KNIGHT SHIFT AND NUCLEAR RELAXATION OF THE $^7$Li, $^{63}$Cu, $^{205}$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$_3$ (=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 $\sigma = 1000$ Scm$^{-1}$, which is one order of magnitude higher as those of the others. In case of (Me,Me-DCNQI)$_2$Cu there is no phase transition but a strong increase of conductivity ($\sigma = 5 \times 10^5$ Scm$^{-1}$) down to 400mK [1]. This DCNQI-salt exhibits, under applied pressure, a metal to insulator phase transition [2] comparable to the $\sigma$-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:

<table>
<thead>
<tr>
<th>Cu - salts</th>
<th>other salts</th>
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<tbody>
<tr>
<td>Valence band spectroscopy [3]</td>
<td>considerable density of states at the Fermi edge in the conductive range.</td>
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<td>ESR [1,4]</td>
<td>no ESR-line of the charge carriers was found, leading to $\Delta B_{\text{pp}} &gt; 1000$ Gauss.</td>
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<tr>
<td>Proton spin lattice relaxation [5]</td>
<td>Korringa like behavior ($T_1^{-1} \cdot T \cdot X^2 = \text{const}$) in all DCNQI salts in the range of high conductivity. no frequency dependence up to 300 MHz</td>
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<tr>
<td>Conductivity[1]</td>
<td>$\sigma(300K) = 1000$ Scm$^{-1}$</td>
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(received October 23, 1989)
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-Me,Me-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

(Me,Me-DCNQI)$_2$Cu: 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 $\tau^{-1} > 10^{-13}$ sec$^{-1}$. The small proton relaxation rate ($T_{1H}^{-1} = 2$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 $^{63}$Cu 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 tetrahedrical arranged CN-groups which can be temperature dependent through crystal distorsion.

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 ($K - \chi$) 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.

(Me,Me-DCNQI)$_2$Tl: 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 ($^{205}$Tl) 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 $T_2$ ($< 10\mu$s). For comparison, the Knight shift of metallic thallium [7] is very large (= 15600ppm).

The Knight shift of $^{205}$Tl 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.
(Me,Me-DCNQI)$_2$Li: 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 $T_1^{-1} = \omega_i/2$[5]. This points to a onedimensional motion of the spin- / charge carriers, being in agreement with the measurements of the Knight shift of the $^7$Li counterion. The resonance line of $^7$Li 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 $^7$Li counterions. The resonance line also shows a temperature independent quadrupolar splitting of about 350 ppm.

Qualitatively the temperature dependence of the relaxation rate of $^7$Li 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 $^7$Li-nuclei, are relaxed by the same mechanism: the interaction with the conduction electrons. The only difference is that in case of $^7$Li we have a dipolar coupling and in case of the protons the scalar one dominates.
Fig. 3: Relaxation rate versus temperature of $^7$Li in (Me,Me-DCNQI)$_2$Li.

Fig. 4: Knight shift (above) and $T_{1H}$ (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.

REFERENCES