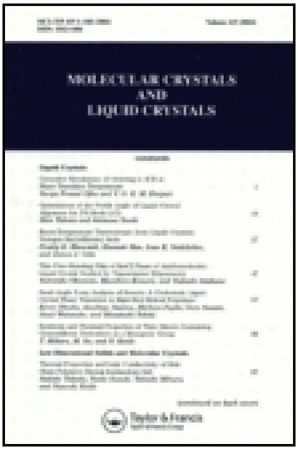

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Abstracts of Other Papers Presented at the Conference

To cite this article: (1982): Abstracts of Other Papers Presented at the Conference, Molecular Crystals and Liquid Crystals, 86:1, 215-331

To link to this article: http://dx.doi.org/10.1080/00268948208073687

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 215
0026-8941/82/8601-0215$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Chemical Properties of Polyacetylenes. H. SHIRAKAWA, Institute of Materials Science, University of Tsukuba, I. HARADA, Department of Pharmaceutical, Tohoku University, Y. FURUKAWA, M. TASUMI, Department of Chemistry, University of Tokyo, and S. IKEDA, Nagaoka Technical College.--IR and Raman Spectroscopy have been used in the investigation of change in chemical properties of polyacetylenes by acceptor and donor doping. Acceptor doping of cis- and trans-polyacetylene creates positively charged part in the polyene chain and uncharged part but being perturbed due to interruption by the charged part. At the initial stage of doping, ungerade C=C stretching vibration appears strongly in IR spectrum with additional two ungerade skeletal modes. The frequency (1397 CM^{-1}) is lower than that of infinitely long polyene system (1460 CM^{-1}) because of lower electron density of this part. Donor doping gives negatively charged part and uncharged part. The IR active ungerade mode appears in higher frequency region (1590 CM^{-1}) which indicates the negatively charged part being high electron density. The IR data will be compared with Raman data which give information on the charged and uncharged parts along polyene chain to discuss the electron transfer reaction of polyacetylene, beta-carotene, and some poly(substituted acetylene)s.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 217
0026-8941/82/8601-0217$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Isomerization Mechanisms from Cis to Trans Form in Polyacetylene. T. YAMABE, K. AKAGI, K. OHZEKI, K. FUKUI, Kyoto Univ., and H. SHIRAKAWA, Tsukuba Univ. --Mechanisms of cis-trans irreversible isomerizations occurring in both thermal treatment and doping to polyacetylene are presented and examined by means of MINDO/3 molecular orbital calculations on some finite polyenes. It is predicted that the thermal isomerization proceeds along the internal rotation of (-CH=CH-) unit around two carbon-carbon double bonds via the transition state having a biradical nature. Meanwhile, the isomerization by doping is rationalized by the mechanism that the cis segment between two doping sites is converted into the trans-cisoid form which rotates easily around two single bonds to yield some trans forms in $(CH)_x$ chain.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 219
0026-8941/82/8601-0219$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Isomerization of Polyacetylene. H.W. GIBSON, S. KAPLAN, A.J. EPSTEIN, H. ROMMELMANN, W.R. SALANECK and J.M. POCHAN, Webster Research Center, Xerox Corporation, Webster, NY 14580--The cis-trans isomerization of polyacetylene has been subjected to coordinated study by infrared spectroscopy, ^{13}C magic angle nuclear magnetic resonance spectroscopy, electron spin resonance spectroscopy, ultraviolet photoelectron spectroscopy, differential scanning colorimetry and conductivity measurements. The results will be discussed in terms of the possible intervention of the trans-cisoid form, sequence lengths, chain lengths and ordered (crystalline) and disordered (amorphous) regions. The importance of thermal history in regard to these parameters and their effects upon electrical properties will be emphasized.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 221
0026-8941/82/8601-0221$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

The Structure of Trans - $(CH)_x$: X-ray Scattering From Oriented Films. C.R. FINCHER JR., C.E. CHEN, A.J. HEEGER and A.G. MACDIARMID, University of Pennsylvania, Philadelphia, PA and J.B. HASTINGS, Brookhaven National Laboratory, Upton, L.I., New York. Results of X-ray scattering studies of oriented films of polyacetylene, $(CH)_x$, will be presented. The data show that the films are of a surprisingly high degree of crystallinity and demonstrate unambigously that the polymer chains are oriented parallel to the fibrils in the aligned polymer. From the observed reflections, the crystal structure is deduced. The space group is $P2_1/c$ with two $(CH)_x$ chains per unit cell. In this space group the $(CH)_x$ chains have a bond-alternating structure; bounds upon the magnitude of the dimerization are set from the observed scattering intensities. Studies of the interchain reflections provide an estimate of an interchain coherence length of only a few lattice constants. Intrachain reflections indicate that the loss of order along the chain is related to the restricted dimensionality of the polymer.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 223
0026-8941/82/8601-0223$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Crystal Structure of Poly(acetylene). FRANK E. KARASZ, JAMES C.W. CHIEN, K. SHIMAMURA and JACOB A. HIRSCH, *UMass*. - The crystal structures of the *trans* and *cis* forms of polyacetylene, $(CH)_x$, and of iodine doped $(CH)_x$, have been studied by selected area electron diffraction. Samples were prepared by *in situ* polymerization (Shirakawa catalyst) on gold electron microscope grids and the diffraction patterns from regions of partially oriented fibrils obtained after drying the nascent polymer were observed. For trans-$(CH)_x$ our results indicate an orthorhombic unit cell containing two monomer units $\mathbf{a}$=7.32 Å, $\mathbf{b}$=4.24 Å and $\mathbf{c}$ (fiber axis)=2.46 Å. Results for the heavily I_2 doped $(CH)_x$ suggest that the iodine, perhaps in trimeric form, intercalates between the $(CH)_x$ chains in an irregular fashion to produce a structure with nematic features.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 225
0026-8941/82/8601-0225$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Oxidation of Polyacetylene. J.M. POCHAN and H.W. GIBSON, Xerox Corporation, Rochester, NY--Oxidation of polyacetylene (PAC) has been monitored via conductivity, infrared and oxygen uptake measurements. It will be shown that the various techniques provide information concerning different aspects of the degradation process. The infrared data indicates that (1) in the absence of UV light, degradation occurs via two distinct first order kinetic processes with a pre-oxidation induction period, (2) in the presence of UV light, no induction period is observed and initial degradation is exponential in character followed by pseudo first order behavior. These data are rationalized in terms of triplet and singlet oxygen and polymer/oxygen energy transfer processes as well as polymer morphology. Kinetic data derived from conductivity measurements provide first order degradation as a function of cis/trans ratio. Activation energies of ~9 Kcal/mole are obtained for cis containing material and 14 Kcal/mole for 100% trans. Two first order rates constant with identical activation energies are observed. A stochastic degradation model is used to describe the two rates. The effects of oxidation on doping behavior as studied via ESR and conductivity will be discussed in light of diffusion models and polymer morphology.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 227
0026-8941/82/8601-0227$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Spectroscopic Studies of AsF_5 Doping of Polyacetylene. J.F. Rabolt, T.C. Clarke and G.B. Street, IBM Research Laboratory, San Jose Fourier Transform infrared measurements have been obtained on lightly doped, intermediately doped and heavily doped polyacetylene. The general features of the IR spectra are very similar for all levels of AsF_5 doping. Specific bands located at 1400, 1180, 900 and 800 cm^{-1} in the lightly doped material are observed to gradually shift to 1385, 1175, 832 and 700 cm^{-1} respectively in heavily doped samples while the position of the medium band at 1295 cm^{-1} does not appear to change. The appearance and intensity of these new IR bands results from a vibronic activation of Raman active modes in the IR due to a coupling of the charge density fluctuation along the polymer backbone(due to charge transfer to the dopant) with skeletal molecular vibrations. Although the shift to lower frequency reflects bond weakening due to electron transfer to the dopant, bond alternation must still exist to some degree in order for this coupling with molecular vibrations to occur.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 229
0026-8941/82/8601-0229$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Thermodynamics and Kinetics of the Reaction Between Arsenic Pentafluoride and Graphite, Polyacetylene and p-Polyphenylene.

A.R. MCGHIE, J. MILLIKEN and J.E. FISCHER, LRSM University of Pennsylvania PA 19104.

--An experiment has been devised in which the simultaneous measurement of heat of reaction,weight gain,and x-ray stage number (for graphite)has been determined isothermally with time as a function of the pressure of the gaseous acceptor arsenic pentafluoride(AsF_5) during reaction with graphite,polyacetylene, and p-polyphenylene.In all cases an initial , rapid,exothermic reaction was observed corresponding to surface adsorption followed by a slower,diffusion-controlled reaction.In graphite,staging is observed above a critical threshold pressure which is dependent on the particle size. Even at the threshold pressure an induction period is observed,followed by a rapid,highly exothermic process after which weight gain increases rapidly with a heat of reaction,$-\Delta H \cong 10$ kcal/mole.Both polyacetylene and p-polyphenylene exhibit much faster diffusion-controlled kinetics but no evidence for distinct staging.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 231
0026-8941/82/8601-0231$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

<u>Swelling of polyacetylene when doped with iodine or sodium</u>. N. MERMILLIOD*, L. ZUPPIROLI* and B. FRANCOIS**. Precise length measurements have been performed on polyacetylene films during their doping by iodine or sodium. The swelling $\Delta V/V$ of the films has been shown to be linear with the iodine concentration x on a large concentration range. A fraction of 1% of iodine per CH unit corresponds to a relative volume increase of 30%. A 1% concentration of sodium corresponds to 1.1% volume increase. The experimental swelling rate for iodine $(\Delta V/xV)_I = 3$ is in perfect agreement with the value that one can calculate from the intercalation model of Baughman et al. During a doping, a compensation and a redoping, the volume of a $(CH)_x$ film increases continuously up to 40% of the initial value. The volume effects of the different dopant species acting on the same film are shown to be cumulative.

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Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 233
0026-8941/82/8601-0233$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

X-Ray Photoelectron Spectroscopic Study of Highly Conductive Bromine-Doped Polyacetylene. I.IKEMOTO, Y.CAO, M.YAMADA, H.KURODA, I.HARADA, Univ. of Tokyo, H.SHIRAKAWA, Univ. Tsukuba, S.IKEDA, Tokyo Inst. Tech.--The bromine-doped polyacetylenes were studied by X-ray photoelectron spectroscopy. The IR, Raman and mass spectra and the electrical conductivity were also measured as a function of bromine content. Below the doping content where the electrical conductivity shows maximum, bromine is found to be more concentrated in the surface region than in the bulk. The C 1s core electron peak is composed of two components with the splitting of about 1.7 eV and their relative intensities varies depending on bromine content. It is likely that a doped polyacetylene consists of metallic domains of high bromine concentration and dopant-free domains. The higher-binding energy component of the C 1s peak is attributed to the positively charged carbon atoms in the metallic domains and the lower-binding energy component is attributed to the carbon atoms in the undoped, low-conducting domains. The amount of charge transfer in the metallic domain is estimated to be about 0.3|e| per carbon atom. A possible reaction mechanism of bromine with polyacetylene is discussed.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 235
0026-8941/82/8601-0235$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Electron Paramagnetic Resonance Saturation Characteristics of Pristine and Doped Poly(acetylene).

JAMES C.W. CHIEN, FRANK E. KARASZ, GARY E. WNEK, JOHN WARAKOMSKI, L. CHARLES DICKINSON, *UMass*. - EPR studies have been made on very slowly doped $(CH)_x$. Using ^{125}I it was possible to prepare samples containing ppm of dopant. The relaxation times of pristine *trans*- and *cis*-$(CH)_x$ have been determined. Exposure to air changes T_1 and T_2 reversibly. For *trans*-$(CHI_y)_x$ from $y=3 \times 10^{-6}$ to 10^{-3}, T_1 first increases then decreases rapidly with increasing y, while T_2 is unaffected. The EPR linewidth is H_1 independent and the neutral soliton concentration [S·] remains constant in this region. In the heavily doped samples, the EPR has Dysonian line shape until it vanishes for $y>2 \times 10^{-2}$. Doping of *cis*$(CH)_x$ with iodine from $y=3.3 \times 10^{-5}$ to 3.9×10^{-4} does not significantly affect the T_1, T_2, linewidth, or its dependence on H_1. For $y>10^{-3}$ the EPR spectra cannot be saturated. The signal vanishes beyond $y>10^{-2}$. The differences between I_2 doped *cis*- and *trans*-$(CH)_x$ is attributable to the much greater mobility of the soliton in the latter. Results on AsF_5 doped materials showed that they are much more inhomogeneous than the I_2 doped substances.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 237
0026-8941/82/8601-0237$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Low Field Proton Spin-Lattice Relaxation in trans-$(CH)_x$. W.G. Clark* and K. Glover*, UCLA, and S. Etemad and M. Maxfield, Univ. of Pennsylvania.--Previous measurements[1] of the proton spin-lattice relaxation rate (T_1^{-1}) as a function of field (H) have shown that highly mobile spins which move diffusively in 1D are present in trans-$(CH)_x$. Of particular interest is the absence of a crossover from 1D to 3D for spin diffusion over the time scale studied which would appear as a more rapid long time decay in the electron correlation function and a field independence to T_1^{-1}. In this paper we report measurements in which the time scale is extended by a factor of 300 using a field cycling technique to measure T_1^{-1} over the range $\sim 7G<H<3.5kG$ between 4.2K and 230K. In all cases $T_1^{-1} \propto H^{-\beta}$ over the entire field range, with β varying slowly from 0.52±.04 at 230K to 0.80±.04 at 4.2K. These results, which suggest that 1D motion persists to extremely long times in $(CH)_x$, are compared to recent models which describe the dynamic properties of solitons.

*Supported by NSF Grant DMR81-03085.

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Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 239
0026-8941/82/8601-0239$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Field Effect Properties of Polyacetylene.*

P.M. GRANT, M. KROUNBI and T.C. CLARKE, IBM San Jose.

--In order to assess the potential of polyacetylene as an active device material, we have measured the C-V characteristics of trans-$(CH)_x$ in the MIS (Metal-Insulator-Semiconductor) capacitor configuration. Our samples were made by growing polyacetylene films on degenerately doped silicon substrates covered by 1000Å of thermally formed SiO_2. The trans-isomerized $(CH)_x$ was then moderately doped. In the resulting MIS package, the degenerate silicon functioned as the metal component, the SiO_2 as the intervening insulator, and the doped $(CH)_x$ as the semidonductor. The results of the C-V measurements are analyzed to determine the carrier concentration and mobility as a function of doping agent, and models of active device performance presented based on these parameters.

*Supported in part by the ONR.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 241
0026-8941/82/8601-0241$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

3-d Variable-Range-Hopping in $(CHI_y)_x$

M. AUDENAERT+, G. GUSMAN, R. DELTOUR, Service de Physique des Solides, CP233, U.L.B., Belgium.--

The temperature dependent electrical conductivity of iodine doped polyacetylene films $(CHI_y)_x$ was measured. Only samples doped at a concentration $y>0.01$ were studied, i.e. in the concentration range where this material is assumed to be metallic.(1) Anyway, a $T^{-1/4}$ temperature dependance of $\ln\sigma$ was deduced from a computer treatment of the experimental data, even though the conductivity of certain samples was altered by the existence of potential barriers. Our data are completely fitted by a model taking account of these potential barriers. This model is supported by an even good fit when applied to temperature dependent thermoelectric power data on iodine doped polyacetylene. The temperature dependance characteristic of a 3-d variable-range-hopping mechanism of conduction suggests that this material behaves like a threedimensional disordered semiconductor.

+ presently supported by IRSIA

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Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 243
0026-8941/82/8601-0243$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Anisotropy in the Thermal Transport of Polyacetylene. P.R. NEWMAN, M.D. EWBANK and C.D. MAUTHE, Rockwell International Science Center, M.R. WINKLE and W. SMOLNCKI, Rohm and Haas Company Research Laboratories, Several recent experimental efforts[1,2] have focused on the measurement of the thermal conductivity of the electrically conducting polymer polyacetylene or (CH)x. These measurements were both made with the heat flow direction parallel to the plane of the as-polymerized material. Typical reported room temperature values[1,2] for the thermal conductivity range between 50 and 100mW/cm-K. We have measured the thermal conductivity in a similar configuration and have found similar results. However, we have also made the measurement with the heat flow normal to the plane of the film and have found dramatically different behavior. The room temperature value for this geometry is approximately 3mW/cm-K. In addition, we have observed similar anisotropic effects in the electrical resistivity, which confirms some earlier observations by some workers at UCLA.[3]

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3. Dr. George Gruner, Dept. of Physics, UCLA (private communication).

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 245
0026-8941/82/8601-0245$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Ion Implantation Applied to Conducting Polymers

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Naval Research Laboratory, Washington, DC 20375

The use of ion implantation to modify the electrical properties of the classical semiconductors is well known. We have extended the use of this technique to covalent polymeric systems; e.g. the organic semiconductor, polyacetylene, $(CH)_x$ and the semi-metal, graphite C_x. Conductivity increases have been observed in these systems. Discussion will center on the spectroscopic studies (ESR, NMR, IR, and XPS) performed after implantation to understand the nature of the polymer-dopant interaction. We believe our results demonstrate the potential use of ion implantation in conducting polymeric systems.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 247
0026-8941/82/8601-0247$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Collective Fields in Polyacetylene: Functional Integral Formalism.* J.S. ZMUIDZINAS, JPL, Caltech and Univ. of So. Calif., and S.E. TRULLINGER and R.J. McCRAW, Univ. of So. Calif. The dynamics of electrons and ions in polyacetylene at zero temperature is investigated by functional integral techniques applied to the Su-Schrieffer-Heeger Hamiltonian.[1] A nearly half-filled electron band is assumed and the exact band structure is used without resorting to the Luttinger approximation. A set of sixteen collective quantum fields is introduced to describe various charge-and spin-density excitations in the system. Electrons and phonons with $k \approx \pm 2k_F$ are integrated out exactly, leading to an effective action for acoustic phonons and collective fields. Implications of this effective action for the physics of linear and nonlinear excitations are discussed. A program of explicit calculation is outlined.

*Research supported by NASA Contract NAS7-100 with JPL, by Caltech President's Fund Grant No. PF-142, and by NSF Grant No. DMR-7908920.

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Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 249
0026-8941/82/8601-0249$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Ab Initio Interpretation of XPS Data - A parallel between the Acenes and Paraphenylenes Series.

J.P. BOUTIQUE, J.J. PIREAUX, J. RIGA, J.J. VERBIST, J.G. FRIPIAT, J. DELHALLE, J.M. ANDRE, Fac. Univ. de Namur, Belgium.

- The lowest acenes and paraphenylenes are the framework of numerous charge-transfer complexes such as aromatic disulfides and their salts. Continuing our research in the field, we would like to stress on the essential characteristics of their electronic structure. The ab initio STO-3G calculations are performed on the first terms in each series, namely naphthalene, anthracene, tetracene, biphenyl, p -terphenyl and p-quaterphenyl, and compared with XPS data. The simulation of the valence bands of naphthalene and biphenyl simplifies the interpretation of XPS spectra, and tests the reliability of the theoretical method. The dominant features of the electronic structure and their evolution are defined and studied in parallel in the two series : the Mulliken populations reflect the degree of delocalization through the molecule and the π levels energies determine important molecular ground state properties.

$(TMTSF)_2X$

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 253
0026-8941/82/8601-0253$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Theory of the Phase Transitions in the (TMTSF)$_2$X Series.

S. BARISIC[1,2] V.J. EMERY,[1,3] S.A. BRAZOVSKII,[4] R. BRUINSMA[3]. 1. Laboratoire de Physique des Solides, Batiment 510, Universite de Paris Sud, 91405, Orsay, France. 2. Institute of Physics of the University, 41001 Zagreb, Croatia, Yugoslavia. 3. Brookhaven Natl. Lab, Upton, N.Y., 11973. 4. L.D. Landau Institute for Theoretical Physics, Moscow, USSR.

- The behavior of the (TMTSF)$_x$X series is analysed within existing theories of quasi-one-dimensional materials. Experiments require that the short- and long-ranged interactions (g_1 and g_2) satisfy $g_1 > 0$ and $2g_2 - g_1 < 0$. A small variation of the bare interactions with pressure changes umklapp scattering (g_3) from a relevant coupling (for $2g_2g_1 > -|g_3|$) to an irrelevant coupling (for $2g_2 - g_1 < -g_3$) and causes a crossover from spin-density-wave (SDW) and $4k_F$ charge-density-wave order to superconducting order. According to the theory, there is no $2k_F$ charge-density response at low temperatures, the SDW transition temperature varies with pressure as $\exp(-A/(P_c - P)^{1/2})$, and P_c increases with the dimerization of the organic stacks-all in qualitative agreement with experiment.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 255
0026-8941/82/8601-0255$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Observation of Antiferromagnetic Resonance (Spin Waves) in $TMTSF_2\ AsF_6$. J.B. TORRANCE and H.J. PEDERSEN, Technical University of Denmark and K. BECHGAARD, H.C. Oersted Institute - The static magnetic susceptibility χ_s of powdered samples of $TMTSF_2PF_6$ remains large below its metal-insulator transition. In contrast, the intensity of the a.c. susceptibility near $g \sim 2.0$ (EPR) rapidly disappears, presumably being shifted far away from $g \sim 2.0$. Recent measurements by Mortensen et al. on single crystals of both the PF_6 and AsF_6 compounds have revealed an anisotropy in χ_s and a spin flop transition. All these features are characteristic of a simple antiferromagnetic insulator. We report here preliminary Q-band (35 GHz) absorption measurements on $TMTSF_2\ AsF_6$ in a search for the absorption at fields far away from $g = 2.0$ ($H = 12.5$ kOe). At 4° K some very weak and broad absorption bands have been observed, whose resonance field depends strongly on sample orientation, shifting by almost a factor three. This absorption is identified as antiferromagnetic resonance. These preliminary results suggest that the amplitude of the spin density wave is much stronger than 1%.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 257
0026-8941/82/8601-0257$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Conduction electron spin resonance and spin lattice relaxation time in radical-cations salts.

P. DELHAES, G. KERYER and J. AMIELL, Centre de Recherches Paul Pascal, CNRS, Domaine Universitaire, 33405 Talence (France).

-- The conduction electron spin resonance (CESR) investigations on organic conductors have been developped and analyzed these last years. A fundamental difference emerges from these experiments between the charge transfer complexes on one hand and the ion-radical salts on the other. At the opposite of the two-chain compounds behavior, the last ones which are one conducting chain compounds always present a linewidth which is decreasing with the temperature. A few examples will be given especially about $TMTSeF_2$- ClO_4, the first organic superconductor under atmospheric pressure. It will be shown that the linewidth temperature dependences can be compared with those obtained on naturel metals so far the electronic system is 2 d or 3 d (i.e. when the longitudinal and transverse conductivities are both coherent). In that case a BORELIUS-GRUNEISEN-like relation can be found. At the opposite this relationship breakdowns when the compounds are 1 d metals. The mechanisms which are involved for the spin-lattice relaxation rate will be also investigated starting from the the ELLIOTT's relation which is not obeyed in these low dimensional electronic systems.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 259
0026-8941/82/8601-0259$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Nonlinear Threshold Phenomena Due to Spin-Density-Wave Transitions in Organic Conductors Including $(TMTSF)_2ClO_4$. W.M. WALSH, JR., F. WUDL, L.W. RUPP, JR., E. AHARON-SHALOM and G.A. THOMAS, Bell Laboratories, Murray Hill, NJ--Below the metal-insulator transitions of $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$ one may restore the metallic conductivity and Pauli paramagnetism by exposure to weak electric fields along the $\hat{a}$ axis. The spin resurrection is accompanied by nonlinear changes in microwave loss. These phenomena are attributed to depinning of charged spin density waves. The influence of weak donor-stack disorder and deuteration will be presented. In addition we have discovered similar behavior in the atmospheric-pressure superconductor $(TMTSF)_2ClO_4$ below $\sim$ 5.5 K. A very weak and highly anisotropic magnetic resonance has also been observed in the perchlorate near 1.6 K, possibly due to antiferromagnetic resonance of the SDW state. This is further evidence that superconductivity does not require suppression of the magnetic precursor state.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 261
0026-8941/82/8601-0261$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Some Infrared Properties of TMTSF 2:1 Salts.*

J.S. CHAPPELL, M.M. LEE, D.O. COWAN, T.O. POEHLER, Johns Hopkins U. and A.N. BLOCH, Exxon Research and Engineering Company--The optical properties of $(TMTSF)_2PF_6$ at room temperature reveal a strong absorption edge at 0.32 eV, attributed to the onset of direct interband transitions in the dimerized lattice. The tight binding transfer integral implied is 0.12 eV, half the magnitude suggested elsewhere.[1] In contrast to monomeric stacks such as TTF-TCNQ, a set of excitations lie within the gap which can be identified as the enhanced absorptions of the totally symmetric TMTSF molecular modes. The electron-molecular vibration coupling responsible for these intense vibronic features is discussed for the case of the organic metals. The ambient pressure superconductor $(TMTSF)_2ClO_4$ is also studied.

*Supported by NSF through grant DMR 80-15318

[1] K. Bechgaard, C.S. Jacobsen, K. Mortensen, H.J. Pedersen, and N. Thorup, Solid State Commun., **33**, 1119 (1980).

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 263
0026-8941/82/8601-0263$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Infrared Study of EMV Interactions and Phase Transitions in the Organic Conductors $(TMTTF)_2X$ and $(TMTSF)_2X$.,

C.Pecile, R. Bozio, and A. Girlando, U. of Padova, R. Bechgaard, U. of Copenhagen, F. Wudl, Bell Laboratories.

We have studied the electron-molecular vibration (EMV) interactions and the Peierls distortions in $(TMTTF)_2X$ and $(TMTSF)_2X$ conductors. Spectral features indicative of strong EMV coupling have been observed for C=C and C-S stretching modes and, unexpectedly, for some modes of the methyl groups. Their intensity increases sharply at the magnetic phase transition in BF_4 but not in the ClO_4 salt. The corresponding vibronic features in the I.R. spectrum of $(TMTSF)_2ReO_4$ show an abrupt increase of intensity starting from almost zero at the 180K metal-insulator transition. The different behaviour of the sulphur compounds is discussed in terms of a greater sensitivity to the small $4K_F$ dimeric distortion observed at room temperature and of a partial suppression of the Peierls instability. The I.R. spectrum of $(TMTSF)_2PF_6$ does not change when the 12K metal-insulator transition is approached indicating the absence of Peierls distortions.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 265
0026-8941/82/8601-0265$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Thermal Transport Properties of $(TMTSeF)_2PF_6$ •

D. DJUREK*, D. JEROME and C. WEYL, Laboratoire de Physique des Solides, Universite Paris-Sud, Orsay, France. The method of "thermal potentiometer" is used to measure the thermal conductance of organic superconductor $(TMTSeF)_2PF_6$ at low temperature for a pressure of 12 kilobars. An abrupt decrease of the thermal conductivity is observed between ∿ 40 and 18K. This result is not inconsistent with the existence of 1-d superconducting fluctuations far above the actual superconducting transition at ∿ 1K previously postulated on the basis of the other experiments and theoretical work. The temperature dependence of the conductivity at low temperature shows that the quasi-particles excited across the pseudo-gap in this way are inelastically scattered by the phonons.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 267
0026-8941/82/8601-0267$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Properties of the $(TMTSF)_2X$ Family of Charge Transfer Compounds.* P.M. GRANT, IBM San Jose.--We present the results of two-dimensional band structure calculations on the $(TMTSF)_2X$ series of charge transfer compounds. Ratios of interchain to intrachain bandwidths are found to be strongly dependent on small changes in interchain cation positions. We believe this behavior to derive from non-linear variations in Se 4p π-orbital overlap between neighboring interchain TMTSF molecules as a function of contact distance. Using simple one-electron concepts, we relate our results to experimental findings on optical properties, normal state transport properties and superconducting critical field behavior.

*Supported in part by the ONR.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 269
0026-8941/82/8601-0269$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Irradiation Induced Defects in Organic Superconductors.

S. BOUFFARD*, M. RIBAULT**, D. JEROME**, K. BECHGAARD***.

We have studied the low temperature phase of $(TMTSF)_2-PF_6$ and TMTSF-DMTCNQ under pressure. In $(TMTSF)_2-PF_6$, a very slight disorder introduced by X-ray irradiation (less than 10^{-3} molecular defect) is able to suppress the superconductivity state at 12 kbars. The transition temperature can be correlated to the residual resistivity. Above this temperature, the effects of irradiation induced defects in $(TMTSF)_2-PF_6$ are essentially the same as in TMTSF-DMTCNQ. Below 100 K, the resistivity curves versus molecular defect concentration show two regimes: the first one is related to the suppression of the superconductivity fluctuations and the second one is the well-known conductivity decrease in the metallic regime.

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TTF-TCNQ AND OTHER TCNQ AND TTF SALTS

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 273
0026-8941/82/8601-0273$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Theory of the Low Temperature Phases in TTF-TCNQ. C.HARTZSTEIN, V.ZEVIN, and M. WEGER, Racah Institute of Physics, Hebrew University, Jerusalem.--Recently[1] we showed that the phase diagram of TTF-TCNQ can be understood from the pressure dependence of the CDW-CDW Coulomb interaction between unsimilar chains. We now investigate the influence of fourth order interaction terms in the phase modulated and amplitude modulated configuration free energies. Two peculiar features are found: i) the above mentioned CDW-CDW bilinear interaction is frustrated in the "4a" commensurate phase, implying that a finite fourth order anharmonic interaction is needed in order to stabilize this phase; ii) a biquadratic interaction term is able to pin the transverse period to "2a" at T<30K and P∿5Kbar[2]. A very good agreement with the experimental phase diagram is obtained from the minimization of the free energy.

[1] C.Hartzstein, V.Zevin and M.Weger, Sol. St. Comm. 36, 545,(1980)/

[2] C.R.Fincher Jr., G.Shirane, R.Comes, and A.F.Garito, Phys. Rev. B21,5424(1980)

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 275
0026-8941/82/8601-0275$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Interstack Spin-Orbit Coupling and ESR Line Broadening in TTF-TCNQ.* F.J. ADRIAN, APL, Johns Hopkins Univ. - Electron spin resonance (ESR) experiments on TTF-TCNQ-like molecules strongly indicate the observed linewidths are due to spin transitions effected by the heavy atom (S or Se) spin-orbit interactions on the donor molecule.[1] This is puzzling, however, because this mechanism is ineffective for electrons in a one-dimensional band. In a single stack of TTF molecules the S spin-orbit interaction can only couple the π-band electrons with energetically inaccessible in-plane (σ) states. It will be shown that the TCNQ π-band states acquire small amounts of TTF σ character via the overlap between TCNQ π and TTF σ orbitals, and, consequently, the TTF spin-orbit interaction can produce transitions between π-band states of adjacent TTF and TCNQ stacks with an accompanying change in electron spin state. The observed ESR line widths agree well with those calculated by orthogonalizing the TCNQ π-states to the TTF σ orbitals and assuming that the correlation time for the spin-orbit coupling matrix elements equals the conduction electron scattering time. *Work supported by Naval Sea Systems Command.

1. Y. Tomkiewicz, E.M. Engler and T.D. Schultz, Phys. Rev. Letters 35, 456 (1975).

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 277
0026-8941/82/8601-0277$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Magnetic properties of pure and irradiated TMTSF-DMTCNQ.

J. AMIELL*, P. DELHAES* and L. ZUPPIROLI**.

E.P.R. experiments have been performed on pure and irradiated TMTSF-DMTCNQ. The pure organic conductor behaves more like a single chain compound than like a usual charge transfer complex. The analysis of the Curie tails in irradiated crystals strongly suggests that defects sitting on the DMTCNQ chains localize spins but change much less the transport properties than defects sitting on the TMTSF conducting chains. A molecular concentration of 1% of paramagnetic centers was found in the "so-called" pure sample. Sitting on the DMTCNQ molecules they are probably responsible of the absence of superconductivity in a TMTSF chains compound which presents large similarities with the $(TMTSF)_2$ X family.

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Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 279
0026-8941/82/8601-0279$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

The low temperature metallic phase of weakly disordered TMTSF-DMTCNQ.

L. FORRO*, A. JANOSSY**, L. ZUPPIROLI*, K. BECHGAARD***.

Hall effect measurements have been performed from 2 K to 300 K on pure and irradiated samples of TMTSF-DMTCNQ. The Hall constant of à pure sample is positive and small at high temperatures $(R(300\ K) = 4.8 \pm 0.9)10^{-11}$ V.cm/A. Gauss) and becomes negative and large below the transition at 41 K $(R(4.2K) = -(3.4 \pm 0.4)10^{-6}$ V.cm/A.Gauss). In an irradiated sample containing 2% of damaged molecules, the Hall effect becomes temperature independant (from 10 K to 300 K $|R(2\%)| < 10^{-9}$ V.cm/A.Gauss). There is no significant difference between the 4.2 K values of the samples containing 0.2% and 1% defects respectively. These results together with longitudinal and transverse resistivity and g values measurements, clearly show that disorder in the TMTSF chain stabilizes the metallic phase of TMTSF-DMTCNQ down to 2 K at least.

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Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 281
0026-8941/82/8601-0281$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

<u>Mott Transition in the Solid Solutions HMTSF $(TCNQ)_x(TCNQF_4)_{1-x}$</u>.* W.A. BRYDEN, J.P. STOKES, D.O. COWAN, T.O. POEHLER, Johns Hopkins U. and A.N. BLOCH, Exxon Research and Engineering Company--Solid solutions between the organic metal HMTSF-TCNQ and isostructural Mott insulator HMTSF-$TCNQF_4$ display a miscibility gap associated with the Mott transition in the range 25-55% TCNQ. Samples in this regime have the visual appearance of single crystals, but are imhomogeneous on a fine scale. The homogeneous and inhomogeneous phases are probed through X-ray techniques and the measurement of static magnetic susceptibility, electron paramagnetic resonance and electrical properties.

*Supported by NSF through DMR 80-15318

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 283
0026-8941/82/8601-0283$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Irradiations induced defects in organic conductors : the mechanisms of the damage production.

L. ZUPPIROLI* and G. MIHALY**. Single crystals of several organic conductors have been irradiated with X rays of several energies. The molecular concentration of defects and damage rates, estimated from the transport porperties of the damaged crystals, have been compared to calculated values in order to decide if the damage is proportional to the number of protons displaced by nuclear collisions or to the total energy absorbed by the crystal in form of electronic excitations. It is demonstrated that, from the point of view of radiation effects, organic metals behave more like usual molecular insulating crystals than like metals. The fraction of destroyed molecules scales with the total absorbed energy. One needs an absorbed energy of 7.1 keV to damage a molecular unit of TMTSF-DMTCNQ, 13.5 keV for a molecular unit of TTF-TCNQ and 147 keV for a molecular unit of TTT_2I_3. The local structures of the molecules are probably responsible of these differences more than the crystal structures or the electronic metallic properties.

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Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 285
0026-8941/82/8601-0285$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

A Summary of Recent Experiments on the Neutral-Ionic Phase Transition in TTF-chloranil.

J.B. TORRANCE, IBM Research, San Jose and C. AYACHE, P. BATAIL, A. GIRLANDO, G. GRÜNER, J. HUBBARD, C.S. JACOBSEN, H. KING, S.J.LAPLACA, J.J.MAYERLE, R.M. METZGER, C. PECILE, Y. TOMKIEWICZ and R. WOLFE.

-- A distinct color change may be induced in TTF-chloranil by either lowering the temperature or by applying pressure. In both cases, this is a Neutral-Ionic transition between a state of quasi-neutral and one of quasi-ionic molecules. The onset of the low temperature transition at 83K is accompanied by anomalies in c_p and ε, but the transition is broad and not discontinuous; in fact it persists from 83K to ~ 50K in temperature and from 6.5 to 11 kbar in pressure (T=300K). Over this range there is a coexistence of Neutral and Ionic stacks. This inhomogeneous charge distribution is stabilized by interstack coulomb interactions, we believe.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 287
0026-8941/82/8601-0287$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Infrared and Raman Studies of the TTF-CH Neutral to Ionic Phase Transition.

A. GIRLANDO, R. BOZIO and C. PECILE, U. Padova and J.TORRANCE, IBM Res., San Jose.

The mixed stack complex of TTF with chloranil (CA) around 80 K exhibit a new kind of phase transition, identified as a transition from a quasi-neutral to a quasi-ionic charge transfer complex. Vibrational data confirm that the transition is essentially a sharp variation of the degree of charge transfer, ρ (from $\simeq$20-30% to $\simeq$60-70%) between CA and TTF units, and show that it is preceeded and followed by a smaller and continuous increase of ρ. Furthermore, IR and Raman data indicate the cohexistence of both the high and low temperature phases, that is, of both quasi-neutral and quasi-ionic TTF and CA units, in a rather broad (90-60 K) temperature range around the phase transition. At low temperature the infrared spectra show the appearance of strong vibronic absorptions, polarized along the stack axis and of frequency coincident with that of the Raman active totally symmetric vibrations. The effect of the vibronic interaction on the vibrational frequencies, and the presence of the vibronic absorptions in relationship to the chain distortion are discussed.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 289
0026-8941/82/8601-0289$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

INFRARED MEASUREMENTS ON PURE AND IRRADIATED NPrQn(TCNQ)$_2$ POWDERS,

K. Kamarås, Central Research Institute for Physics, P.O.Box 49, H-1525 Budapest, Hungary, and J. Kürti, L.Eötvös University, H-1088 Budapest, Hungary

Infrared spectra of NPrQn(TCNQ)$_2$ (NPrQn = = N-n-propylquinolinium) pure and irradiated by neutrons and gamma-rays, respectively, have been measured vs. temperature. The defect concentration dependent phase transition observed before in the susceptibility, d.c. conductivity and dielectric constant, is seen in the behaviour of the activated a_g modes. The splitting of several peaks at low temperatures supports the picture of the phase transition to be due mainly to localization of electrons on two molecules within the TCNQ tetrades.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 291
0026-8941/82/8601-0291$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Frequency Dependent Conductivity of Quasi-One Dimensional Electronic Conductors.

G. GRUNER, A. ZETTL, and W.G. CLARK, Department of Physics, University of California, Los Angeles, CA, 90024

The frequency and temperature dependent electrical conductivity $\sigma(\omega,T)$ is measured in a one dimensional model system quinolinium-ditetracyanoquinodimethanide $Qn(TCNQ)_2$. Detailed results are presented for Re $\sigma(\omega)$ and Im $\sigma(\omega)$ over a broad temperature range. The nature of the dielectric-to-metal transition is discussed, and the experiments are described by a model by Alexander, Bernasconi, Schneider, Biller and Orbach. The relation between frequency and field dependent transport phenomena in random highly anisotropic systems will also be discussed.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 293
0026-8941/82/8601-0293$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Neutron Scattering from one-dimensional conductors. K. CARNEIRO, University of Copenhagen and Risø National Laboratory.-- Neutron scattering offers unique insight into the structural (i), lattice-dynamical (ii), and magnetic properties (iii). The following is presented. (i): New structural instabilities, and their relation to electronic properties of ZnOP and TEA$(TCNQ)_2$. (ii):Differences in the giant Kohn anomaly for commensurate and incommensurate systems are demonstrated by KCP(Br), K(det)CP, and TEA$(TCNQ)_2$. (iii): Results of the search for a spin-density wave in $(TMTSF)_2PF_6$.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 295
0026-8941/82/8601-0295$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

The Phase Transition of KTCNQ as Studied by ^{14}N Nuclear Quadrupole Resonance. A.COLLIGIANI, R.AMBROSETTI, Ist.Chim.Quant., CNR, Pisa, Italy and J.MURGICH, IVIC, Caracas, Venezuela.--The NQR technique has been used for the first time to study the phase transition of alkali metals-TCNQ complexes. In fact, the dependence of ^{14}N NQR frequencies and amplitudes turned out to carry detailed information on the behavior of individual sites at the phase transitions. The measurements, done between r.t. and 190 °C, revealed a very peculiar trend of the eight ν_+ and ν_- lines pertaining to the low-temperature dimeric phase. At 142°C the eight-line spectrum disappeared abruptly and was replaced by two main lines pertaining to the normal high-temperature phase. Just above 122°C, the phase-transition temperature previously reported[1], and till 142°C the coexistence of the two phases has been clearly verified. The NQR frequencies showed no hysteresis whereas the amplitudes displayed a strong one around 122°C. A tentative interpretation is given under the hypothesis of the existence of an incommensurate phase[2] connected to a spin-Peierls transition.

[1] J.G.Vegter et al, Chem.Phys.Letters, 3, 427 (1969)
[2] S.Plesko et al, Phys.Stat.Sol.(a), 61, 87 (1980).

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 297
0026-8941/82/8601-0297$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Spectroscopic Properties of Semiconducting Cu-TCNQ Films. R. S. POTEMBER, T. O. POEHLER, and D. O. COWAN, Johns Hopkins U.*, A. N. BLOCH, Exxon Corp., and P. BRANT and F. L. CARTER, Naval Research Lab.--Polycrystalline metal organic semiconductors sandwiched between metallic electrodes exhibit fast current-controlled bistable electrical switching and memory behavior. The effects are observed in films of either Cu or Ag complexed with electron acceptors TCNE, TNAP, TCNQ, substituted TCNQ molecules, and several other acceptors. The polycrystalline semiconducting films used in electrical switching devices have been investigated by Auger, X-ray photoelectron, and diffuse infrared reflectance spectroscopy. These measurements reveal that the charge-transfer complex is primarily composed of Cu(I) and radical-anion $\mathrm{TCNQ}^{\overline{\cdot}}$. Detailed spectroscopic measurements of the complex subsequent to the application of an electric field indicate that the field is responsible for formation of a mixed valence species. This mixed valence complex responsible for the high conductivity state of the films will be described in detail.

*Supported by NSF Grant DMR80-15318 and US Navy.

PHYSICAL PROPERTIES OF VARIOUS LOW-DIMENSIONAL CONDUCTORS

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 301
0026-8941/82/8601-0301$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Frequency(field) Dependent NMR Relaxation in the Interrupted Strand Model,

J.R. COOPER, Institute of Physics of the University, Zagreb, Yugoslavia.

It is possible that the interrupted metallic strand model or other models with weakly localised electronic states, may apply to some linear chain or polymer conductors. A characteristic of these models is that because of localisation the electron energy spectrum is locally discrete, with level spacing $\Delta \simeq E_F/n$, for a segment of n units. However, since n is a random variable,the average density of states is continuous. Recently(1) we calculated the NMR T_1 arising from the usual electron-nuclear hyperfine contact interaction, within this model. The discrete levels were assumed to be broadened with an energy half-width Γ due to the effect of adjacent segments or phonons. Using the standard procedures, we found that for $kT \gg \Delta > \Gamma$

$$T_1^{-1} = \frac{AkT}{\Delta}\left[\frac{\Gamma}{(\mu_B H)^2 + \Gamma^2} + O\left(\frac{\Gamma}{\Delta^2}\right)\right]$$

That is, the temperature dependence of T_1 is the same as for the band case(delocalised states $\Gamma \gg \Delta$) but T_1^{-1} has a Lorenztian field/frequency dependence, and is enhanced at low fields by Δ/Γ .

(1) J.R.Cooper and V.Zlatić, to be submitted.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 303
0026-8941/82/8601-0303$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Localized and Extended Electron States in a One Dimensional System with Bond Distortion.

B.BULKA, Institute of Molecular Physics, Polish Academy of Science, Poznan, Poland.

A tight-binding one-dimensional model, in which hopping integrals t are modulated with a periodicity incommensurate with a lattice constant a is considered. We numerically investigated a convergence of the self-energy of the Green's function, which is expressed as a continued fraction. For example, for a wave vector $Q=3.0/a$ and an amplitude of the distortion $\delta=0.1t$ electron states are extended and form the bands: $0.26t<|E|<2.0t$ and $|E|<0.06t$. The result is similar to that with solitons in a system, when a narrow band around $E=0$ exists. In the case $\delta>t$ all states are localized.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 305
0026-8941/82/8601-0305$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

From Mott to Anderson localization in electron irradiated 1T-TaS_2. H. MUTKA*, L. ZUPPIROLI* and P. MOLINIE**. The relations between electronic transport, the periodic lattice distortion (PLD) associated to charge density waves (CDW) and disorder are studied experimentally in 1T-TaS_2. Disorder is introduced by means of electron irradiation which is able to displace lattice atoms. The defects stable around room temperature are due to displacements in the tantalum sublattice. The experimental methods used in this work to explore disordered 1T-TaS_2 are conductivity and Hall effect measurements and electron microdiffraction. The irradiation induced defects act strongly on the CDW ; they pin its phase and are thus able to suppress the phase transitions where the PLD orders to form a commensurate superstructure. The localized electronic ground state of the pure material can be destroyed by slight disorder to obtain metallic transport properties. Further irradiation induced disorder leads to a new localization. This sequence is interpreted as a change from Mott to Anderson localization.

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Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 307
0026-8941/82/8601-0307$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Donor-Acceptor Inter-Chain Coulomb Scattering In a One-Dimensional Charge Transfer Conductor.* S. K. LYO, Sandia National Laboratories Albuquerque.**-- The contribution of donor-acceptor inter-chain electron-electron scattering to the d.c. resistivity is calculated for one-dimensional charge transfer metallic conductors. The resistivity arises from U-processes when the relative signs of the slopes of the donor and acceptor bands are the same and from N-processes when they are opposite. Application of the model to TTF-TCNQ is discussed.

*Supported by the U.S. Dept. of Energy (DOE) under contract DE-AC-4-76-DP00789.

**A U.S. DOE facility.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 309
0026-8941/82/8601-0309$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Anisotropy in Magnetic Susceptibility Using A Torsion Method. M. MILJAK and J.R. COOPER, Institute of Physics of the University, Zagreb, Yugoslavia.

We have constructed a simple quartz fibre torsion apparatus for measuring the torque exerted on a single crystal by a uniform magnetic field, and have used it to measure the anisotropy in magnetic susceptibility (χ)of the organic conductors HMTSF-TCNQ* and $(TMTSF)_2PF_6$** in the temperature range 1.7 to 300K and fields up to 0.8 T. The method is sensitive, adequate resolution was obtained using only 0.14 and 1.1 mg crystals respectively.

The anomalous diamagnetism of HMTSF-TCNQ was thus found to be strongly anisotropic and temperature dependent. It is largest for H along the low conductivity direction.

For $TMTSF_2PF_6$ there is a large increase in torque at 0.55 Tesla for fields approximately perpendicular to the needle axis which is ascribed to the antiferromagnetic spin-flop transition reported by other groups. However in our experiments this large effect does not persist up to the Neél temperature(12K) but disappears between 5 and 6K.

*
** Single crystals prepared by K. Bechgaard,Copenhagen.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 311
0026-8941/82/8601-0311$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Non-linear dielectric properties of $NbSe_3$ below the Peierls transition at 145 K, D. Djurek, M. Prester, S. Tomic, Institute of Physics, University of Zagreb, Zagreb, Yogoslavia.--We have developed a technique of the measurement of dielectric function ε in non-linear region when ε is dependent on electric field. The electric field pulse, is applied to the sample and the time derivative of corresponding current response is interpreted in terms of field dependent dielectric function. The method is applied to the measurement of dielectric function of $NbSe_3$ below the Peierls transition temperature T_p at 145K. The strong exponential decrease of ε with electric field E has been found i.e. $\varepsilon \sim e^{-E/E_c}$. The characteristic electric field E_c is temperature dependent and diverges by approaching T_p as a consequence of quasi-particle excitations across the Peierls gap.

SYNTHESIS AND PROPERTIES OF NOVEL ORGANIC AND INORGANIC MATERIALS

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 315
0026-8941/82/8601-0315$06.50/0

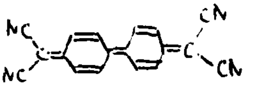
Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Synthesis of New Charge-transfer Complexes.1)

T. NOGAMI and H. MIKAWA, Osaka U., Japan

Organic charge-transfer complexes of tetracyanodiphenoquinodimethane (**1**) were isolated. N-methylquinolinium and N-methylphenazinium ions were used as cations. They were not high conductive with the conductivities of 10^{-8} $(\Omega cm)^{-1}$. We also tried to synthesize tetracyanoanthraquinodimethane (**2**). Although we could not synthesize it yet, we have isolated the new acceptor **3**, which seems to be the precursor of **2**. From the charge-transfer absorption measurements of **3** with several donor molecules, **3** was estimated to have the comparable electron affinity to 1,3,5-trinitrobenzene. Besides **3**, we obtained another new acceptor **4** as a byproduct. **4** was estimated to have the comparable electron affinity to m-dinitrobenzene by the measurements of the CT-absorption.



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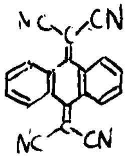

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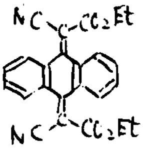

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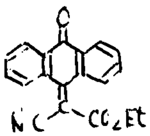

4

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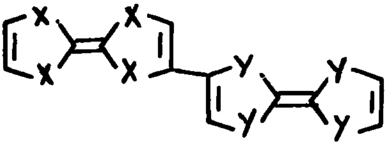
Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 317
0026-8941/82/8601-0317$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Bi-TTF and Bi-TSF. V.Y. LEE, R.R. SCHUMAKER, E.M. ENGLER and J.J. MAYERLE, IBM Research Lab, San Jose. --A high yield, single step preparation of bi-TTF 1 from TTF is described. Physical properties including conductivity data on a variety of electrochemically grown crystalline CT salts are presented. The application of this synthesis to the preparation of bi-TSF 2 and the mixed sulfur-selenium system 3 will be discussed.

1. X=Y=S
2. X=Y=Se
3. X=S, Y=Se



Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 319
0026-8941/82/8601-0319$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Electrochemical Synthesis of a New Series of Ionic Radical Salts. Conductivity and Structural Data.

J.M. FABRE, C. GALAINE and L. GIRAL, USTL, 34100 Montpellier, France - The method of electrolytic crystal growth is used for a number of systems containing new unsymmetrical donors (TTF, TSF type) and inorganic counterions. Dimethyltrimethylen tetrathiofulvalen (DMTMTTF), for example, is oxidized electrochemically at a platinum anode and give conductive salts : tetrafluoborate, hexafluoroarsenate, perchlorate. . . .The electrical conductivity and the structural data of these salts are given. The series containing a donor with four sulfur atoms then, four selenium atoms, are compared.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 321
0026-8941/82/8601-0321$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Electronic Structure of the Naphthothia- and Naphthoselena-diazines: Theoretical and Experimental Approaches. J.P. BOUTIQUE, J. RIGA, J.J. VERBIST, J.G. FRIPIAT, J. DELHALLE, J.M. ANDRE, Fac. Univ. de Namur, Belgium. - Pursuing our research on the electronic structure of organic potential conductors, we present new theoretical and experimental results on the naphtothia- and naphthoselena-diazines [1]. Ab initio STO-3G calculations and X-ray photoelectron spectra indicate which resonance formulae are the more appropriate to describe the compounds and allow to discuss the role of the S3d orbitals in such structures. In the specific case of naphtho[1,8-cd ;4,5-c'd'] bis [1,2,6] thiadiazine, we compare the XPS valence band with a simulated spectrum, derived from our calculations. The agreement is good and helps in the valence levels assignation. The experimental data obtained on the selenium analog show strong similarities : the evolution of the valence peaks intensities informs about the chalcogenide atomic orbital participation in the highest occupied π levels.

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Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 323
0026-8941/82/8601-0323$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Electronic Properties of [3.3]TTF-Phan TCNQ-Crystals.

D. SCHWEITZER, MPI Abt. Mol. Physik, CHU TAOPEN, C. KRIEGER and H.A. STAAB, MPI Abt. Org. Chemie, Heidelberg, Jahnstr. 29, West Germany

[3.3]TTF-Phan-TCNQ-crystals with a composition of 1:4 (Angew.Chem. 92,51, 1980; Angew.Chem. Int.Ed.Engl. 19,67,1980)) are semi-conductors with room temperature conductivities along the needle axis of about $10^{-2}(\Omega cm)^{-1}$. Between 50 K and 400 K the conductivity changes over 12 orders of magnitude. Polycristalline pills of this material show very similar conductivity behaviour. Only one strong sharp ESR-signal was observed in the crystals. From the weak anisotropy of the g-value and the isotropic g-value this ESR-signal could be assigned to TCNQ anions. In contrast to the conductivity measurements the ESR-signal was temperature independent down to 50 K and corresponds to a more metallic behaviour. Therefore we concluded that the TTF-Phan-TCNQ-crystals are of a two dimensional structure. This assumption could be confirmed by the x-ray structure analysis.

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 325
0026-8941/82/8601-0325$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

X-Ray Structure Determination on Crystallized Cation Radical Salts.

Dieter Wehe, Anorg.-Chem. Institut, 6900 Heidelberg

Structures of the high conducting radical cation salts $(Perylene)_2(PF_6)_{1.1}0.8\ CH_2Cl_2$ (I) and the AsF_6 analoge (II) were determined[1,1a]. The structures are very similar to known structures[2,3] especially the perylene-stacks. Analytical data could be confirmed by structure determination and also by diffusions on rotation photographs. A new less conducting modification of (I) showed the same geometry an and intensity of reflections but the diffusions now look like diffuse reflections and are more intense. The more disordered modification (I) with partial charche transfer thus can explain the higher conductivity[4].
Annother non conducting radical cation salt[5] Dimethylphenazine PF_6 ($M_2P\ PF_6$) shows no stack of the planar M_2P cation. Comparison with the other $M_2P^+X^-$ salts will be reported.

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Mol. Cryst. Liqu. Cryst. (1980) in press

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Z. Phys. Chem. B33,319,(1936)

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Solid State Comm., Vol.35 945

4) J. B. Torrance,
Acc. Chem. Res. 12 (1979) 79

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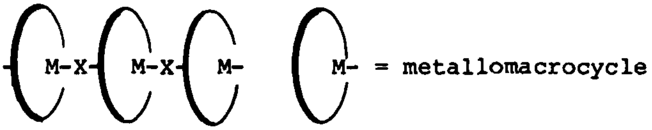
Universität Heidelberg (1980)

1a) C. Kröhnke, V. Enkelmann und G. Wegner
Angew. Chemie in press

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 327
0026-8941/82/8601-0327$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

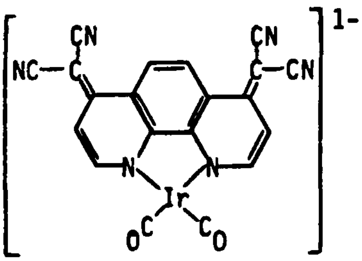
Rational Control of Electronic Structure and Lattice Architecture in Electrically Conductive Molecular/Macromolecular Assemblies. T.J. MARKS, C.W. DIRK, C.R. KANNEWURF, J.W. LYDING, and K.F. SCHOCH, JR., *Northwestern U.*--The properties of low-dimensional molecular materials are critically dependent on the capricious and relatively unpredictable forces that dictate the configurational and metrical aspects of stacking architecture. We discuss here chemical and physical studies of conductive polymeric materials in which the molecular subunits are rigorously constrained to a "face-to-face" orientation. The properties of these assemblies vary dramatically from "molecular metals" to integral oxidation state insulators. Such characteristics reflect, in a highly informative way, differences in dopant, macrocycle, molecular and electronic structure, and intrastack, interplanar architecture.



Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 329
0026-8941/82/8601-0329$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Synthesis and Solid State Properties of A New Planar Iridium (I) Complex. L.V. INTERRANTE, A.L. GILLIE and J.S. KASPER, General Electric Corporate Research & Development, P.O. Box 8, Schenectady, NY 12301.--The preparation, characterization and solid state electrical conductivity of the iridium (I) dicarbonyl complex of the new redox-active ligand, 4,7-bis(dicyanomethylidene)-4,7-dihydro-1, 10-phenanthroline $(C_{18}H_6N_6{}^{2-})$ [see figure] will be reported. This monoanionic complex has been isolated as salts of various organic and inorganic cations and electrical conductivity measurements have been carried out on these salts before and after partial oxidation with iodine. The results of these electrical measurements and of a crystal structure determination currently in progress on the triphenylmethylphosphonium salt will be described and discussed in the context of other work on "one-dimensional conductor" systems. [Work supported, in part, by AFOSR.]



Mol. Cryst. Liq. Cryst., 1982, Vol. 86, p. 331
0026-8941/82/8601-0331$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

Synthesis and Optical Properties of Some New One-Dimensional Compounds of Pt and Pd.

G.C.PAPAVASSILIOU and D.LAYEK, The National Hellenic Research Foundation, Athens, Greece.

The present work describes the synthesis and optical properties of linear chain halogen bridged compounds of the type $M(NH_3)_4M(NH_3)_4X_2Y_4$ and $M'_2M(NH_3)X_3M(NH_3)X_5$ (where $M = Pt$ or Pd, $M' = K^+$ or NH_4^+, $X = Cl, Br$ or I and $Y = HSO_4^-$ or ClO_4^-) and the compound $Pt(NH_3)_4PtCl_4(HSO_4)_x$ $(1 > x > 0.5)$. The single crystal reflectance and Raman spectra of halogen bridged compounds show an anisotropic behaviour. The resonance Raman enhancement has been observed only in the case of polarization with the wave vector parallel to the chain axis. All halogen bridged compounds are insulator or semiconductor with the conductivity ranging from 10^{-12} to 10^{-6} $\Omega^{-1}cm^{-1}$. The conductivity and reflectance spectrum of $Pt(NH_3)_4PtCl_4(HSO_4)_x$ in a pellet is the same as that of KCP pellet.