

NMR INVESTIGATIONS OF THE ORGANIC METALS AND SUPERCONDUCTORS α -(BEDT-TTF) $_2$ I $_3$, β -(BEDT-TTF) $_2$ I $_3$ AND α_t -(BEDT-TTF) $_2$ I $_3$

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^1H and ^{13}C spin lattice relaxation rates as well as ^{13}C Knight shifts of the quasi two dimensional organic metals α -, β - and α_t -(BEDT-TTF) $_2$ I $_3$ are reported. In β - and α_t -(BEDT-TTF) $_2$ I $_3$ at temperatures below 100K the Korringa relation is fulfilled. Near the critical temperature of 8K of the stable superconducting state of α_t -(BEDT-TTF) $_2$ I $_3$ an enhancement of the proton spin lattice relaxation rate due to superconducting fluctuations is observed. The observed individual ^{13}C Knight shifts, as measured by magic angle sample spinning and cross polarisation methods range between -6 and +244 ppm for α - phase and -10 and +125 ppm for β - and α_t - phase crystals.

1. INTRODUCTION

Since in organic metals the conduction band arises from delocalized molecular orbitals the understanding of the electronic properties on a microscopic level is of importance. High resolution ^{13}C NMR investigations can provide such information because spin densities derived from Knight shifts for individual carbons reflect directly the charge density [1-3].

Here we report ^1H and ^{13}C NMR investigations on the three title compounds. α -(BEDT-TTF) $_2$ I $_3$ is an organic metal at temperatures above 135K. At 135K a metal insulator phase transition occurs [4]. Crystals of β -(BEDT-TTF) $_2$ I $_3$ are organic metals down to low temperatures and have a superconducting state at ambient pressure below 1.3K [5]. They have a second metastable superconducting state at 8K [6]. Crystals of α_t -(BEDT-TTF) $_2$ I $_3$ have at ambient pressure a stable superconducting state below 8K [7,8].

2. EXPERIMENTAL, RESULTS AND DISCUSSION

^{13}C Knight shifts were measured on α -, β - and α_t -(BEDT-TTF) $_2$ I $_3$ crystals, using magic angle sample spinning and cross polarisation methods. Besides samples with natural abundance of ^{13}C , 10% ^{13}C enriched crystals were used as well in the case of α -(BEDT-TTF) $_2$ I $_3$ and α_t -(BEDT-TTF) $_2$ I $_3$ (enriched in the positions 1-6 of BEDT-TTF, see fig.1), since cross polarisation was not very efficient for the C positions 1-6. In the spectra of the ^{13}C enriched samples the intensities of the lines of the carbons to which the protons are attached (positions 7-10, see fig.1) are very weak. Therefore this range is shown separately in fig.2 for samples with natural abundance. The Knight shifts of these carbons are given with respect to pure BEDT-TTF. As a reference for the Knight shifts of the other carbons (pos.1-6) the insulating state below 135K of α -(BEDT-TTF) $_2$ I $_3$ was used. The chemical shifts of the carbons of the BEDT-TTF molecules in these crystals below 135K are very similar to those of pure BEDT-TTF as can be seen from fig.1, while above 135K in the metallic region the Knight shifts range between -6 and +244 ppm (see figures 1 to 3 and the table).

Figure 3 shows ^{13}C spectra at 68MHz and 300K of BEDT-TTF (top) and β -(BEDT-TTF) $_2$ I $_3$ (bottom), both with ^{13}C in natural abundance, as well as of α - and α_t -(BEDT-TTF) $_2$ I $_3$ (middle part), both ^{13}C enriched. The insert on top shows the spectrum of the center (pos.1,2) and middle carbons (pos.3-6) of a polycrystalline BEDT-TTF sample in higher resolution.

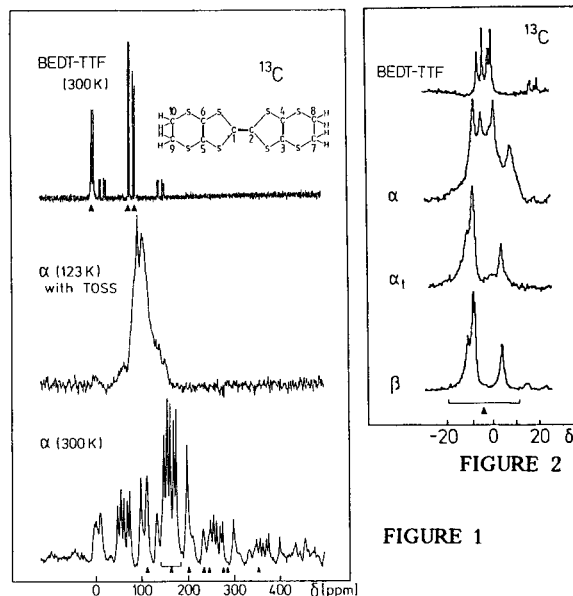


FIGURE 1: ^{13}C spectra at 50MHz of BEDT-TTF (top, natural abundance, 300K), α -(BEDT-TTF) $_2$ I $_3$ at 123K (middle, ^{13}C enriched sample, insulator below 135K) and α_t -(BEDT-TTF) $_2$ I $_3$ at 300K (bottom, ^{13}C enriched sample, metal at temperatures above 135K). δ is given relative to TMS.

FIGURE 2: ^{13}C spectra (natural abundance) at 68 MHz and 300K of the carbons to which the protons are attached (positions 7-10, see fig.1) of BEDT-TTF (top), α -, α_t -(BEDT-TTF) $_2$ I $_3$ and β -(BEDT-TTF) $_2$ I $_3$.

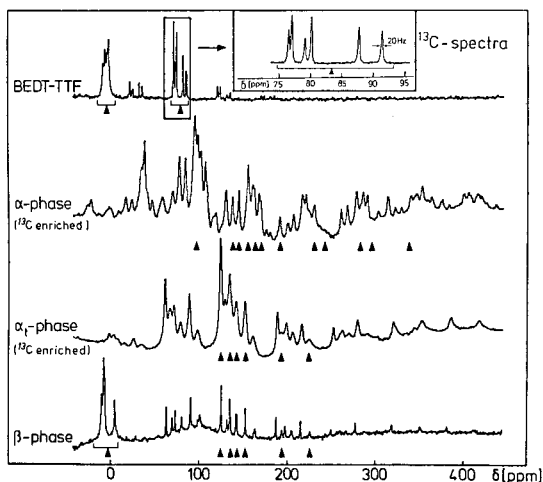


FIGURE 3

^{13}C spectra of polycrystalline BEDT-TTF, α -, α_t - and β -(BEDT-TTF) $_2\text{I}_3$ at 68 MHz and 300 K (see text).

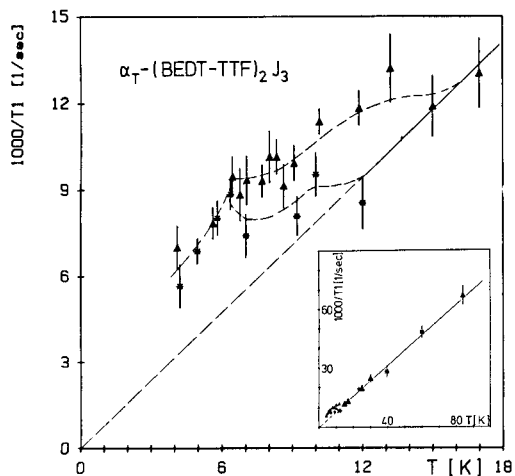


FIGURE 4

^1H Spin lattice relaxation rates (measured at 13.5 MHz) of single crystals of α_t -(BEDT-TTF) $_2\text{I}_3$ for the magnetic field perpendicular (\blacktriangle) and parallel ($*$) to the c^* -axes (see text).

All carbons are resolved due to the low symmetry in the BEDT-TTF crystal. In order to separate the center ^{13}C bands from spinning side bands the spinning frequencies were varied (between 3 and 5 KHz). In addition TOSS experiments were performed. In figures 1 and 3 the center bands are marked by \blacktriangle . The Knight shifts and the ^{13}C spin lattice relaxation times at 300 K are listed in the table.

The ^1H spin lattice relaxation rates of β - and α_t -(BEDT-TTF) $_2\text{I}_3$ were measured at several frequencies in the temperature range 4.2 – 380 K. Below 100 K the Korrington relation is fulfilled, while above 100 K the relaxation is dominated by a strong contribution due to

TABLE

^{13}C Knight shifts κ [ppm] and ^{13}C spin lattice relaxation times T_1 [msec] of α - and α_t -(BEDT-TTF) $_2\text{I}_3$ (Knight shifts of α_t - and β -(BEDT-TTF) $_2\text{I}_3$ crystals are identical [8]). Due to the low crystal symmetry and the number of BEDT-TTF molecules in the unit cell of α -(BEDT-TTF) $_2\text{I}_3$ [4] all carbon positions of the inner and middle carbons appear twice (inner: 1,1' and 2,2'; middle: 3,3'–6,6'). In addition the Korrington enhancement factor η is shown. For the definition of η see reference [2].

Position	κ	T_1	η	Position	κ	T_1	η
$\underline{\alpha}$:				$\underline{\alpha}_t$:			
1,1',2,2'	244	15	16	1,2	125	19	47
	199	27	13		92	42	39
	187	26	15				
	146	19	34				
					62	97	36
	144	27	25	3-	51	120	44
	104	57	22	6	44	130	55
	82	60	35		34	135	90
3,3'-	76	60	41		5.5	750	-
6,6'	69	87	34	7-	-6.7	110	-
	57	109	38	10	-7.3	110	-
	50	109	48		-9.7	450	-
	11	85	-				
7,7'-	9.7	-	-		-2.7	-	-
10,10'	3.0	-	-		-6.0	-	-

flipping of the CH_2 - groups. Figure 4 shows the ^1H spin lattice relaxation rates of α_t -(BEDT-TTF) $_2\text{I}_3$ (single crystals) below 20 K for the magnetic field parallel and perpendicular to the c^* -axes. The insert in figure 4 shows the relaxation rates up to 100 K.

Similarly as in the case of β -(BEDT-TTF) $_2\text{I}_3$ [9] the relaxation rates deviate from the Korrington law near the superconducting transition. This is ascribed to fluctuation effects. Here in the case of α_t -(BEDT-TTF) $_2\text{I}_3$ the increase of the relaxation rates is much weaker than for the crystals of β -(BEDT-TTF) $_2\text{I}_3$ [9]. This behaviour might be explained by the fact that α_t -(BEDT-TTF) $_2\text{I}_3$ crystals behave at low magnetic fields like anisotropic three dimensional superconductors and only at magnetic fields above 1.5 T like typical two dimensional superconductors [10]. Nevertheless a weak directional dependence of the relaxation rate can be observed as well. A detailed discussion of this subject as well as of the spin densities at individual carbon sites will be given elsewhere [11].

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