ABSTRACT SUBMITTED
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<u>Self-Consistent Crystal Potential and Band Structure of</u>
<u>3D trans-$(CH)_x$.</u> **P.M. GRANT and I.P. BATRA,** <u>IBM</u> Research
<u>Lab.</u>--We have made the first calculation of the crystal potential,
charge density and band structure of 3D trans-$(CH)_x$. Our compu-
tational technique was the self-consistent pseudopotential method.
With this method, we have been able to partition the total energy
into one-electron, exchange and Madelung contributions and sepa-
rate out interchain interaction terms. From our results, we obtain
estimates of the soliton coupling constant and interchain soliton
isolation. We also determine the interchain transfer integrals and
the electronic anisotropy of ideally crystalline trans-$(CH)_x$.

(X) Prefer Standard Session

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persed ions in sites with low frequency vibrational modes.

11:00

DE 11   The Electronic Properties of $\left|CH(FeCl_4)_{.061}\right|_x$.*
Y. W. PARK, J. C. WOO, K. H. YOO, W. K. HAN, C. H. CHOI, Seoul National U., Seoul, Korea, T. KOBAYASHI and H. SHIRAKAWA, U. of Tsukuba, Ibaraki, Japan.--The temperature dependence of dc conductivity, thermopower and electron paramagnetic resonance (EPR) results on $\left|CH(FeCl_4)_{.061}\right|_x$ are reported. The dc conductivity and thermopower measurements indicate metallic charge transport along the polyacetylene chain interrupted by the interfibril contact resistances and also 'dragged' by the dopant ions below 50 K. The initial measurements of EPR show Dysonian lineshape with very broad linewidth ($\Delta H \simeq$ 600G at room temperature). The temperature dependence of EPR absorption intensity implies that there exist localized magnetic moments with antiferromagnetic interaction. The observed g value (g≃2.03) suggests the dopant anion is in a form of $(FeCl_4)^-$.

11:12

DE 12   Electrical Impedance Measurements of Polyacetylene Electrodes in Electrochemical Cells,* S. R. KURTZ, W. H. SMYRL, and D. S. GINLEY, Sandia National Laboratories, Albuquerque, NM 87185.-- We report the results of small signal impedance measurements for electrochemically doped polyacetylene electrodes. This experiment is performed concurrently with coulometry measurements that monitor the concentration of the dopant species. At high dopant concentrations, the open circuit cell voltage versus charge curve displays hysteresis. Simultaneously, hysteresis is observed in the charge transfer portion of the electrode impedance. This observation suggests other processes, in addition to diffusion, determine the reversibility of electrochemical doping of polyacetylene.

11:24

DE 13   Frequency Dependence of the Conductivity and Dielectric Constant of $CH(IrCl_6)_y$ and $CH(I)_y$.   J. I. GITTLEMAN and S. BOZOWSKI, RCA Labs, and E. K. SICHEL, GTE Labs -- We have measured the ac properties of polyacetylene doped with $H_2IrCl_6 \cdot 6H_2O$ and I_2 from 10^5 to 10^7 Hz at room temperature. We find in both cases that the conductivity is only weakly dependent on frequency, in agreement with previous work[1,2]. However, we find that the dielectric constant of $CH(IrCl_6)_y$ is anomalously large, $\sim 10^4$. We suggest that the large dielectric constant can be modeled by an effective medium theory assuming that the $CH(IrCl_6)_y$ is a mixture of conducting and insulating regions. TEM evidence in support of the model will be presented. The results for $CH(IrCl_6)_y$ will be contrasted with $CH(I)_y$ where TEM evidence shows a uniform distribution of dopant in the polyacetylene and the dielectric constant is significantly lower.

[1] P.M. Grant and M. Krounbi, Sol. Stat. Comm. 36, 291 (1980).
[2] A.J. Epstein, H.W. Gibson, P.M. Chaikin, W.G. Clark, and G. Grüner, Chemica Scripta 17, 135 (1981).

11:36

DE 14   Isomerization Kinetics in $(CH)_x$*, E.A. Imhoff and D.B. Fitchen, Cornell U., Ithaca, N.Y. The kinetics of isomerization of polyacetylene films have been inves-
tigated using sequences of Raman spectra excited at different laser wavelengths. These selectively enhanced spectra reveal distinctly different time development for different trans features. The most complete studies were made at 102 and 130°C, with excitation at 457.9 and 670.9 nm. The blue spectra are less affected by complicating changes in the optical constants of the sample during isomerization. Disappearance of the cis features proceeds with at least two thermally-activated rate constants; the slower is $\sim 10^{13}$ s^{-1} exp(-1.32eV/kT) The appearance of the sharp trans peaks (at 1066 and 1454 cm^{-1}) is governed by this one slow rate. Other components of the broad trans bands accompanying these peaks grow with a range of rates, including some much faster than this slow rate. The spectra recorded with red excitation show interesting but more complicated behavior. These results are compared with those of other techniques and with models of non-uniform isomerization.

11:48

DE 15   Bond Length Determination in Polyacetylene T. C. CLARKE, R. D. KENDRICK, and C. S. YANNONI, IBM San Jose. Using nutation NMR spectroscopy we have been able to determine directly the carbon-carbon bond lengths in polyacetylene. For trans-polyacetylene we find double and single bond lengths of 1.36 and 1.44 Å respectively; the double bond in cis-polyacetylene is found to be 1.38 Å. These experiments also provide new insights into the mechanisms of polymerization and cis-trans isomerization in polyacetylene. Thus, we find that the two carbons of a given acetylene monomer unit end up doubly bonded to one another in the resulting cis-polymer. However, on isomerization the bonding sequence is scrambled to give an essentially equal probability that these two carbons will be separated by a single or a double bond. Interestingly, at 77°K we do not observe a rapid interchange of the single and double bonds in trans-polyacetylene in the manner predicted for chains containing a soliton defect, suggesting that the majority of the carbons in the trans isomer are on conjugated segments which do not contain such mobile species.

12:00

DE 16   Tetrahedral Cross-Links in Polyacetylene. C. T. WHITE and M. L. ELERT, Naval Research Laboratory and PATRICK BRANT, Exxon Chemical Company.--We propose that tetrahedral cross-links are formed during the cis to trans conversion of polyacetylene. Results of cluster calculations at the semi-empirical Hartree-Fock level, including limited configuration interaction, demonstrate the stability of such defects. The many-body part of the calculation shows that concomitant with the cross-link formation a neutral soliton-like defect is generated on each chain participating in the cross-link. These defects can be subsequently quenched by π-bond formation or additional cross-link formation. Our results are consistent with the observed burst of spins accompanying cis to trans conversion as well as the increased embrittlement of the sample with isom-erization.

12:12

DE 17   Self-Consistent Crystal Potential and Band Structure of 3D trans-$(CH)_x$. P.M. GRANT and I.P. BATRA, IBM Research Lab.--We have made the first calculation of the crystal potential, charge density and band structure of 3D trans-$(CH)_x$. Our computational technique was the self-consistent pseudopotential method. With this method, we have been able to partition the total energy into one-electron, exchange and Madelung contributions and separate out interchain interaction terms. From our results, we obtain estimates of the soliton coupling constant and interchain soliton isolation. We also determine the interchain transfer integrals and the electronic anisotropy of ideally crystalline trans-$(CH)_x$.

BAND STRUCTURE OF 3D trans-$(CH)_x$

OBJECTIVES:

- PREDICT SINGLE PARTICLE 3D PROPERTIES OF IDEALLY CRYSTALLINE trans-$(CH)_x$

- STUDY IMPLICATIONS FOR SOLITON PHYSICS

- GENERATE NUMERICAL DATA BASE FOR CALCULATION OF OTHER PHYSICAL PROPERTIES

COMPUTATIONAL DETAILS

- SELF - CONSISTENT PSEUDOPOTENTIAL

- LOCAL EXCHANGE

- BASIS SET:
    - 367 PW'S AT Γ (163 eV)
    - 125 PW'S LOWDIN (204 eV)

- SELF - CONSISTENCY:
    - 16 k - POINTS IN BZ
    - CONVERGENCE:

        10^{-4} eV MEAN SQUARE

        10^{-1} eV MAXIMUM DIFFERENCE

- TOTAL ENERGY: - 658.46 eV

    (- 646.54 eV ATOMIC)

- BASIS SET CONVERGENCE:
    - 420 PW'S LOWDIN (272 eV)
    - TOTAL ENERGY - 668.17 eV

trans − (CH)$_x$

Charge Distribution within Unit Cell
a − direction
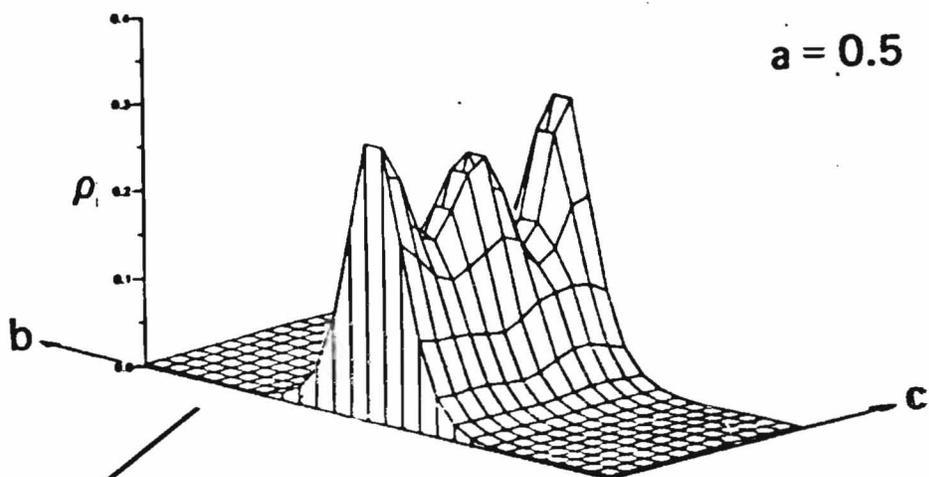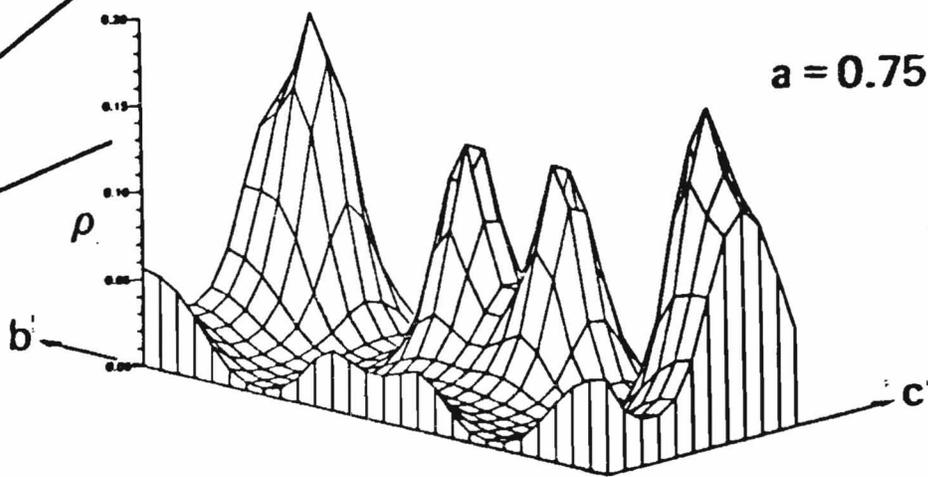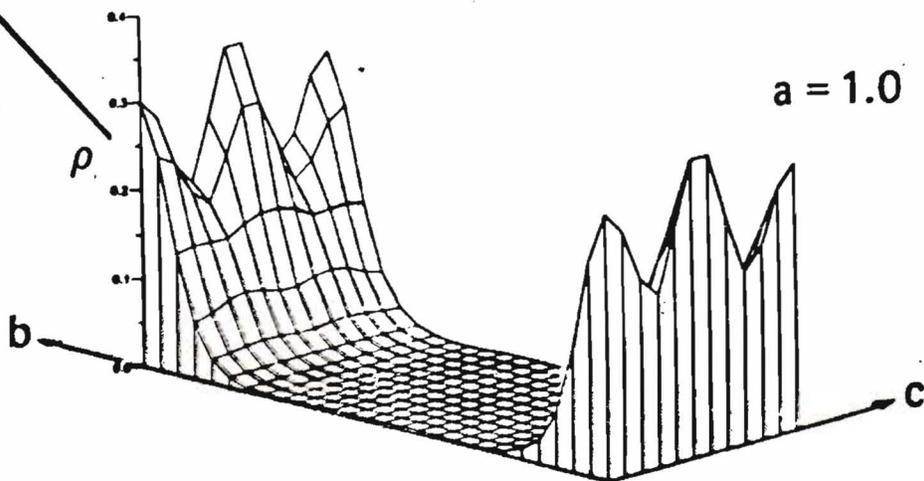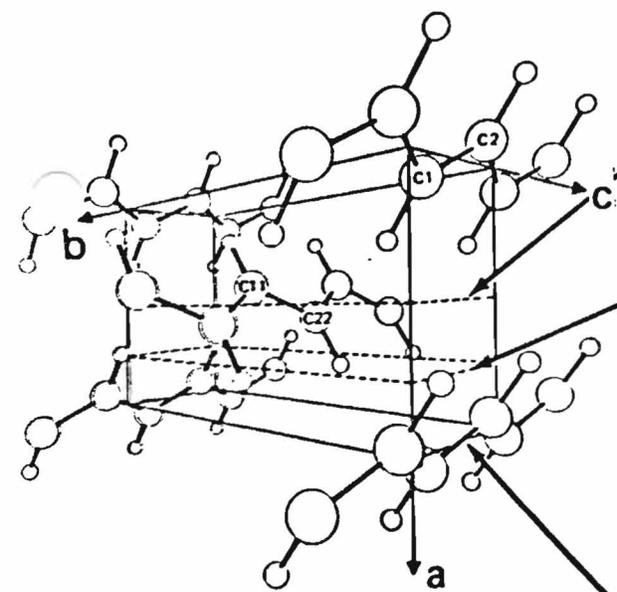
trans - (CH)x

Charge Distribution within Unit Cell

c-direction
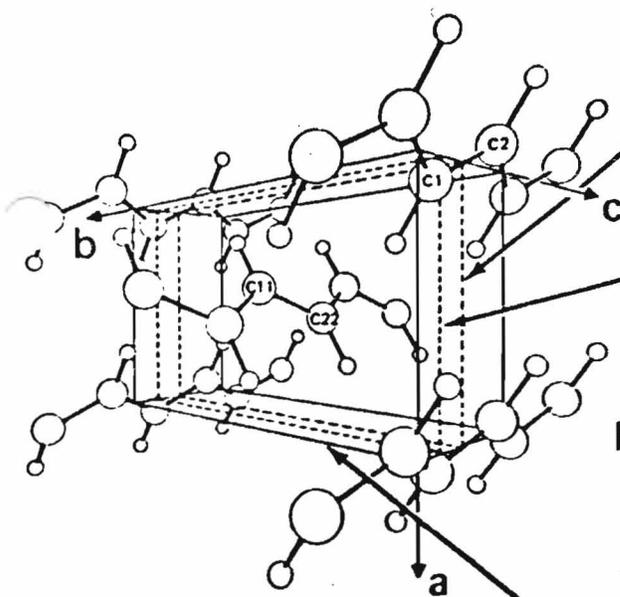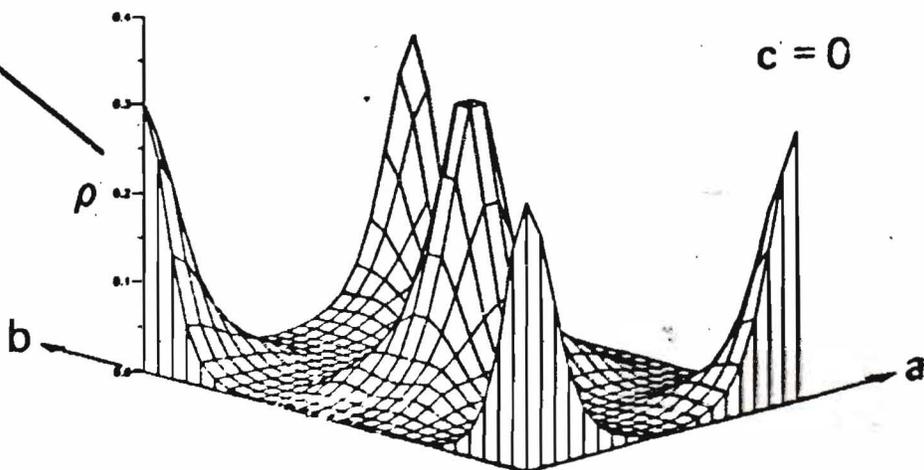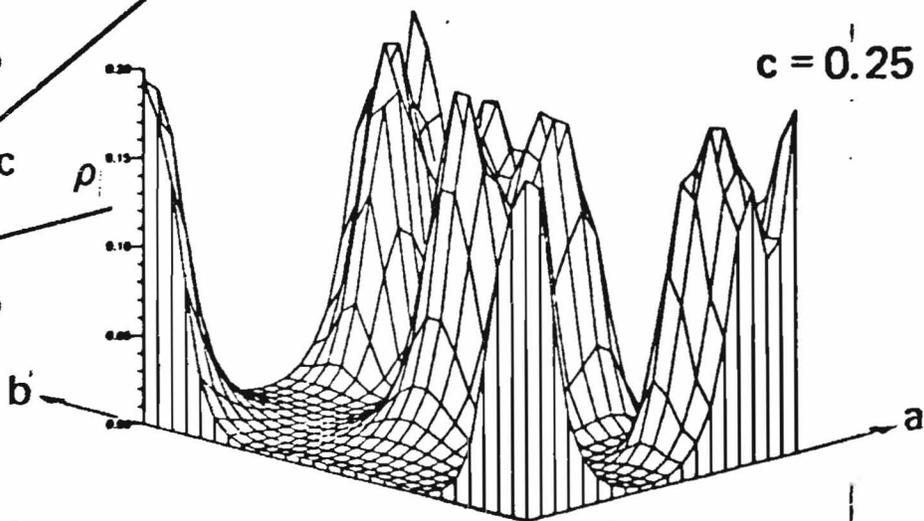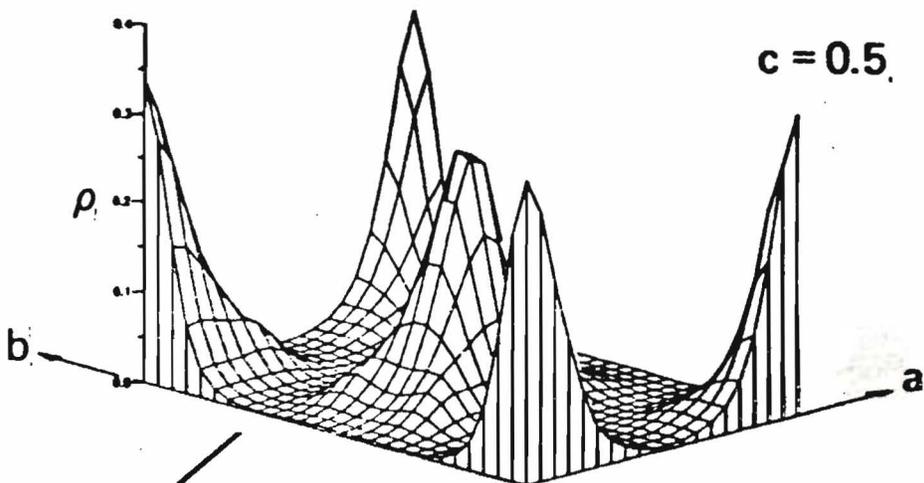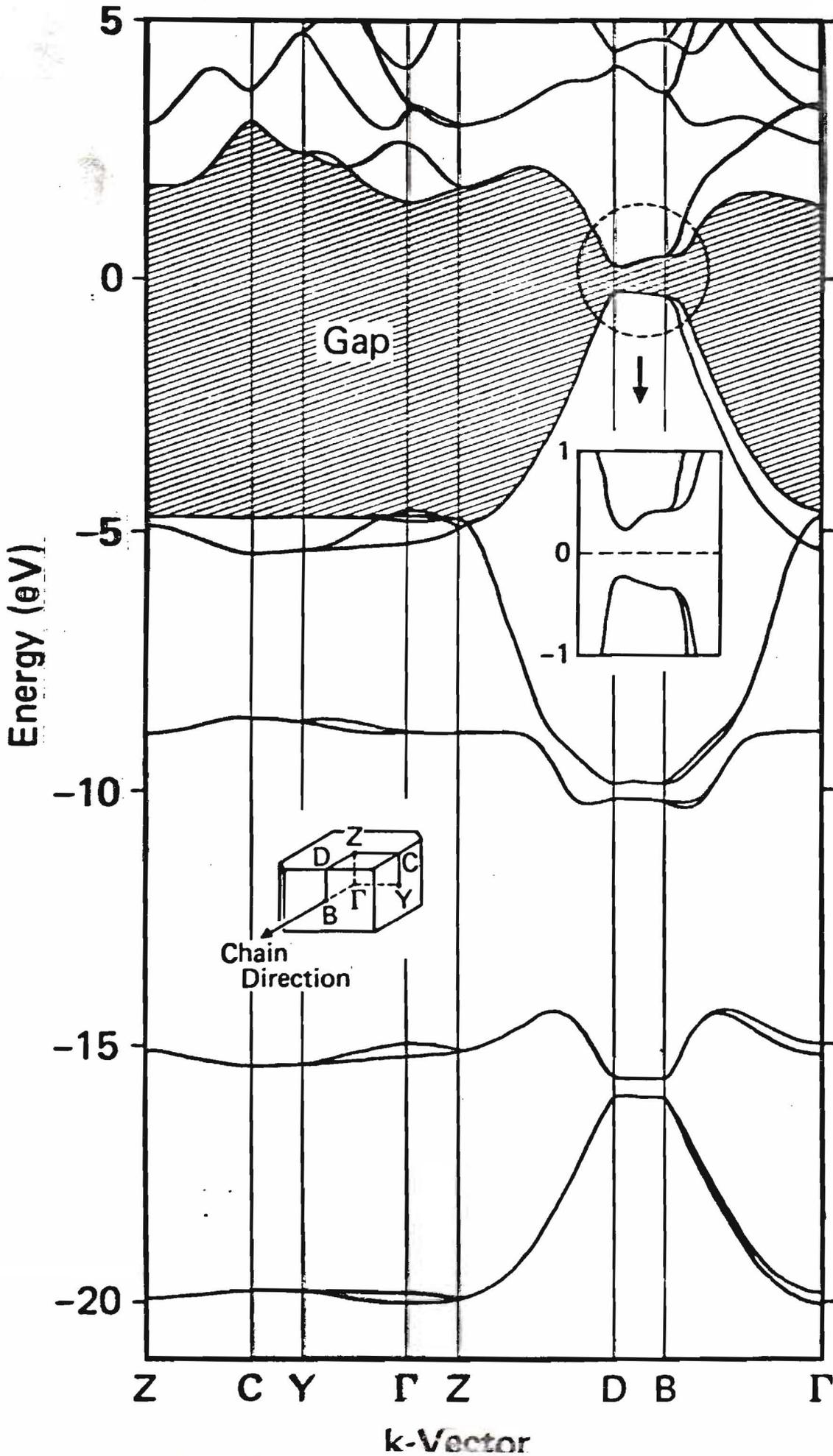
trans-$(CH)_x$

$E_G = 0.5\,eV$

$t_\perp = 25\,meV$

CONCLUSIONS

- ANISOTROPY IN trans - $(CH)_x$

  - 50 - 100 $(t_\parallel / t_\perp)$

  - GREATER THAN CHARGE TRANSFER SALTS: 10-20 IN $(TMTCF)_2 X$

  - $t_\perp$ OF ORDER SIMILAR TO /2:1 CT SALTS

- SOLITON WALL FORMATION

  - BRAZOVSKII, GORKOV, SCHRIEFFER CRITERION:

    $$t_\perp \geq 2\Delta/\pi c \quad (\sim 450 \text{ meV})$$

  - SOLITON WALLS UNLIKELY IN CRYSTALLINE trans - $(CH)_x$

FUTURE

- CALCULATE OPTICAL PROPERTIES
$$\epsilon(\omega), \quad \text{Im}\,\epsilon^{-1}(\omega), \quad D(E, \omega)$$

- LATTICE DYNAMICS

- SUGGESTIONS ?