which have pointed to a predominantly one dimensional motion of the paramagnetic spins within the anion stack.

In this paper, we like to present further experiments on $(\text{fluoranthenyl})_2^+$-$XF_6^-$ salts in which the anion (X=P so far) is replaced by the larger atoms As and Sb. We can show that qualitatively comparable results are obtained which confirm therefore our models applied recently[5] to the nuclear relaxation.

EXPERIMENTAL

All NMR measurements were performed with a conventional broad band pulse spectrometer (at 44 MHz and partially at 22 MHz), which is described in detail elsewhere[5]. The probe consisted of a single coil arrangement used for both frequencies. A commercial helium vapor cryostat (Leybold Heraeus) was used to cool the sample in the temperature range from 15 to 300 K.

The nuclear-spin-lattice relaxation rates were measured with 90°-τ-90° pulse sequences. T_1^{-1} was deduced either from the slope of ln $(M_\infty - M(\tau))$ versus τ in the case of a single exponential behavior or evaluated as a mean value of a T_1^{-1}-distribution. Pulsed ESR experiments were performed with the same set up using lower B_0 and B_1-fields, cw-measurements were performed with a conventional Varian X-Band Century-Line ESR spectrometer E 1009.

(FLUORANTHENYL)$_2^+$XF$_6^-$

The stable radical-cation-salt crystals, shiny black needles, were grown by anodic oxidation of the fluoranthenes in the presence of the XF_6^--anion as described in the literature[1,6]. They exhibit a phase transition at about 180 K as found by X-ray analysis[7], ESR[3] and conductivity measurements[8].

The fluoranthene molecules (FA) are arranged in stacks along the a axis with unusually small distances of about 3.3 Å. The stacks are packed leaving channels in which the XF_6^--octahedra are located. The aromatic rings are alternatingly rotated by 180° giving rise to the unusual molecular overlap shown below.

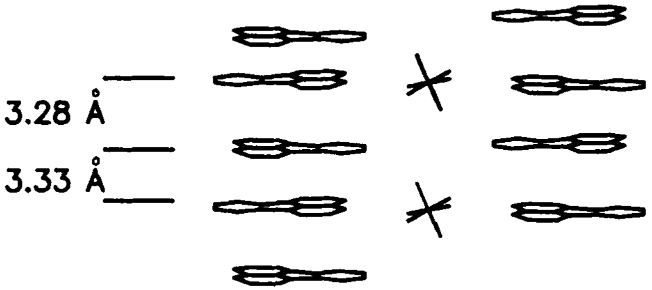

FIGURE 1. The molecular arrangement in the stacking direction of (fluoranthenyl)$_2$XF$_6$ salts.

EXPERIMENTAL RESULTS

a) NMR The proton- and fluorine-spin-lattice relaxation rates T_{1H}^{-1} and T_{1F}^{-1} at 44 MHz as function of the reciprocal temperature are given in fig. 2 for $(FA)_2PF_6$ and fig. 3 for $(FA)_2AsF_6$ and $(FA)_2SbF_6$.

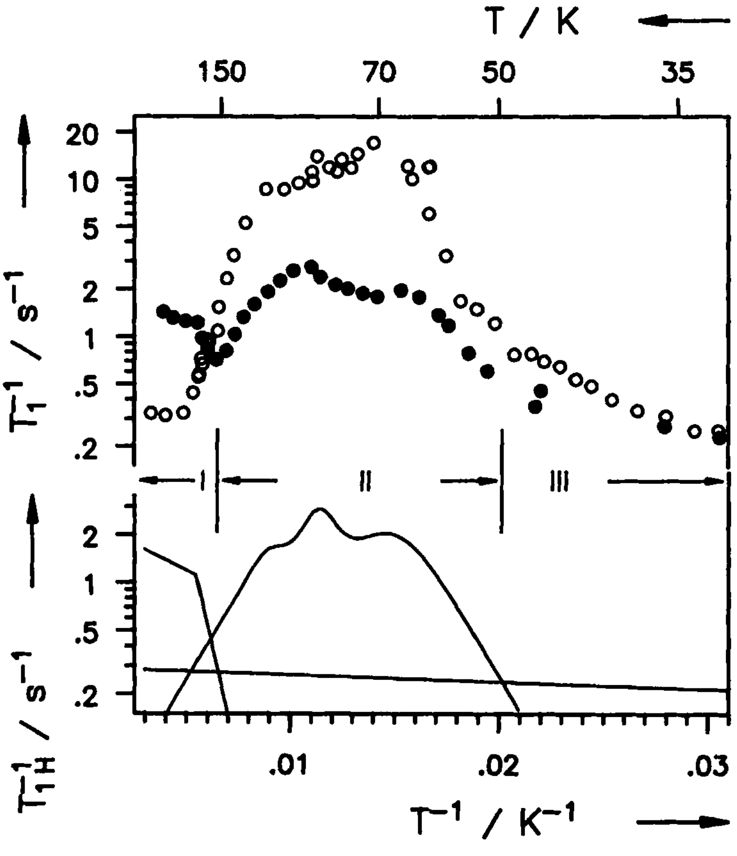

FIGURE 2 · Proton-(●) and fluorine-(o) relaxation rates as function of the reciprocal temperature of $(FA)_2PF_6$. In the lower part, the separation of three relaxation processes is shown, each being predominant in one of the temperature ranges I-III.

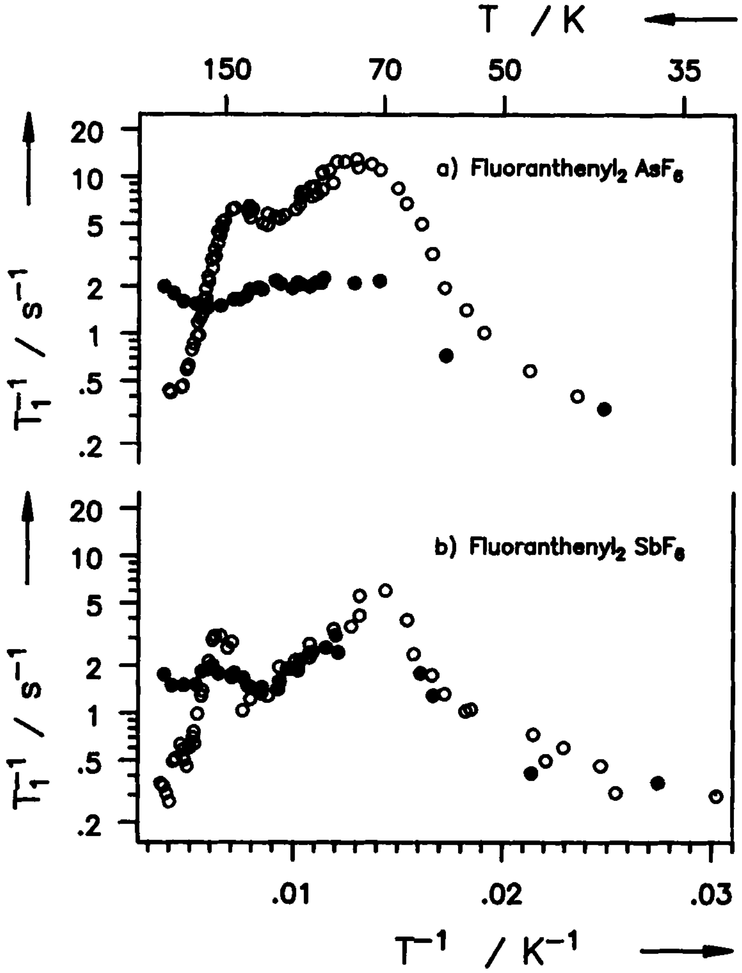

FIGURE 3. Proton-(●) and fluorine-(o) relaxation rates as function of the reciprocal temperature for (a) $(FA)_2AsF_6$ and (b) $(FA)_2SbF_6$.

In all cases, the relaxation curves show - at least qualitatively - a similar behaviour: quite a temperature independent slope above about 160 K (range I), two more or less pronounced maxima in range II at 95/62 K (FA_2PF_6), 110/80 K

(FA_2AsF_6), 140/90 K (Fa_2SbF_6) and at temperatures lower than 40 K (range III) the convergence of all rates to a constant value of about 0.4-0.2 sec^{-1}. This description holds for both, the proton and the fluorine relaxation as well, but in the absolute values there are striking differences, depending on the range of temperature: whereas the proton relaxation is an order of magnitude larger than T_{1F}^{-1} in range I, its maxima (range II) are much lower than that of the fluorines.

b) ESR The amplitude of the cw-ESR signals at 9.5 GHz as a function of the reciprocal temperature is represented in fig. 4.

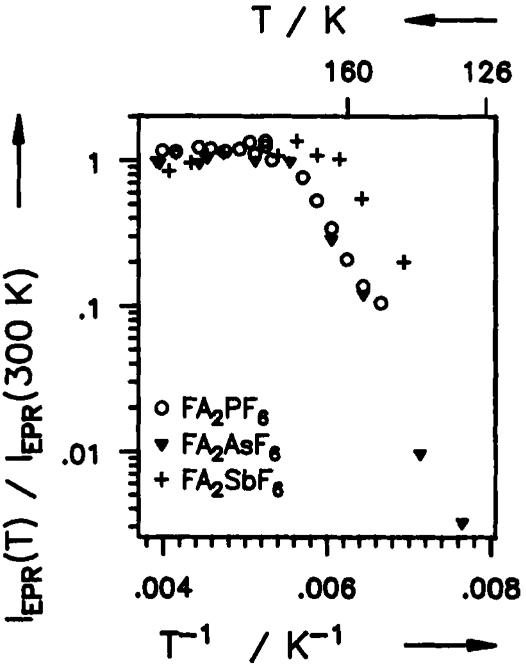

FIGURE 4. EPR-intensity as function of the reciprocal temperature for the three cation salts.

The signals - intensity and linewidth - are nearly constant above T_c (T_c = 183 K (PF_6), 176 K (AsF_6), 166 K (SbF_6) and decrease below this temperature with nearly identical activation energies of about 0,12 eV.

DISCUSSION

In the previous paper[5], the proton relaxation was attributed to a superposition of three processes, each being predominant in one of the three temperature ranges mentioned above and shown in fig. 2, lower part.

In range I we observe the interaction between the protons and mobile paramagnetic species which can be described in case of a preferential quasi 1-dimensional electronic motion according to ref. 9 by a frequency dependent Korringa (κ)-relation

$$(T_{1H\kappa}T)^{-1} = C_1 \left[\frac{1 + [\, 1 + (\omega_e \tau_\perp)^2 \,]^{1/2}}{2\,(1 + (\omega_e \tau_\perp)^2)} \right]^{1/2} + C_2 \qquad (1)$$

C_1 is the product of 4 factors: the bare Korringa-relaxation rate, the electronic diffusion time within the chain $\tau_\parallel^{-1/2}$, the escape time $\tau_\perp^{-1/2}$ and the enhancement factor K_o due to multiple electron-nucleus scattering. C_2 represents the limiting high-field relaxation rate, which is attributed to the sum of scalar contribution and of the dipolar interaction.

In range II, the origin for the relaxation was identified as anisotropic reorientational jumps of the XF_6-octahedra due to their hindering-potential in the crystalline state, whereas the cations are fixed in the lattice. Relaxation of nuclear spin-pairs undergoing isotropic or anisotropic reorientation is well known in the literature [10-13].

$$T_{1H}^{-1} = \Sigma_{\alpha=1,2}\, K_{HF}^{\alpha}\, \tau_{HF}^{\alpha}\left(\frac{1}{1+((\omega_H-\omega_F)\tau_{HF}^{\alpha})^2} + \frac{3}{1+(\omega_H\tau_{HF}^{\alpha})^2} + \frac{6}{1+((\omega_H+\omega_F)\tau_{HF}^{\alpha})^2}\right) \tag{2}$$

and for the fluorine nuclei:

$$T_{1F}^{-1} = \Sigma_{\alpha=1,2}\, K_{FH}^{\alpha}\, \tau_{HF}^{\alpha}\left(\frac{1}{1+((\omega_F-\omega_H)\tau_{HF}^{\alpha})^2} + \frac{3}{1+(\omega_F\tau_{HF}^{\alpha})^2} + \frac{6}{1+((\omega_F+\omega_H)\tau_{HF}^{\alpha})^2}\right) + K_{FF}^{\alpha}\, \tau_{FF}^{\alpha}\left(\frac{1}{1+(\omega_F\tau_{FF}^{\alpha})^2} + \frac{4}{1+(2\omega_F\tau_{FF}^{\alpha})^2}\right) \tag{2'}$$

with $K_{FH}^{\alpha} = (N_H/N_F)\, K_{HF}^{\alpha}$, ω_i = nuclear Larmor frequencies, τ_{ii}^{α} = correlation time for like and τ_{ij}^{α} unlike spin pair interactions, K_{ii}^{α} = amplitude factors, containing the magnetogyric ratios of the moments and their separation, with $\alpha = 1.2$, meaning a twofold reorientation of the anion.

Turning now to the case of fixed paramagnetic centers (range III) spin diffusion limits the relaxation rate of the bulk nuclei[14] and we apply as usually:

$$T_{1eloc}^{-1} = 4\pi N D \rho \tag{3}$$

with N = number of the fixed paramagnetic centers, D = diffusion constant and ρ = geometrical factor containing the magnetic field B_o. The contribution of each of these processes (1)-(3) to the total relaxation is represented schematically in fig. 2 (lower part) for the proton relaxation rates of $(FA)_2PF_6$. The values of the individual parameters are given

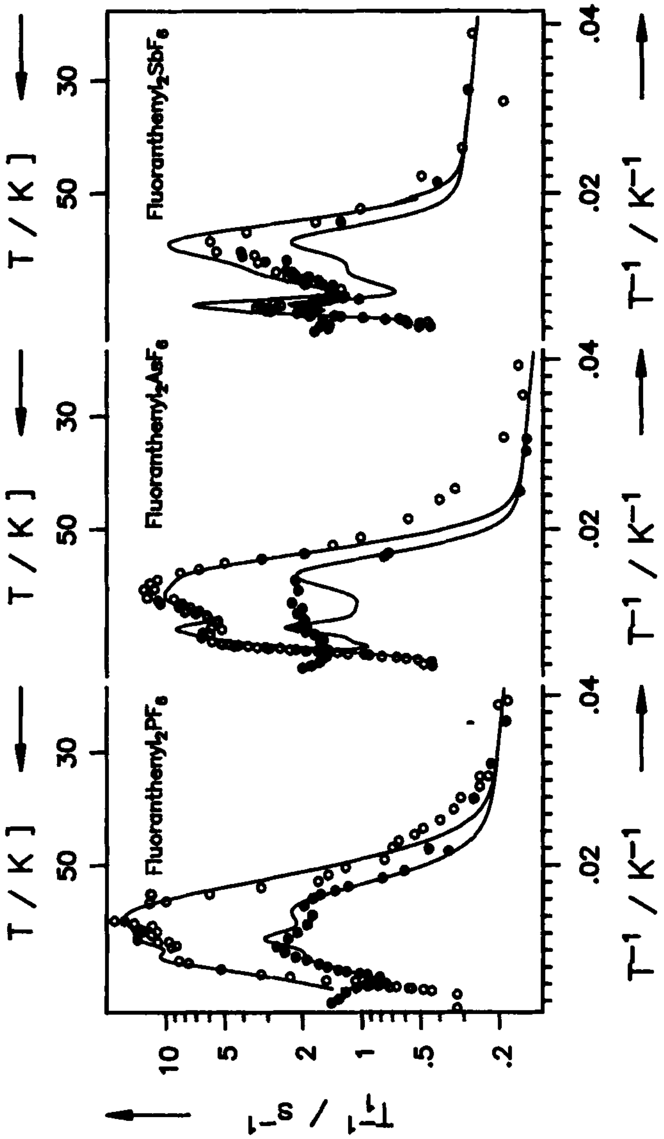

FIGURE 5. Comparison of the experimental and calculated relaxation rates of (a) (FA)$_2$PF$_6$ (b) (FA)$_2$AsF$_6$ and (c) (FA)$_2$-SbF$_6$.

in table 1, the superposition of (1)-(3) is drawn in fig. 5 through the experimental points.

fluoranthenyl$_2^+$		PF_6^-	AsF_6^-	SbF_6^-
T_c	K	183 ± 1	176 ± 2	166 ± 2
$\tau_{\infty 1}$	s	$0.13 \cdot 10^{-13}$	$0.6 \cdot 10^{-14}$	$0.8 \cdot 10^{-15}$
ΔE_1	eV	0.126	0.164	0.224
$\tau_{\infty 2}$	s	$0.3 \cdot 10^{-10}$	$0.1 \cdot 10^{-11}$	$0.3 \cdot 10^{-12}$
ΔE_2	eV	0.045	0.065	0.073
K_{HF}	s^{-2}	$0.6 \cdot 10^{8}$	$0.6 \cdot 10^{8}$	$0.6 \cdot 10^{8}$
K_{FF}	s^{-2}	$0.8 \cdot 10^{9}$	$0.56 \cdot 10^{9}$ *)	$0.32 \cdot 10^{9}$ *)
n_e	e^-/FA	$1.2 \cdot 10^{-2}$	$1.3 \cdot n_e(PF_6)$	$1.2 \cdot n_e(PF_6)$
N	mole/mole	$1 \cdot 10^{-4}$	$0.7 \cdot N(PF_6)$	$1.25 \cdot N(PF_6)$

TABLE 1 Parameters of the calculated curve in fig. 5. n_e represents the number of mobile paramagnetic species/fluoranthenyl which is taken from ref. 5. *These values are calculated using the ratios of fluorine-fluorine separations[15].

As far as process (1) is concerned, $(T_{1K}\ T)^{-1}$ just follows the concentration n_e of the mobile species (fig. 4) because the diffusion and escape times do not vary in the temperature range of interest.

If we compare now the proton and fluorine relaxation it is obvious that the fluorine nuclei do not see these mobile paramagnetic states (process (1) in range I) at all, which led to the conclusion that the mobile species reside in the fluoranthenyl stacks only[5]. Therefore, the fluorine relaxation can be fit by eqn. (2') and eqn. (3) solely. In range II of course, T_{1F}^{-1} exceeds T_{1H}^{-1} due to the strong fluorine-fluorine interaction which does not contribute to T_{1H}^{-1}.

Applying now the scheme discussed for $(FA)_2PF_6$ to the salts with AsF_6 and SbF_6 as anions, there are no further parameters for the fit of their data. The relaxation due to paramagnetic spins is given by the temperature dependence of the ESR-signals (fig. 4), the amplitude factor K_{HF} is kept fixed and K_{FF} depends reciprocly on the sixth power of the fluorine-fluorine distance which increases from P to As and Sb[15].

"Free" variables are the activation energies ΔE and the τ_∞'s of the anisotropic reorientational motion, which however determine the shape only, not the amplitudes of the curves. In fig. 5 the solid lines represent the theoretical curves for all three salts. The individual parameters are listed below the figure.

If one bears in mind that the proton- and fluorine-relaxation is coupled via eqn (2) and (2'), the fits can be considered satisfying, all the more so since no correlation time distribution is used[16].

The exchange of the anions seems not to alter significantly the properties of this kind of crystals, although there are clear trends with increasing size of the anions.

The anisotropy of the reorientational motion increases for heavier anions as indicated by the increasing separation of the two maxima in range II, due to the difference in the hindering potentials.

The anion octahedra seem to be more "squeezed" between the fluoranthenyl stacks which may explain the occurance of the phase transition at lower temperature.

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