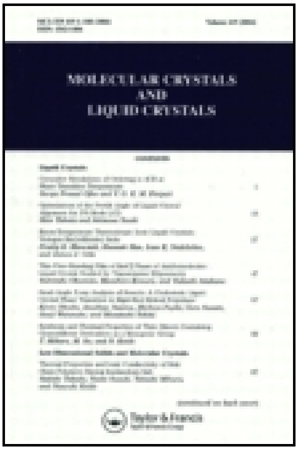

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Overhauser Shift on Radical Cation Salts of Fluoranthene

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To cite this article: G. Denninger , W. Stöcklein , E. Dormann & M. Schwoerer (1985): Overhauser Shift on Radical Cation Salts of Fluoranthene, Molecular Crystals and Liquid Crystals, 120:1, 233-236

To link to this article: http://dx.doi.org/10.1080/00268948508075792

Mol. Cryst. Liq. Cryst. 1985, Vol. 120, pp. 233-236
0026-8941/85/1204-0233/$10.00/0

Printed in the United States of America

OVERHAUSER SHIFT ON RADICAL CATION SALTS OF FLUORANTHENE

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Abstract Hyperfine interaction, proton spin relaxation and dynamic proton spin polarization were determined for the radical cation salts of fluoranthene: $(FA)_2^{\dot{+}}PF_6^-$ and $(FA)_2^{\dot{+}}SbF_6^-$ by observation of the Overhauser shift.

INTRODUCTION

The radical cation salts $(FA)_2PF_6$ and $(FA)_2SbF_6$, respectively are conducting crystals with a good 2:1 stoichiometry. They show a quasi metallic phase above $T_c \sim 180$ K and a semiconducting phase[1] below T_c. Their strong single line ESR spectrum originates from the charge carriers[2,3]. It is motionally narrowed with a width ΔH_{pp}=10 mGauss for T = 300 K and 7.5 mGauss for T = 190 K. Due to this extremely narrow line its shift due to the nuclear field of the protons (Overhauser shift) can be analyzed in detail[4].

EXPERIMENT

After recording a conventional ESR spectrum the external field B_0 is fixed to the center of the line. By applying an additional radiofrequency field and sweeping through the range of the proton Larmor frequency a shift of the ESR resonance field is observed. This shift ΔB_{ov}, predicted by Overhauser[5], is due to switching off the average nuclear field of the protons by saturating the proton NMR. In first order approximation the shift ΔB_{ov} produced by N protons ($N = 20$ for $(FA)_2PF_6$) per electron is given by

$$\Delta B_{ov} = -(2 \cdot g_e \mu_B)^{-1} \cdot N \cdot \mathcal{P} \cdot \bar{A}_{zz} \qquad (1)$$

where $\bar{A}_{zz}$ is the averaged z-component of the proton's hyperfine tensors. If the ESR is saturated the polarization $\mathcal{P}$ is a dynamic nuclear polarization (DNP) and thus exceeds the thermal nuclear spin polarization $\mathcal{P}_o$.

RESULTS

1. The magnitude of the shift (≈ 1 mGauss at T = 293 K for $(FA)_2PF_6$) yields the product $\mathcal{P} \cdot \bar{A}_{zz}$. We observe a dependence on the incident microwave power P:

$$\Delta B_{ov} \propto \mathcal{P}_o \cdot \left[1 + V \cdot \frac{\alpha P}{1 + \alpha P}\right] \qquad (2)$$

$V = \mathcal{P}_{max}/\mathcal{P}_o - 1$ is the Overhauser enhancement factor. By measuring $\Delta B_{ov}(P)$ down to small microwave powers P the enhancement factor V was determined. For $(FA)_2PF_6$ at T = 185 K we deduced a value of $V = 400 \pm 60$. This yields $\bar{A}_{zz}/g_e \mu_B = -1.1$ Gauss.

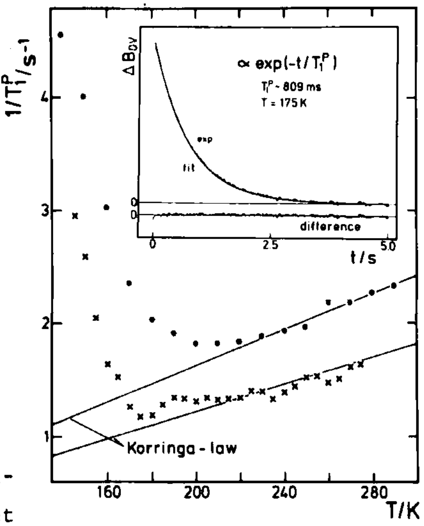

FIGURE 1 Proton $1/T_1^p$ versus T determined by the Overhauser shift method. (•) $(FA)_2SbF_6$, (×) $(FA)_2PF_6$

2. After sudden switch-off of the rf-field a monoexponential decrease of the shift is observed (inset fig.1). It can be shown experimentally and theoretically that one observes directly the longitudinal spin lattice relaxation time T_1^p of the protons. Fig. 1 shows $1/T_1^p$ versus T. The straight line indicates the Korringa law $T_1^p \cdot T$ = const. to be obeyed for T > 200 K. Below T_c the relaxation rate rises because further relaxation me-

chanisms for the protons[6] become important. A consequence is the decrease of ΔB_{ov} (fig.3).

3. By applying rf-pulses of variable length τ the DNP can be manipulated as usual in NMR spectroscopy. Fig. 2 shows the variation of the ESR line shift with the pulse length τ. The experimental data (•) are fitted by:

$$\Delta B_{ov}(\tau) = \Delta B_{ov}(\infty)[1-\cos\{\frac{\pi \cdot \tau}{T_{180^o}}\} \cdot \exp(-\tau/2 \cdot T_2^{eff})] \qquad (3)$$

where $\Delta B_{ov}(\infty)$ is the shift for an infinitely long rf pulse. T_{180^o} is the time for an 180^o-pulse. The fit yields $T_2^{eff} \approx 16$ µs. The value is in good agreement with the T_2^{eff} deduced from the line width of the shift signal ($T_2^{eff} \approx 13$ µs).

4. It should be pointed out that all the results are obtained with tiny single crystals and show a clear anisotropy with respect to the crystal axis. We observe $T^p_{1\perp}/T^p_{1\parallel} = 1.15$ and $(\Delta B_{ov})_\perp/(\Delta B_{ov})_\parallel \approx 3$, where "⊥" and "∥" denote the direction of the needle axis with respect to B_o.

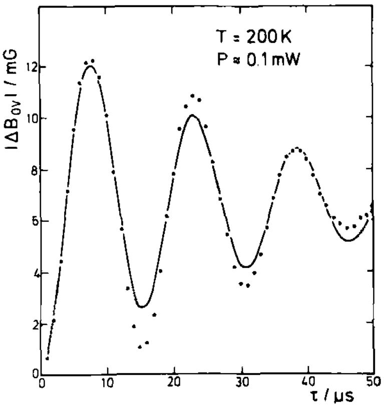

FIGURE 2 shift ΔB_{ov} versus rf-pulse length τ

5. The temperature dependence of ΔB_{ov} shows a strong variation near T ≈ 185 K. Above 190 K one observes $(1/\Delta B_{ov}) \propto T + \text{const.}$ Below 190 K the shift decreases similar to the decrease of the ESR-intensity (fig. 3).

6. The ratio ν_e/ν_p is independent on the magnetic field which acts on the electrons and protons. Thus the anisotropy of ν_e/ν_p reflects the anisotropy of the spin orbit coupling and is unaffected by demagnetization effects.

7. No shift ΔB_{ov} induced by the phosphorus or fluorine nuclei was

detected outside the error limit of 0.5 % of the proton value.

CONCLUSION

The Overhauser shift method is highly sensitive to determine the proton spin relaxation times T_1 and T_2^{eff} and their angular dependence in tiny single crystals of organic conductors. Furthermore the Overhauser enhancement and the average hyperfine tensor components can be determined directly. Thus the experiments yield specific informations on the interactions of the almost free charge carriers.

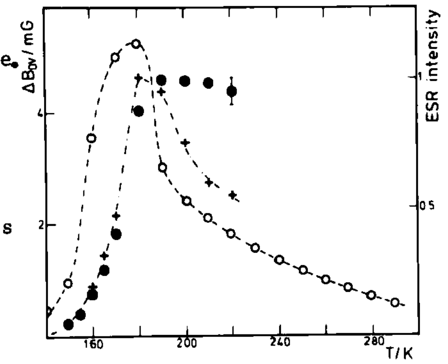

FIGURE 3 ΔB_{ov} versus T for $(FA)_2PF_6$ (+) and $(FA)_2SbF_6$ (o) (•) ESR intensity for $(FA)_2PF_6$

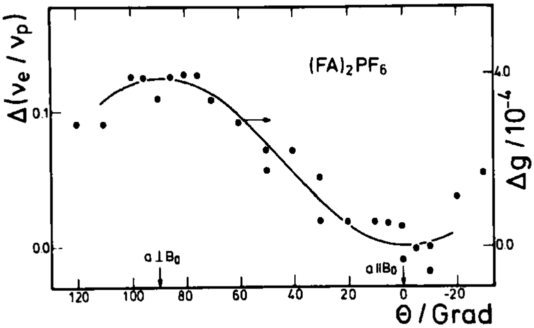

FIGURE 4 (•):$\Delta(\nu_e/\nu_p)$ $(\theta) = \nu_e/\nu_p$ (θ) - ν_e/ν_p (0)
solid line: Δg (θ) = g (θ) - g (0)

ACKNOWLEDGEMENTS

We acknowledge valuable discussions with M. Mehring, J.U. v. Schütz and K.P. Dinse. This work was supported by Stiftung Volkswagenwerk

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