POLYACETYLENE : LA CHASSE AUX SOLITONS

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Résumé - Des expériences électriques, magnétiques et optiques dans le polyacétylène sont recensées et des résultats nouveaux sont présentés concernant l'isomérisation cis-trans par dopage AsF_5 (étude Raman) ; la coexistence des spins localisés et itinérants (expérience RPE) même dans des échantillons dopés doucement ; et la variation en temps (échelle des nanosecondes) de l'effet photoélectrique. Des arguments expérimentaux pro-soliton sont critiqués et l'avis est exprimé qu'il manque des évidences directes de l'existence des solitons mobiles dans le polyacétylène.

Abstract - Electric, magnetic and optical experiments on polyacetylene are reviewed and new data are presented concerning Raman studies of the AsF_5-induced isomerisation of cis samples, ESR results implying the coexistence of localized and itinerant spins even in slowly doped films at all doping levels, and time-resolved photoresponse of trans-polyacetylene in the nsec regime. It is argued that at present there is still very little direct experimental evidence for soliton motion in polyacetylene.

Introduction:
Since several years it has been noticed that a perfect polyene chain is a tempting model to illustrate some field-theoretical phenomena and to carry out gedankenexperimente of cosmological importance /1/. Schrieffer, Su, and Heeger /2/ and Rice /3/ have independently and nearly simultaneously shown that excitations in such a chain would have soliton-like properties. In this context a "soliton" is a bond-alternation defect as shown in Fig. 1: a domain-wall separating -regions from regions. Other authors might prefer to call this soliton "free radical", "dangling bond" or "Pople-Walmsley defect" /4/.

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

As a nonbonding electron this defect will carry a magnetic moment and give rise to an ESR signal. If the polyene chain is doped (oxidized) this dangling electron is likely to be the first one to be removed. Then there still remains a domain-wall, but now it carries a charge and no spin. The separation of electric and magnetic properties is one of the fascinating features of solitons in a polyene chain /5/. Other idealized solid state systems have been proposed, where solitons are even more spectacular and carry fractional charges /6/.

During the last ten years about two and a half thousand papers have appeared on solitons, five hundred on polyacetylene and a hundred on solitons in polyacetylene (Fig. 2). There is little surprise about the theoretitians' and experimentalists' hope that solitons would be not only a beautiful mental construct but also entities somehow related to physical observation and thus resistant to Ockham's razor /7/.

It is the tendency of this report to point out that up to now solitons in polyacetylene have pretty well managed to escape direct detection and that most evidences of their existence could also be interpreted in a non-solitonic way. This state of affairs will be found to be reminiscent of the well-kown French folk song "La chasse aux papillons" where what is chased turns out to be something other than butterflies /8/. Of course, this shortcoming has to be blamed to the demiurge, who has created the material world as a but imperfect copy of the pure ideas, as demonstrated by previous authors /9/. The relevant aspects of the stated imperfection are the finite length of real polyene chains and the existence of various defects, which act as soliton traps.

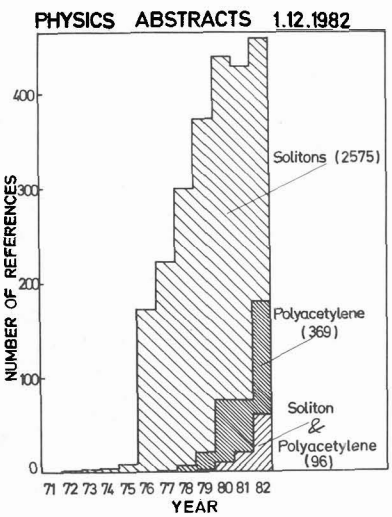

Fig. 2: Last decade's topic-relevant scientific output

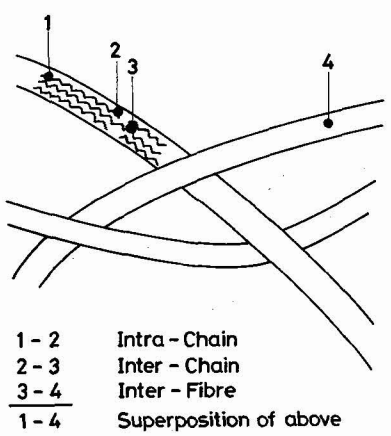

Fig. 3: Artist's view of a magnified picture of polyacetylene

Electric Conductivity:

Fig. 3 shows an artist's view of a magnified picture of "real" polyacetylene. Chains of finite lengths are somehow bundeled to form fibres. Hypothetical subminiature probes are inserted to measure the electric resistance: 1 and 2 along a chain segment, 2 and 3 between chains and 3 and 4 between fibres. It is reasonable to expect at least three different transport mechanisms: intra-chain, inter-chain, and inter-fibre. Measurements - even at high frequencies - can only be carried out between probes 1 and 4, so that there will be a superposition of all mechanisms. If the theory for each mechanism has e.g. two free parameters, any set of experimental data can be fitted.

It is up to the skill of the experimentalist to choose conditions where one mechanism is dominant. In undoped trans polyacetylene the resistance between 2 and 3 might be the most important. For this case Kivelson has developed the theory of intersoliton hopping /10/: there are charged and neutral solitons, both free to move along their chain segments, but they cannot leave these segments. They can, however, exchange their charge: the charge hops from a charged soliton to a neutral one. Epstein has carried out measurements of the temperature and frequency dependence of the conductivity of undoped trans polyacetylene and finds remarkably good agreement with Kivelsons's theory /11/.

Very recently, Summerfield /12/ has worked out an alternative theory: general hopping between random sites (their energy density being open to a fit). This theory does not make specific use of solitons, the sites between which to hop could be just any impurity. Summerfield's theory, see and behold, fits Epsteins's data not worse than Kivelson's theory (Fig. 4)! Moreover, Summerfield's theory also fits the imaginary part of the conductivity, which has become available since Chroboczek's measurement, some weeks ago /13/, and which is less consistent with intersoliton hopping.

The conductivity of doped samples can be explained by several non-solitonic mechanisms, amongst others fluctuation-induced tunneling between metallic particles /14/. Apparently the claim of having observed solitons cannot be based on conductivity measurements.

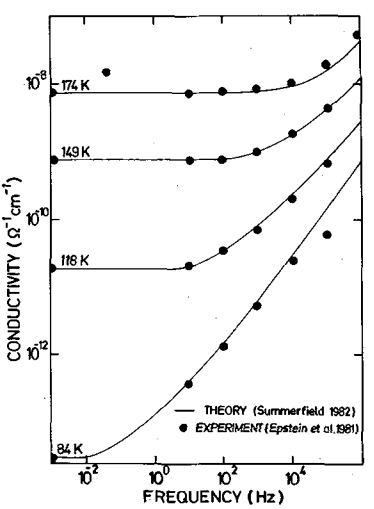

Fig. 4: Summerfield's general hopping theory fitted to Epstein conductivity data

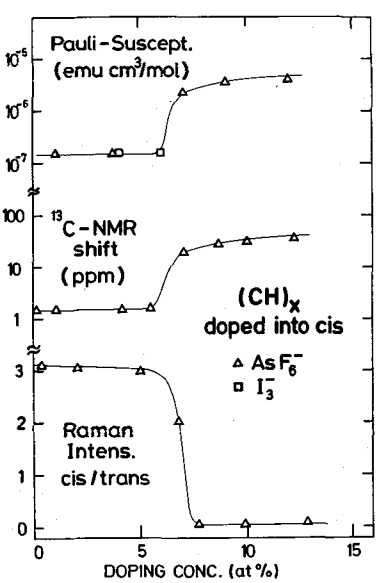

Fig. 5: Correlation of steps when doped into cis polyacetylene

Magnetic Properties:
In undoped trans polyacetylene an ESR signal is seen, corresponding to several hundred ppm of free electron spins. The line appears to be motionally narrowed and there is an Overhauser effect /15/. Are these spins solitons ? Why not ? But the justification of calling them so lies entirely in our knowledge of the dynamics of a polyene chain: mobility along the chain seems to imply solitonhood. If our phantasy were wide enough to imagine other spin carriers we would be less sure!

Doping reduces the number of free spins in polyacetylene /16/, consistent with the above mentioned concept of converting neutral solitons into charged but spinless ones. Admittedly this is an evidence for solitons, but a very indirect one: it is always insatisfactory to deduce the existence of something from the non-observation of something else. What, if doping somehow were to produce such a crazy band structure that most electrons went into band states or doubly occupied localized states below the Fermi level ? Even without the help of solitons most of the paramagnetism would vanish !

In 1980 Peo et al. have reported at various spring meetings /17/ that in polyparaphenylene and also in polyacetylene no Pauli susceptibility could be observed up to a certain doping level. These results were reproduced by several groups /18/, and contradicted by others /19/. In some cases a sudden rise of the Pauli susceptibility was found at a critical doping concentration. This step could be correlated with a similar behaviour in the NMR line shift and line width /20/ and was interpreted as insulator-to-metal transition due to the overlap of solitons in trans polyacetylene.

At that time, at least all the results of our group were obtained on samples originally in the cis modification. It was believed that even moderate doping completely converted cis into trans. The NMR investigation, however, has shown that - up to the critical concentration - a large fraction of the samples remained in the cis configuration. Subsequent work of Clarke and Scott /21/ has confirmed this view even if there remains some questions on the amount of the cis-to-trans conversions. Recent Raman measurements /22/ of various concentrations of AsF_5 doped into cis polyacetylene show a pronounced step at the same critical concentration, when the ratio of cis and trans Raman lines is plotted. Fig. 5 shows the correlation of these steps in susceptibility, NMR line shift, and Raman intensity. Therefore it is reasonable to assume structural changes at Peo's step rather than soliton overlap.

This summer, together with D. Davidov, we have been involved in new ESR studies /23/. Absolute susceptibility measurements are very difficult by the ESR technique because of spindepth problems. So the existence of the above step could not yet be checked by this method (Fig. 6). In all samples, however, both in cis and in trans (thermally converted before doping), two ESR lines are seen: a broad one with little motional narrowing, Curie-law temperature dependence and long relaxation time; the other narrow, fast relaxing and with temperature-independent intensity (Pauli susceptibility). So we conclude that in doped polyacetylene there is "always" coexistence of itinerant electrons in extended band states and of localized spins. This does not necessarily imply the formation of metallic islands in an otherwise undoped matrix (Tomkiewicz's "Thousand Islands" hypothesis /19/), but it reveals inhomogeneities at least on a microscopic level, e.g. due to chain length distribution and random clusters of the dopant.

If, in spite of the above criticism of indirect proofs of existence, magnetic measurements could satisfactorily corroborate the soliton concept, all evidence would very likely be masked by these inhomogeneities - at least up to the present day this seems to have widely occured.

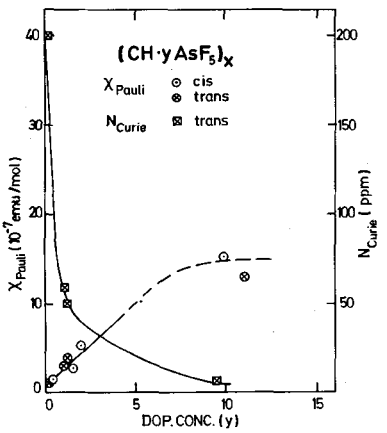

Fig. 6: Coexistence of localized and itinerant spins in polyacetylene

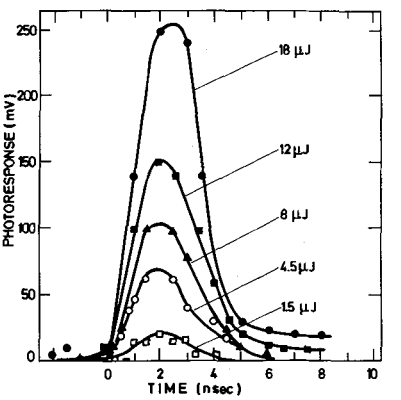

Fig. 7: Nanosecond photoresponse of undoped trans polyacetylene (room temperature)

Optical Behaviour:
Optical investigations are expected to probe very local properties and so they are - perhaps - most helpful in the search for solitons in, alas, imperfect polyacetylene. Usually the midgap absorption /24/ and soliton-induced infrared vibrational modes predicted by Mele and Rice /25/ are considered as signature of solitons. Both features have been observed to occur upon doping /25, 26/. Because it was suspected, however, that immobile chemical defects might lead to similar optical properties as solitons would, attempts have been made to look for optical effects after a presumed photogeneration of solitons. Photogeneration of solitons in polyacetylene has been proposed by Su and Schrieffer /27/ and used by Etemad to explain his finding of photoconductivity in trans but not in cis samples /28/. Kiess et al. /29/ have tried to see the Mele-Rice line during photoconductivity. They failed, however, to observe it, although their light intensity was high enough to produce more photoconductivity than the doping-induced conductivitiy in a parallel experiment, where the line had been seen. We have repeated Kiess' experiment with a pulsed laser using even three orders of magnitude more intensity and still did not see any Mele-Rice line !

Therefore we decided to do a time-resolved photoconductivity measurement to get an estimate of the lifetime of photogenerated solitons. Fig. 7 shows the response of undoped trans polyacetylene to laser pulses of about 2 nsec (nitrogen pumped dye laser, $h\nu \sim 2$ eV)/30/. As is clearly seen, there is no photoresponse longer than the 2 nsec laser pulse (except for a heating tail at high intensities). From the pulse height and the electrode separation the migration distance of the photogenerated carriers (Schubweg) can be obtained. Assuming unity (!) quantum efficiency we thus obtain $\mu\tau \sim 8 \times 10^{-14}$ cm/V. If the mobility μ is guessed to be 1 cm^2/Vsec (from conductivity and doping concentration /31/), we would get $\tau \sim 8 \times 10^{-14}$ sec !

This value for τ is extremely short, but it is not at all unreasonable. The laser pulse will preliminarily excite electrons and holes. These should relax into solitons and antisolitons within the time of a lattice vibration, i.e. 10^{-13} sec. Most of the electrons and holes could recombine immediately, before they have a chance to get separated by the field and before they relax into solitons. A few, however, do escape (τ is an average value), they will migrate to chain ends or other traps, where they certainly will arrive within a nanosecond (before the laser pulse is over). Part of this migration the charge carriers might carry out in the form of solitons, but it will be very difficult to "prove" this. From the time on when the charge carriers sit on chain ends there is no more need to call them solitons: they are just trapped charges. They will get slowly released from their traps and in constant trap-and-release cycles give rise to long-time photoconductivity as measured by Etemad et al. /32/. The gap state is certainly not sensitive to whether charge carriers migrate as solitons or whether they sit as electrons on chain ends. Therefore the electron-energy-loss experiment of Salaneck /33/ and the absorption measurements of Orenstein and Baker /34/ do not really reveal the existence of solitons even though the carriers have been photogenerated. The bleaching experiment of Vardeny et al. /35/ does not indicate soliton motion in the sense used here either: it just tells that dipoles diffuse. Therefore it is safe to state that the optical evidence for solitons in polyacetylene is not yet overhelming.

Discussion:
During the discussion at the end of the oral presentation of this report A. Heeger drew the attention of the audience to a poster of Vardeny et al. /36/, where the Mele-Rice line is found in a photoconductivity experiment (the effect saturates easily so that the intense light in Zürich and especially in Stuttgart did not facilitate observation). When I was willing to admit this important experimental result as strong evidence for the existence of solitons, B. Horovitz pointed out, that the Mele-Rice line is not specific for solitons: any charge on the chain will induce the line, including charges trapped on chain ends.

Conclusion:
Incorporating all the discussions in Les Arcs in which I have been involved, mentioning Popper's /37/ caveat, that a theory can never be proved but only disproved, and leaving open the possible usefulness of finite-polyene soliton-algorithms in future bio-computers /38/, I still can terminate this report with the statement that there seems to be a profound difference between butterflies and solitons: both are very likely to exist (tertium comparationis), but butterflies do not only exist, they also have been observed in a rather direct way (differenta specifica).

Acknowledgement:
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References

/1/ see e.g.
CAMPBELL D.K., and BISHOP A.R., Phys.Rev.B 24 (1981) 4859
BISHOP A.R., CAMPELL D.K., and FESSER K., Mol.Cryst.Liq.Cryst. 77 (181) 253
and KIVELSON S., these proceedings

/2/ SU W.P., SCHRIEFFER J.R., and HEEGER A.J., Phys.Rev.Lett. 42 (1979) 1698

/3/ RICE M.J., Phys.Lett. A 71 (1979) 152

/4/ POPLE J.A., and WAMSLEY S.H., Mol.Phys. 5 (1962) 15

/5/ IKEHATA S., KAUFER J., WOERNER T., PRON A., DRUY M.A., SIVAK A., HEEGER A.J., and MAC DIARMID A.G., Phys.Rev.Lett. 45 (1980) 1123
for a review see e.g.
ETEMAD S., HEEGER A.J., and MAC DIARMID A.G.,
"Polyacetylene, $(CH)_x$: The Prototype of Conducting Polymers",
to be published as volume 33 of "Annual Reviews of Physical Chemistry"
CAMPBELL D.K., BISHOP A.R., and FEESER K.,
Phys.Rev. B 26 (1982) 6826
BRAZOVSKII S.A., Zh.Eksp.Teor.Fiz.Pis'ma Red. 28 (1978) 659
JETP Lett. 28 (1978) 606 ;
Zh.Eksp.Teor.Fiz. 78, (1980) 677
Sov.Phys.-JEPT 51 (1980) 342
TAKAYAMA H., LIN-LIU Y.R., and MAKI K.,
Phys.Rev. B 21 (1980) 2388
HOROVITZ B., Phys.Rev.Lett. 46 (1981) 742
Phys.Rev. B 22 (1980) 1101

/6/ SU W.P., SCHRIEFFER J.R., Phys.Rev.Lett. 46, (1981) 738
BAK P., Phys.Rev.Lett. 48 (1982) 692
SCHRIEFFER J.R., Mol.Cryst.Liq.Cryst. 77 (1981) 209
RICE M.J., and MELE E.J., Mol.Cryst.Liq.Cryst. 77 (1981) 223

/7/ MOODY E.A., "The logic of William of Ockham", Russel & Russel, New York, 1965

/8/ BRASSENS G., "La chasse aux papillons"
in "La Mauvaise Réputation", Philips 9101 043 (record)

/9/ PLATO: "Timaeus", Athens, ca. 350 B.C.

/10/ KIVELSON S.: Phys.Rev.Lett. 46 (1981) 1344

/11/ EPSTEIN A.J., ROMMELMANN H., ABKOWITZ M., and GIBSON H.W.,
Mol.Cryst.Liqu.Cryst. 77 (1982) 81 see also
MOSES D., CHEN J., DENENSTEIN A., KAVEH M., CHUNG T.C., HEEGER, MAC DIARMID A.G., and PARK Y.W., Solid State Commun. 40, (1981) 1007

/12/ CHROBOCZEK J.A., and SUMMERFIELD S.: these proceedings
and SUMMERFIELD S., CHROBOCZEK J.A., and ROTH S.: to be published

/13/ CHROBOCZEK J.A.,and SUMMERFIELD S.: Ref. 12

/14/ ABELES B., Appl.Sol.State Sci. 6, (1976) 1
SHENG P., Phys.Rev.B 21 (1980) 2180
SHENG P., SICHEL E.K., GITTLEMAN J.I., Phys.Rev.Lett. 40 (1978) 1197
TOMKIEWICZ Y., SCHULTZ T.D., BROM H.B., CLARKE T.C., and STREET G.B.:
Phys.Rev.Lett. 43 (1979) 1532
TOMKIEWICZ Y., SCHULTZ T.D., BROM H.B., TARANTO A.R., CLARKE T.C., and STREET G.B., Phys.Rev. B 24 (1981) 4338

/15/ see e.g.
WEINBERGER B.R., EHRENFREUND E., PRON A., HEEGER A.J., and MAC DIARMID A.G., J.Chem.Phys. 72 (1980) 4749 and
NECHTSCHEIN M., DEVREUX F., GREENE R.L., CLARKE T.C., and STREET G.B., Phys.Rev.Lett. 44 (1980) 356

/16/ WEINBERGER B.R., KAUFER J., HEEGER A.J., PRON A., and MAC DIARMID A.G., Phys.Rev. B 20 (1979) 223
and IKEHATA et al., Ref. 5
and DAVIDOV et al., Ref. 23

/17/ PEO M., and ROTH S., Verhandl. DPG (VI) 15 (1980) 168
and Europhys.Conf.Abstr. 3G (1980) 315
ROTH S., and PEO M., Colloid & Polymer Sci 259 (1981) 279
ROTH S., and PEO M., Spring Meeting of the Electrochemical Society, St.Louis, May 1980 (post deadline paper)

PEO M., ROTH S., DRANSFELD K., TIEKE B., HOCKER J., GROSS H., GRUPP A., and SIXL H., Solid State Commun. 35 (1980) 119
PEO M., ROTH S., and HOCKER J., Chemica Scripta 17 (1981) 133
/18/ IKEHATA et al., Ref. 5
EPSTEIN A.J., ROMMELMANN H., DRUY M.A., HEEGER A.J., and MAC DIARMID A.G., Solid State Commun. 38 (1981) 683
/19/ TOMKIEWICZ et al., Ref. 14
/20/ PEO M., FÖRSTER H., MENKE K., HOCKER J., GARDNER J.A., ROTH S., and DRANSFELD K., Solid State Commun. 38 (1981) 467
/21/ CLARKE T.C., and SCOTT J.C., Solid State Commun. 41 (1982) 389
/22/ YACOBY Y., PEO M., and ROTH S., to be published
/23/ DAVIDOV D., ROTH S., and NEUMANN W., to be published in Z.Physik and these proceedings
/24/ e.g. SUZUKI N., OZAKI M., ETEMAD S., HEEGER A.J., and MAC DIARMID A.G., Phys.Rev.Lett. 45 (1980) 1209;
ERRATUM Phys.Rev.Lett. 45 (1980) 1463 and
FELDBLUM A., KAUFMANN J., ETEMAD S., HEEGER A.J., CHUNG T.-C., and MAC DIARMID A.G., Phys.Rev. B 26 (1982) 815
/25/ MELE E.J., and RICE M.J., Phys.Rev.Lett. 45 (1980) 926
/26/ ETEMAD S., PRON A., HEEGER A.J., and MAC DIARMID A.G., Phys.Rev. B 23 (1981) 5137 and
TANAKA J., TANAKA M., FUJIMOTO H., SATO N., and INOKUTI H., these proceedings
/27/ SU, W.P., and SCHRIEFFER J.R., Proc.Nat.Acad.of Sci. 77 (1980) 5626
/28/ ETEMAD S., OZAKI M., HEEGER A.J., and MAC DIARMID A.G., Proc.Int.Conf. on Low Dimensional Synthetic Metals, Helsingor, Denmark, August 1980
Chemica Scripta 17 (1981) 159
ETEMAD S., MITANI M., OZAKI M., CHUNG T.-C., HEEGER A.J., and MAC DIARMID A.G., Solid State Commun. 40 (1981) 75
LAUCHLAN L., ETEMAD S., CHUNG T.-C., HEEGER A.J., and MAC DIARMID A.G., Phys.Rev. B 24 (1981) 3701
/29/ KIESS H., BAERISWYL D., and HARBEKE G., Bull.Am.Phys.Soc. 27 (1982) 240 and Verhandl. DPG (VI) 17 (1982) 734
and KIESS H., KELLER R., BAERISWYL D., and HARBEKE G., Solid State Commun. 44 (1982) 1443
/30/ YACOBY Y., ROTH S., MENKE K., KEILMANN F., and KUHL J., to be published
/31/ CHIANG C.K., FINCHER C.R., PARK Y.W., HEEGER A.J., SHIRAKAWA H., LOUIS E.J., GAU S.C., and MAC DIARMID A.G., Phys.Rev.Lett. 39 (1977) 1098
At 4.2 K an "effective mobility" of polyacetylene has been determined to be as high as some 100 $cm^2/Vsec$;
RÖSS W., PHILIPP A., SEEGER K., EHINGER K., MENKE K., and ROTH S., submitted to Solid State Commun. and
EHINGER K., BAUHOFER W., MENKE K., and ROTH S., these proceedings
/32/ ETEMAD S., MITANI M. et al., Ref. 28
/33/ SALANECK W.R., GIBSON H.W., PLUMMER E.W., and TONNER B.H., Phys.Rev.Lett. 49 (1982) 801
/34/ ORENSTEIN J., and BAKER G.L., Phys.Rev.Lett. 49 (1982) 1034
SHANK C.V., YEN R., FORK R.L., ORENSTEIN J., and BAKER G.L., Phys.Rev.Lett. 49 (1982) 1660 and these proceedings
/35/ VARDENY Z., STRAIT J., MOSES D., CHUNG T.-C., and HEEGER A.J., Phys.Rev.Lett 49 (1982) 1657 and these proceedings
/36/ VARDENY Z., ORENSTEIN J., and BAKER G.L., these proceedings
/37/ WELLMER A., "Methodologie als Erkenntnistheorie. Zur Wissenschaftslehre K.R. Poppers". Suhrkamp, Frankfurt/Main 1967
/38/ CARTER L.F., Naval Research Laboratory, Washington DC, NRL Memorandum Report 3940 (1979) 121; 4335 (1980) 35; 4717 (1982) and lecture at NATO-ARI, spring 1982