

KNIGHT SHIFT AND NUCLEAR RELAXATION OF THE ${}^7\text{Li}$, ${}^{63}\text{Cu}$, ${}^{205}\text{Tl}$ COUNTERIONS IN METALLIC DCNQI-SALTS

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ABSTRACT: The highly conductive (Me,Me-DCNQI) radical anion salts with Li, Tl or Cu as metallic counterions were investigated by NMR. The Li-salt exhibits no Knight shift, the Tl-salt a small one and the Cu-salt a large Knight shift in comparison with the respective metals, indicating the trend of a quasi onedimensional charge carrier migration (Li-salt) to a quasi 3-dimensional behavior (Cu-salt).

INTRODUCTION

All radical anion salts of X,Y-DCNQI (X,Y = CH_3 ($\equiv\text{Me}$), Cl, Br, I, OCH_3) with metallic counterions (Li, Na, K, Rb, Ag, Tl, Cu) are highly conductive at room temperature. The copper salts are exceptional with a conductivity of $\sigma \approx 1000 \text{ Scm}^{-1}$, which is one order of magnitude higher as those of the others. In case of $(\text{Me,Me-DCNQI})_2\text{Cu}$ there is no phase transition but a strong increase of conductivity ($\sigma \approx 5 \cdot 10^5 \text{ Scm}^{-1}$) down to 400mK [1]. This DCNQI-salt exhibits, under applied pressure, a metal to insulator phase transition [2] comparable to the σ -behavior of all other Cu-systems with decreasing temperature. From these experiments the question results in how far the "degree of anisotropy" is responsible for the difference between the copper- and the non-copper salts. To lighten up this question, recently we have performed different experiments with the following results:

	Cu - salts	other salts
Valence band spectroscopy [3]	considerable density of states at the Fermi edge in the conductive range.	no density of states at the Fermi level.
ESR [1,4]	no ESR-line of the charge carriers was found, leading to $\Delta B_{pp} > 1000$ Gauss.	ESR-line at $g \approx 2$ linewidths of 0.3G to 100G
Proton spin lattice relaxation [5]	Korringa like behavior ($T_1 \cdot T \cdot \chi^2 = \text{const}$) in all DCNQI salts in the range of high conductivity. no frequency dependence up to 300 MHz	frequency dispersion with $T_1^{-1} \sim \omega^{-1/2}$ down to 22 MHz
Conductivity[1]	$\sigma(300\text{K}) \approx 1000 \text{ Scm}^{-1}$	$\sigma(300\text{K}) \approx 100 \text{ Scm}^{-1}$

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All measurements show that the copper salts behave as quasi 3-dimensional metals and that the non-copper salts seem to be strictly onedimensional. Here we present results on 2,5-Me₂-DCNQI with Li, Tl and Cu as metallic counterions. Knight shift- and relaxation rate measurements of the metallic ions show that there is a decrease of the anisotropy in the salts going from Li over Tl to Cu.

RESULTS and DISCUSSION

(Me₂-DCNQI)₂Cu: As shown in the proton spin lattice relaxation (T_{1H}^{-1}), there is a Korringa like behavior and no frequency dispersion up to 300 MHz. Using a quasi onedimensional model [6] we consider this salt as a system with an interstack hopping rate of the charge carriers of $\tau_i^{-1} > 10^{13} \text{ sec}^{-1}$. The small proton relaxation rate ($T_{1H}^{-1} \approx 2 \text{ sec}^{-1}$) in relation to the higher values of the non-copper salts, is in agreement with the interpretation of a far reaching spectral density. At room temperature ⁶³Cu shows a Knight shift of 2000 ppm in respect to the diamagnetic reference CuCl. The shift increases up to 3300 ppm with decreasing temperature (Fig.1) concomitantly with the temperature dependence of the conductivity [1], and exceeds that of metallic copper (2370 ppm) [7] below 170K.

For the explanation of the shift we have to introduce a S-spin density at the Cu nuclei. This can happen via:

(1) the polarisation of the Cu 3d-orbitals by the tetrahedral arranged CN-groups which can be temperature dependent through crystal distortion.
or / and via

(2) a hybridization between 2p-orbitals of the CN-group and the 3d-orbitals of the copper counterion, which can lead to N-Cu-N bridges.

In the latter case, the Knight shift ($K \sim \chi$) should be temperature independent as in metallic copper, because the static susceptibility (Fig.1) shows no increase (except a Curie contribution at low temperature) lowering the temperature. In case that the contribution of (1) and (2) are temperature dependent, the similarity of $\sigma(T)$ and Knight shift(T) can be understood.

(Me₂-DCNQI)₂Tl: This salt behaves one-dimensional in ESR, proton spin lattice relaxation and conductivity like all other non-copper salts. Nevertheless it is the first non-copper salt, where a strong Knight shift of the metallic counterion (²⁰⁵Tl) is observable (Fig.2). Coming from low temperature the Knight shift is constant and rises abruptly between 50K and 100K. Above that range there is a slow increase of the Knight shift observable up to 220K reaching 3800 ppm, where the Tl-signal was lost due to the very short T_2 ($< 10 \mu\text{sec}$). For comparison, the Knight shift of metallic thallium [7] is very large ($\approx 15600 \text{ ppm}$).

The Knight shift of ²⁰⁵Tl is directly correlated to the ESR-susceptibility (Fig.2) as it is expected in the case of an interaction between the conducting DCNQI-chain and the metallic counterion. This interaction was also indicated in earlier measurements: the ESR line is much broader in the Tl-salt [4] in comparison to the alkaline- [4] and Ag-salts [1] and the g-value is greater as well as. We assume from these results that the Tl-salt is an intermediate state between Cu and the alkalines as far as the anisotropy is concerned.

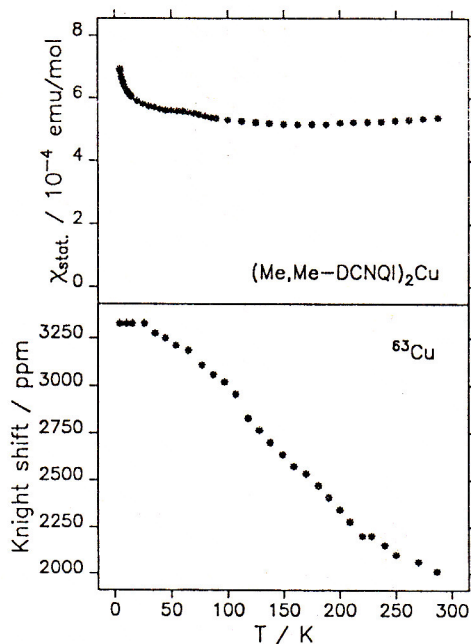


Fig.1: Knight shift and static susceptibility of the copper salt.

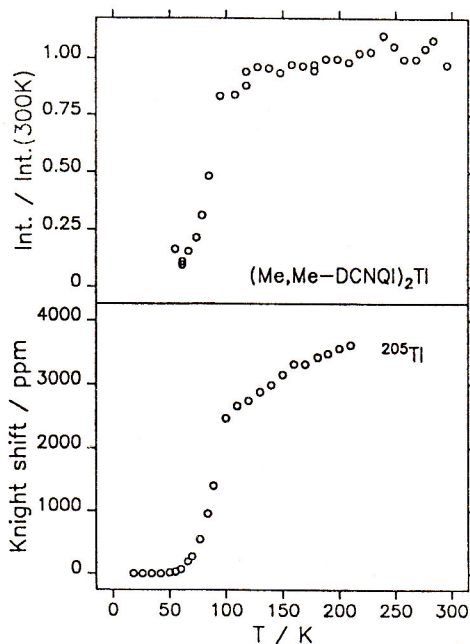


Fig.2: Knight shift and ESR intensity of the thallium salt.

(Me,Me-DCNQI)₂Li: In the high temperature range the proton spin relaxation rate is governed by the interaction with the conduction electrons (Korringa like behavior). In this temperature range it exhibits a frequency dependence with $T_{1H}^{-1} \sim \omega^{-1/2}$ [5]. This points to a onedimensional motion of the spin- / charge carriers, being in agreement with the measurements of the Knight shift of the ⁷Li counterion. The resonance line of ⁷Li does not show any shift relative to a diamagnetic Li reference in the whole temperature region (Fig.4). This fact implies that there is no spin-density of the conduction electrons at the ⁷Li counterions. The resonance line also shows a temperature independent quadrupolar splitting of about 350 ppm.

Qualitatively the temperature dependence of the relaxation rate of ⁷Li behaves similar to that of the protons (Fig.3 and Fig.4) if we neglect the strong maximum at 75K which results from the reorientation of the methyl-groups in the DCNQI molecule. Therefore we conclude that both, the protons and ⁷Li-nuclei, are relaxed by the same mechanism: the interaction with the conduction electrons. The only difference is that in case of ⁷Li we have a dipolar coupling and in case of the protons the scalar one dominates.

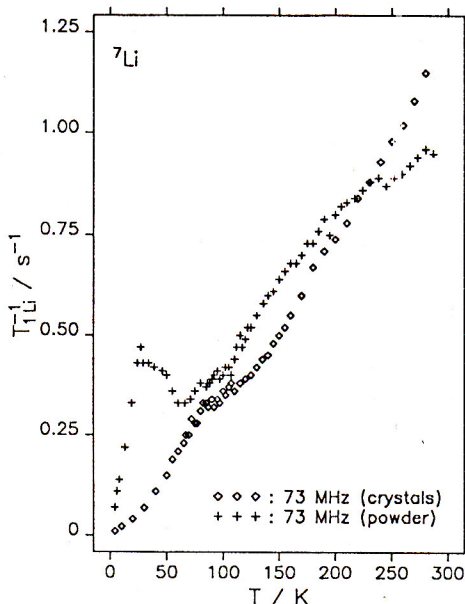


Fig.3: Relaxation rate versus temperature of ${}^7\text{Li}$ in $(\text{Me,Me-DCNQI})_2\text{Li}$.

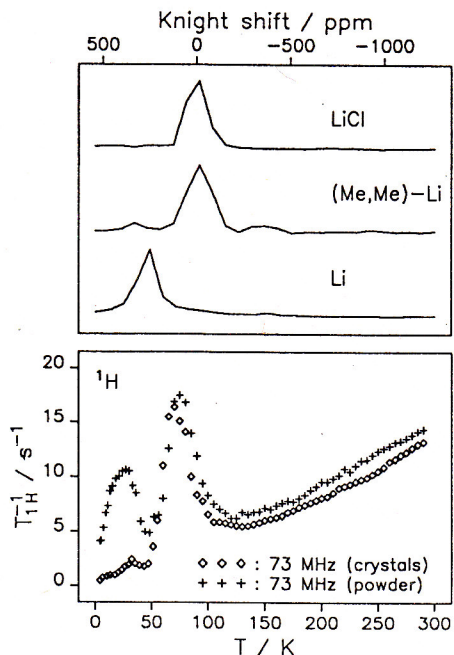


Fig.4: Knight shift (above) and $T_{1\text{H}}^{-1}$ (below) in the Li-salt.

It must be mentioned that there are striking differences in the relaxation rate below 60K when using an assembly of many good single crystals instead of a powder sample (poor crystal quality). In case of poor crystal quality a maximum appears, which is due to a change in the dynamics of the total S-spin system, which contains the conduction electrons and the localized paramagnetic impurities. Therefore, protons as well as Li-nuclei are influenced in a similar manner.

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