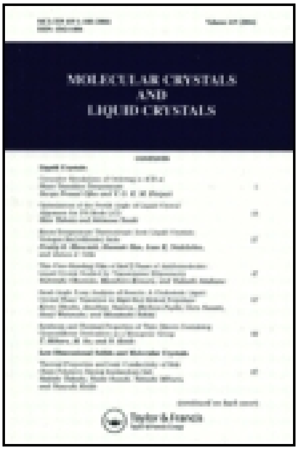

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Undoped Trans - $(CH)_X$: Magnetic Resonance and Structure

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UNDOPED TRANS - $(CH)_x$: MAGNETIC RESONANCE AND STRUCTURE

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Abstract Arguments are given that soliton conditions might be best realized at the surfaces of the fibrils constituting the Shirakawa polyacetylene. The implications of this hypothesis on the interpretation of magnetic resonance and other experiments are discussed.

Ever since the proposition of the soliton model by Su, Schrieffer and Heeger (SSH)[1] to account for the properties of trans - polyacetylene, $(CH)_x$, its applicability was always a subject of controversy. The SSH model deals with an ideal situation: it describes a single polymer chain with a two-fold degenerate dimerized ground state, which gives the possibility of mobile paramagnetic neutral solitons, corresponding to the domain-walls between the two ground state configurations. Polyacetylene, as it is prepared by the Shirakawa technique, is far from being ideal: its intrinsic properties can be easily hampered by its fibrous morphology, incomplete crystallinity and chemical impurities. Confrontation of the model with the reality is not an easy task: attempts to observe the topological defects directly by crystallographic means have failed up to now. Sophisticated magnetic resonance techniques have been used to spy out "soliton properties" through the spin dynamics in $(CH)_x$; their often complicated interpretation can easily be misled if one does not pay enough attention to the actual

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nature of the material.

In this contribution, we try to summarize results and informations coming from magnetic resonance, morphological and crystallographic studies and to consider their implications together. Our aim is to try to show up "soliton properties" as well as the limitations imposed by the real $(CH)_x$ upon the applicability of the SSH model. We shall consider the "soliton story" first from magnetic resonance, then from a structural point of view. We would like to show that several surprizing phenoma and complications could have a common simple reason: looking for special one-dimensional effects, we think that we deal with a three-dimensional solid and we observe surface phenomena. We think that the ideal "soliton conditions" might be best realized at the surfaces of the fibrils. The consequences of this assumption are discussed.

Dynamic nuclear polarization (DNP) and nuclear spin-lattice relaxation time (T_1) measurements showed the existence of highly mobile electronic spins in trans-$(CH)_x$.[2] The motion was found highly anisotropic, with diffusion constants of $D_{//} \sim 10^{-3}$ cm^2/sec and $D_{\perp} \sim 10^{-9}$ cm^2/sec respectively along and perpendicular to the polymer chain: values supporting the previsions of the SSH model. ESR studies revealed however many complications[3], leading to the supposition that a fraction of the paramagnetic centers observed in trans-polyacetylene is immobile.[4] The ratio of immobile to mobile spins was found to vary from sample to sample and to be very sensitive to oxygen contamination. It was proposed that ESR properties, like line-width (ΔH) and line-shape, were mainly sensitive to fixed spins (their own line-width would be several Gauss), while mobile spins visiting many proton sites dominate the relaxation, keeping T_1 fairly reproducible. These observations gave the possibility to use ESR line-width as a measure of quality from the "soliton point of view". We want to remind the following observations:

1./ The smallest ESR line-width can be attained by the quickest thermal isomerization, heating the sample at the highest temperature (200-210 °C just for one minute), which is not necessarily the best from other points of view, producing high spin concentrations (1 spin for 1000 CH units).[4]

2./ Cooling down the $(CH)_x$, the mobile spins are gradually trapped. The temperature dependence of the number of mobile spins is not a single energy activated form; an approximate description needs to suppose a continuous distribution of trapping energies from $E_0 \sim -650$ K to zero.[5]

3./ Mobile spins get trapped upon oxygen exposure too: a part of this effect is instantaneous and reversible by pumping off the oxygen.[6]

Although the interpretation of T_1 required to take into account the second observation[7], the relaxation time was found to be less sensitive to these trapping effects. The reason is that, as long as a common spin temperature for the nuclei is established, their relaxation is governed by the mobile spins and gives their correct diffusion constant.[8,9] We add two NMR results to the above list of observations:

4./ In case of weakly coupled nuclei, ^{13}C or ^2H, it was found that their relaxation is inhomogeneous. The fast part of the relaxation, which can be assigned to direct relaxation on the mobile spins, concerns only 30 % of the nuclei.[10]

5./ An NMR nutation experiment showed that double and single bond lengths are not averaged out by the fast motion of the solitons, i.e. there are no solitons on most of the chains.[11]

Now we turn to discuss some morphological and structural aspects of trans-$(CH)_x$. As it is well known, the Shirakawa synthesis of $(CH)_x$ gives a fibrous material, with a fiber thickness varying from about 100 to 1000 Å. This morphology results in an enormous specific surface of the order of 10 to 100 m^2/g. In other words, while in an ordinary solid the fraction of atoms situated in the first surface layer is of the order of 10^{-8}, in case of $(CH)_x$ 5 to 20 % of the chains are at the surface. This peculiarity has been extensively discussed in the context of possible use of $(CH)_x$ as electrode material in a battery, but it has rarely been considered to play an important role in the properties of the undoped material.

The small number of Bragg reflections observed in diffration *experiments on the trans-$(CH)_x$ does not allow a full refinement* of the structure. Many ambiguities concern the value of the bond alternation and its perpendicular ordering in the crystal structure; The different possibilities for in-phase and out of phase alternation of neighboring chains change the symmetry of the elementary cell as well as the value of the calculated lattice energy. On the other hand, moving solitons would destroy the perpendicular order of the bond alternation, giving rise to the apparition of the otherwise absent (001) (chain direction) reflection in the form of one dimensional (uncorrelated in the perpendicular direction) diffuse scattering. This has not been clearly observed yet.

Baughman and Moss[12] calculated the interchain electrostatic energy for different perpendicular order configurations. They pointed out that this interchain interaction lifts the two-fold degeneracy associated with the bond alternation in an ordered crystal, inhibiting the free motion of solitons predicted by the single chain SSH model. While in a single chain model, chain-ends and breaks in the conjugation represent a repulsive potential for the solitons, pushing them to the middle of the chains, the interchain interaction forces to localize them at the chain-ends (or push them out of the chains if it is possible). Introducing a soliton at a chain-end and moving it on the chain needs a linearly diverging energy proportional to the distance from the chain-end. The existence of a finite number of spin carrying bond alternation defects in the real material brings about disorder in the crystal, reducing the activation energy of the motion to a few hundred of degrees of Kelvin for the spin concentration practically observed.

We would like to point out the existence of an other factor which helps to overcome the trapping effect of three dimensionality: it is the fact that several percent of the chains are at the surface. Chains at the surface experience a considerably reduced electrostatic field of the other chains, compared to those inside the crystal. Moving solitons are easily created on these chains: this results in a "disordered surface layer" which gives a disordered (partially averaged out) electrostatic field only to the next inner layer, thereby facilitating the existence of moving solitons in the second layer too. We expect the trapping energy coming from the interchain interaction to build up slowly (in 5 to 10 atomic layers) while getting deeper into the fibers to the above estimated value.

Keeping in mind that a few atomic surface layers can easily represent even 1/2 of the material, the above arguments lead us to propose that moving solitons observed in trans-$(CH)_x$ are in the first few atomic layers, at the surfaces of the fibrils,[13] where conditions of the one dimensional physics described by the SSH model are best approximated.

Although thermodynamics is hardly applicable to discuss variations on the scale of 50 lattice constants, to gain some qualitative insight into the isomerization process, we adopt the argumentation of Baughman and Moss.[12] For a given conjugation length L and interchain interaction E_0 (soliton-lattice interaction energy in their notation), a critical temperature is defined

$$T_0 = LE_0/2R \ln 2$$

above which the trans polymer formed is disordered, while below the bond alternation of the chains are ordered. For bulk material this temperature is estimated to be of the order of 200 to 1000 K, depending on the structure. We expect E_0 to be small at the surface and to increase slowly up to the bulk-value getting deeper into the fibers of the real material. As E_0 is spatial dependent, T_0 becomes spatial dependent too. In the middle of the fibers, T_0 will be higher than the temperature T_i we use to isomerize our cis-$(CH)_x$

to trans, but $T_0 < T_i$ close to the surface.

Qualitatively we expect to have ordered polymer inside the fibers covered by a finite thickness of disordered layer. The higher the isomerization temperature, the thicker the disordered layer. (Of course we do not expect a clear phase separation at this small distance scale.). The other effect of thermal treatment is the creation of paramagnetic centers, the mechanism of which is not exactly known. Chemical reactions, like cross-linking or reactions with impurities etc., interrupt the π electron conjugation, producing bond alternation defects. The higher the temperature and the longer the thermal treatment, the higher the produced spin (defect) concentration. This adds further disorder, increasing the thickness of the disordered region and reducing effective interchain interaction inside the fibrils. Although it is not evident, for the sake of simplicity we suppose here that a homogeneous spin distribution is created by thermal isomerization. Spins close or at the surfaces will be mobile, while spins inside the fibrils will be trapped by the interchain interaction.

This picture gives a natural explanation for the coexistence of mobile and fixed spins, whose ratio will depend on the fiber diameter and isomerization temperature T_i, in agreement with observation 1./. Moreover a natural distribution of trapping energies is found as a function of distance from the surface, from 0 to several hundreds degrees K, in agreement with observation 2./. We note that to produce attractive potential for the soliton, one needs to imagine chemical defects like hydrogene substitution with some other groups, leaving the π conjugation intact.[14] It is unlikely to have an important concentration of this kind of defects in $(CH)_x$. The interplay of surface disorder and interchain interaction offers a natural explanation for the observed trapping phenomena without evoking chemical impurities of exotic nature.

The single ESR line results from asmall exchange interaction between the spins, as originally proposed.[4] However in the present picture, trapping of the spins upon cooling is accompanied by a more and more important spatial separation between mobile and fixed spins, as the "cylinder" of mobile spins becomes thinner and thinner. This increasing inhomogeneity may help to explain the inhomogeneous broadening of the ESR line as well as the coexistence of solid state and Overhauser effects in DNP below 150 K.

The reversible part of oxygen trapping (observation 3./) was interpreted as a consequence of surface absorption of oxygen.[5] A complete description of oxygen effect at room temperature requires to take into account diffusion of O_2 molecules into the fibrils and irreversible reactions as well. Below 200 K however, the oxygen effect is completely reversible[5] and it concerns as much as 60 % of the spins at this temperature. Decreasing the temperature, its relative importance is gradually decreasing due to the thermal trapping..These observations support strongly the above developped image of decreasing thickness surface "cylinder" of mobile spins.

The strong dipolar coupling between protons allows to overcome this spatial inhomogeneity and to establish a common spin temperature in the whole fibril. This common spin temperature is however easily destroyed by reducing the proton concentration.[9] As homonuclear coupling of ^{13}C or ^{2}H in enriched samples is weaker, we can suppose that only nuclei being close to or inside the mobile spins containing regions relax fast. Thus the observation 4./ tells us that this volume is about 30 % of the total volume.[10] In case of 200 Å thick fibers, this corresponds to a 5 lattice constants thick mobile spins containing surface layer! According to observation 5./, not all the chains are soliton bearing even in this volume.

From a structural point of view, it is better to study highly crystalline samples, like the one obtained by the Durham synthesis at 120 °C[15], but it won't probably contain moving solitons. We think that the less crystalline sample (small fiber diameter, high preparation temperature) may offer the best chance to look for the

(001) diffuse reflection.

Soliton properties, monitored either by magnetic or other means, has always been found to have small time constants upon doping, giving the impression of fast and homogeneous doping, while electrochemistry showed that the diffusion of the dopant into the fibrils is very slow and it is nearly impossible to attain a homogeneously doped material.

In this paper, we proposed that many observations on trans-polyacetylene can be interpreted as surface phenomena. The specific morphology of the Shirakawa $(CH)_x$ amplifies surface effects, which, in common solid state physics, are $\sim 10^{-8}$ times smaller than bulk effects. We argued that disorder introduced by bond alternation defects brings about nearly ideal one dimensional conditions in the surface, which involves about 5 to 30 % of the material. This is why we believe that the physics described by the single chain SSH model can be experimentally inferred on the Shirakawa trans-$(CH)_x$. In a bulk crystalline material, interchain interactions should lift the degeneracy of the polymer's ground state, excluding the existence of moving solitons. The concept of disordered surface was successfully used to reinterprete various magnetic resonance results. A more detailed account will be published elsewhere.[16]

REFERENCES

1. W.P. Su et al., Phys. Rev. Lett., 42, 1698 (1979).
2. M. Nechtschein et al., Phys. Rev. Lett., 44, 356 (1980).
3. N.S. Shiren et al., Solid State Commun., 44, 1157 (1982).
4. K. Holczer et al., Phys. Rev. B, 23, 1051 (1981).
5. F. Genoud et al., J. de Phys. C3, 44, 291 (1983).
6. K. Holczer et al., Solid State Commun., 49, 881 (1981).
7. F. Devreux et al., Mol. Cryst. Liq. Cryst., 77, 97 (1981).
8. J.C. Scott and T.C. Clarke, J. de Phys. C3, 44, 365 (1983).
9. M. Ziliox et al., this volume.
10. M. Ziliox et al., Solid State Commun., 51, 393 (1984).
11. T.C. Clarke et al., J. de Phys. C3, 44, 369 (1983).
12. R.H. Baughman and G. Moss, J. Chem. Phys., 77, 6321 (1982).
13. We are indebted to J.J. André, who first raised this idea.
14. M. Kertesz et al., Mol. Cryst. Liq. Cryst., 77, 341 (1981).
15. H. Kahlert and G. Leising, this volume.
16. J.J. André and K. Holczer, to be published.