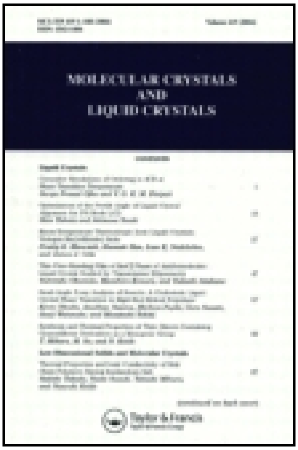

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Absence of Knight-Sheft in the Metallic State of Polyacetylene

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ABSENCE OF KNIGHT-SHIFT IN THE METALLIC STATE OF POLYACETYLENE

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Abstract: NMR spectra on ^{13}C of cis-$(CH)_x$ have been recorded using the magic angle spinning technique. Inspite of doping with AsF_5 up to a level of ~ 7at%, $(CH)_x$ does not convert to the trans modification. No Knight shift or other line shift is observed up to this dopant concentration. Above 7at% a line shift of about 30 ppm is found. To extend the soliton model to cis-$(CH)_x$ bi-solitons or bi-polarons are proposed.

Introduction

It is well known that polyacetylene becomes conducting by doping[1] but the mechanism of the electrical conductivity is not yet understood. Measurements of the magnetic susceptibility[2] have shown that the charge carriers are apparently spinless and do not contribute either to a Curie susceptibility (as one would expect for localized charge carriers) or to a Pauli susceptibility (as expected for charge carriers in a conduction band). Therefore the concept of solitons in conjugated polymers has been developed.[3] These solitons are conjugational defects (domain walls separating chain segments of inversed bond alternation) and are spinless when charged.

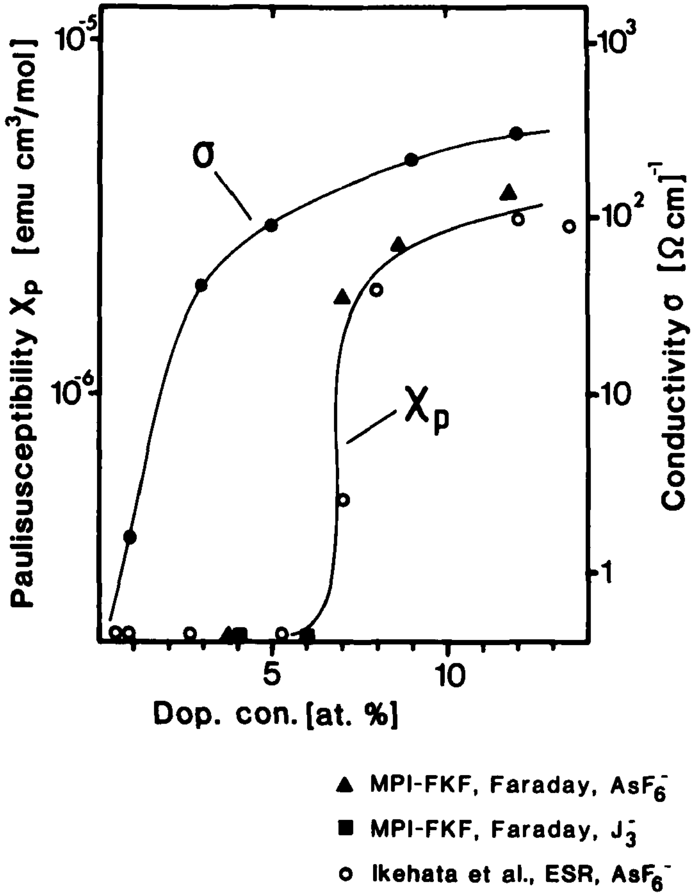


Fig. 1: Compilation of experimental data on the Pauli susceptibility.

Pauli Susceptibility

Fig. 1 shows a compilation of experimental data on the Pauli susceptibility of polyacetylene doped with AsF_5 or iodine. The abscissa represents the doping level assuming a charge transfer of one electron per three iodine atoms, or one AsF_5 molecule, respectively. The ordinate shows the susceptibility as determined from Faraday balance or ESR measurements.[2]

It is remarkable that a "universal" curve can be drawn, showing essentially no Pauli susceptibility up to - and a sharp rise at - the critical doping level of 7at%.[4] For comparison the electrical conductivity is also included in the figure. It is evident that the insulator-to-metal transition occurs at a much lower doping level in the conductivity than it does in the susceptibility so that a region exists where polyacetylene has a strong response to electric but no response to magnetic fields.

We want to point out that this magnetic anomaly is not observed in <u>every</u> sample; there <u>are</u> samples showing a finite Pauli susceptibility below a doping level of 7at%. The data compiled in Fig. 1 represent only the lower contour of all available experimental values. We believe, however, that the physical relevance of the experimental results is this very contour; data above this contour can be explained by inhomogenous doping, which often occurs and leads to samples mixed of dopant-rich and undoped parts.

Although the magnetic anomaly is seen both in static susceptibility and in ESR measurements the importance of the physical implications calls for further conformation by additional independent methods. Therefore the present NMR measuremnts were carried out.

Experimental

Films of polyacetylene were prepared at - 78°C by the usual Shirakawa method[5] and doped by contact to AsF_5 gas. Our doping procedure consists of condensing AsF_5 in a nitrogen cold trap and warming several times till the vapour pressure rises to a few millibar for some seconds thus exposing the sample to short gas "bursts". Between these bursts the vessel is connected to a diffusion pump for about half an hour to remove AsF_3 and other unwanted gases. By this method we often (but not always) get samples with no Pauli susceptibility if the doping level is below 7at%. The doping level is determined by weight uptake.

NMR data have been recorded for naturally abundant ^{13}C in $(CH)_x$ at room temperature on a Bruker CXP 200 spectrometer working at 50.3 MHz (in a field of 4.7 Tesla), using proton decoupling combined with magic angle spinning of the sample (4 kHz).[6]

Results

Fig. 2 shows the spectra observed in polyacetylene doped with various concentrations of AsF_5[7]. The frequency is expressed in ppm deviation from a standard line (tetramethylsilane). The solid curves are averaged from our original chart recordings, the error bars indicating the noise level. The NMR absorption (vertical scale) is plotted in arbitrary units which are not identical for the various concentrations.

In undoped polyacetylene we observe a narrow line (linewidth ~ 4 ppm) at 127 ppm, which is attributed to cis-$(CH)_x$. The small satellite at 136 ppm originates from traces of trans-$(CH)_x$ and is well known to become predominant after thermal annealing.[8] Up to now it has been generally assumed that even slight doping (well below 1 at%) leads to an almost complete cis-to-trans conversion. As can be seen from Fig. 2 the sample remains mainly in the cis-configuration even after doping to as much as 5.6%. The preservation of the cis-modification is a very important result and has far reaching consequences for the soliton concept as will be discussed later.

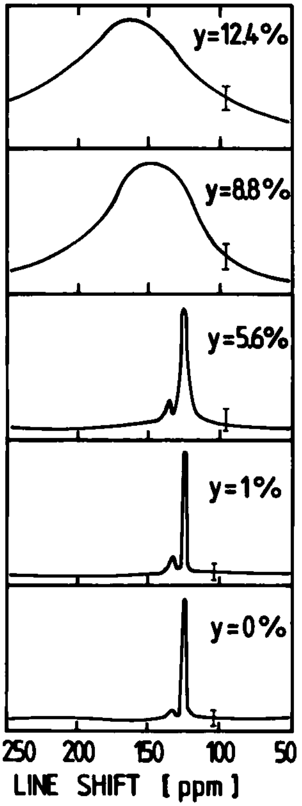


Fig. 2: Observed NMR absorption of ^{13}C in $[CH(AsF_5)_y]_x$ as a function of frequency for 5 different concentrations of AsF_5. The concentrations y are indicated in at % and the frequency is expressed in ppm deviation from the frequency of the tetrametylsilane (TMS) reference.

The second important result of our NMR data in Fig. 2 is the absence of any line-shift up to y = 5.6%. At higher doping levels a line-shift and a line-broadening occurs. This line-shift as a function of doping concentration is plotted in Fig. 3.

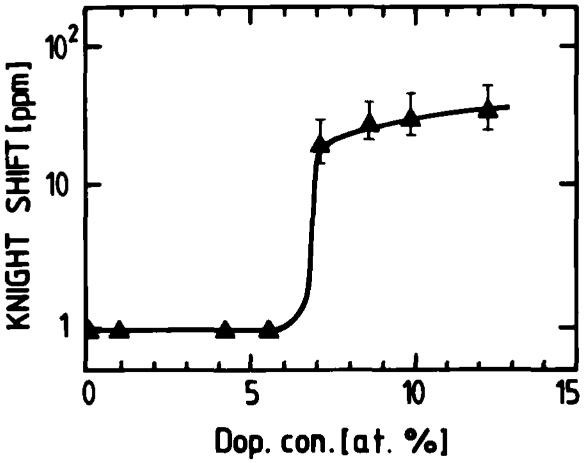


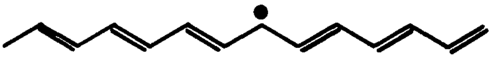
Fig. 3: Knight-shift as function of doping concentration

Discussion

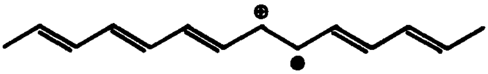
The parallelism in the NMR line-shift (Fig. 3) and the Pauli susceptibility (Fig. 1), seems to confirm the magnetic anomaly by an independent and local method. It is reasonable to interprete the line-shift at about 7% as Knight-shift, which - in ordinary metals - is proportional to the Pauli susceptibility. It is difficult, however, to understand why doping does not lead to a line-shift at all. Even if there were no magnetic reason for a line-shift, there should be a shift due to charge transfer from the polymer chain to the dopant (chemical shift).

Therefore in many discussions it was argued[9] that by some yet unknown reason the NMR measurements do not see all of the polyacetylene sample - in particular they might just see the undoped parts of an inhomogeneous sample. Then both the failure to see the cis-to-trans conversion and the absence of a line-shift would be trivial. Line intensity measurements, however, exclude this possibility. From the comparison of our line intensity to that of a simultanously measured standard (i.e. the sample holder) we know that "most" of the ^{13}C nuclei of our sample do contribute to our NMR line (certainly much more than 50%).

If one accepts the magnetical anomaly in polyacetylene and if one accepts that the samples remain in the cis-configuration after doping, then the soliton concept has to be modified. Many authors[10] have pointed out, that solitons are only stable in trans-$(CH)_x$. In cis-$(CH)_x$ the energy of the polymer chain is not equal on both sides of the domain wall and the soliton will move out of the chain leaving behind the low-energy configuration (Fig. 4). If one wants to keep the soliton model, bi-solitons will have to be constructed. If they are charged the attractive lattice force (the tendency to eat up the high energy part of the chain between the solitons) will be balanced by Coulomb repulsion as soon as the solitons have sufficiently approched each other (uncharged solitons will annihilate).[11]

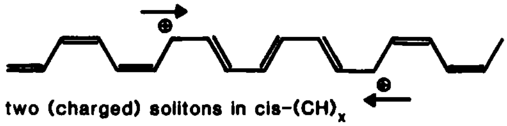


(neutral) soliton in trans-$(CH)_x$



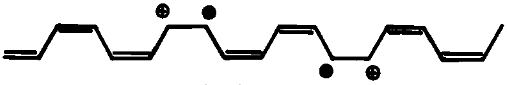
polaron = neutral + charged soliton

(neutral) soliton in cis-$(CH)_x$



two (charged) solitons in cis-$(CH)_x$

bi-polaron in cis-$(CH)_x$



two polarons in cis-$(CH)_x$

bi-soliton in cis-$(CH)_x$

Fig. 4: Solitons and polarons in trans-$(CH)_x$, bi-solitons and bi-polarons in cis-$(CH)_x$

Such bi-solitons can also be envisaged as bi-polarons, where a single polaron is the combination of a charged and a neutral soliton. If two polarons combine to a bi-polaron the neutral parts will annihilate and the charged parts form the bi-soliton. Bi-polarons are well known from other parts of solid state physics (e.g. $WO_{3-\delta}$[12] or Ti_4O_7[13]) and might turn out more useful in a "universal" description of conjugated polymers than "simple" solitons.

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