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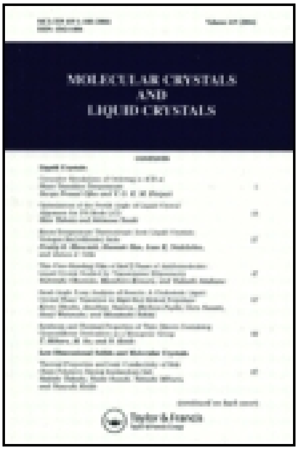

Molecular Crystals and Liquid Crystals

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Abstract

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HIGHLY CONDUCTING DERIVATIVES OF POLYACETYLENE AND POLYPYRROLE FORMED IN THE REACTION WITH SELECTED PROTONIC ACIDS AND METAL HALIDES - SYNTHESIS AND APPLICATION

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It has been found that polyacetylene can be used in chemical analysis for selective determination of nitrate ion in dilute aqueous solutions. If such solutions are acidified with sulphuric acid the log σ vs. NO_3 concentration plots are linear over the NO_3^- concentration range 2-40 mM. Several new conducting derivatives of chemically polymerized polypyrrole have been prepared in the reaction with selected metal halides such as: $FeCl_3$, $SbCl_5$, and others. The products have been characterized by elemental analysis and conductivity measurements.

ANALYSIS OF RESIDUAL IMPURITIES IN POLYACETYLENE FILM BY NEUTRON ACTIVATION METHOD

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Neutron activation analysis was attempted to identify residual impurity nuclides and their concentration in cis and trans $(CH)_x$ films prepared by different purification methods. $(CH)_x$ films (ca. 1-10 mg) were sealed in polyethylene bags and irradiated by thermal neutron (2.3×10^{13} n/cm^2 sec) for 1-30 min. with a pneumatic facility installed in Kyoto University Reactor. Comparators of 20 μg ^{55}Mn and/or 500 μg ^{23}Na on Millipore Filters were irradiated together with the samples. Concentration of impurity nuclide is given as y in $(CHImp_y)_x$, where Imp is impurity nuclide in the sample. Major impurity nuclides in cis film synthesized and purified by usual procedure were found to be Al (1.3×10^{-3}) and Ti(6.2×10^{-4}) originated from residual catalyst with minor components of As, W, Ir, and Au (10^{-6} - 10^{-8}). No difference in impurity concentration was observed between cis and trans films, indicating that the impurities did not volatilized during thermal isomerization under dynamic pumping. Washing of as-prepared films with HCl solution caused a greater decrease in the concentration of Ti and Al about an order of magnitude but incorporation of Cl at the level of 10^{-4}. Effect of these impurities on chemical doping will be presented.

EXCITONS AND SOLITONS IN POLYACETYLENE

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The nature of photoexcitations in polyacetylene, $(CH)_x$, is a subject of current theoretical and experimental interest. Our initial work using the technique of transient absorption spectroscopy revealed the presence of two metastable gap states after photoexcitation. Recent experiments have allowed us to more fully characterize these centers. One excitation, which has an absorption peak at $\sim$1.4 eV, is intrinsic in nature. We believe it is a bound state of two spin 1/2 SSH solitons and is the "exciton-like" state of the Peierls insulator. In addition to this fundamentally single-chain excitation, higher pump photon energy results in the separation of an electron-hole pair to different chains. These carriers are rapidly trapped at neutral soliton sites, yielding charged solitons. To account for this overall picture of excitations, the SSH framework must be modified to include the essential role of electron-electron repulsion.

KINETIC STUDY OF DEGRADATION IN CONDUCTING POLYMERS.

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Research in the chemistry of conducting polymers has for the most part focused on finding new dopants, understanding the doping process, and investigating the role of the dopant in the conduction process. Little attention is given to the nature of the dopant-polymer interaction in conducting polymers. We will report a study of the dopant-polymer interaction in oxidized polyacetylene and the polyheterocycles. The experiments consisted of holding doped trans-$(CH)_x$ or a polyheterocycle at a constant elevated temperature in either dynamic vacuum or air and monitoring the change in resistivity over a period of time. Rate constants and activation energies were calculated for a process which results in a loss of conductivity. It was found that the degradation of electrical conductivity in doped polyacetylene was dopant independent. The polyheterocycles exhibited superior stability. The results will be presented as well as a rationale (based upon an understanding of the reactivity of the oxidized polymer backbone) for the synthesis of stable conducting polymers.

EFFECT OF MOLECULAR OXYGEN UPON SOLITON T_M AND T_1 RELAXATION MEASURED BY ESE TECHNIQUES

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When samples of pristine polyacetylene and composites of polyacetylene with structural polymers are exposed to molecular oxygen (either $^{16}O_2$, $^{17}O-^{17}O$) at reduced temperature a purely physical interaction is observed. This interaction results in an enhancement of both neutral soliton phase memory and spin-lattice relaxation rates consistent with electron Heisenberg spin exchange and electron dipolar mechanisms. Exposure at higher temperature results in the chemical incorporation of oxygen into the polymer structure as a crosslink incorporating diamagnetic oxygen. A detailed investigation of the chemical process provides insight into the distribution of crossbridges and the reaction trajectories of solitons scattered by crossbridging barriers.

POLARIZATION DEPENDENT EXAFS IN Br-DOPED ORIENTED POLYACETYLENE

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X-ray absorption spectra of the Br K-edge were taken on $(CHBr_y)_x$ with $0.046 = y = 0.42$ using the synchroton radiation at HASYLAB. A highly stretch-oriented $(CHBr_{0.12})_x$ sample enabled the study of the polarization dependence of the EXAFS structure. The analysis of the EXAFS spectra yielded defined distances to neighbouring C and Br atoms. A detailed structural model will be presented: the linear Br_3^- molecules as well as the $(CH)_x$ chains are oriented parallel to the polymer fibrils. The Br-Br and Br-C distances indicate a commensurate intercalation of the Br_3^- molecules with respect to the $(CH)_x$ chains.

POLYMERIZATION REACTIONS OF MONOSUBSTITUTED ACETYLENES

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Polyacetylene is an attractive material because its conductivity can be enhanced several magnitude orders by doping. Its sensitivity to moisture and oxygen are however negative properties, since they limit the possible technological applications.
With the aim of preparing polymers with increased stability and comparable electrical properties, we examined the catalytic activity of several transition metal complexes towards monosubstituted acetylenes H-C≡C-R (R = C_6H_5, CH_2OH, CH_2Cl, CH_2Br, CH_2NHEt_2, $CH_2NHEtMe$). Polymers are obtained in simple reaction conditions. Stability and spectral properties of the synthesized polymers have been examined.

POLY(TRIMETHYLSILYLACETYLENE) - A USEFUL PRECURSOR TO A SOLUBLE FORM OF POLYACETYLENE AND NEW POLYACETYLENE DERIVATIVES.

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The intractability of most conductive polymers, including polyacetylene, has limited the number and types of applications found for them to date. We have found that a soluble polyacetylene derivative, poly(trimethylsilylacetylene) (PTMSA), can be prepared in good yield with molecular weights ranging up to $5\text{x}10^5$ by polymerization with a new class of catalysts formed by mixing WCl_6 with organolithium or organo-magnesium reagents. Reversible doping of PTMSA with I_2 induces semiconductivity (10^{-4} S/cm) in the polymer. A soluble copolymer of acetylene with TMSA having greater than 80% acetylene subunits can be obtained by desilation of PTMSA with tetraalkylammonium fluorides. Results of doping of this solubilized form of polyacetylene and additional synthetic transformations to other previously unknown polyacetylene derivatives will also be discussed.

This work performed at Sandia National Laboratories, supported by the U.S. Department of Energy, under contract DE-AC04-76DP00 789.

ELECTRICAL CONDUCTIVITY OF DOPED POLYMERS.

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Polymeric hydrocarbons which are intrinsically insulators may be doped to have conductivities as high as 1000 Ω^{-1} cm^{-1}. Examples are polyacetylene $(CH)_x$ and polypyrroles $(C_2(CH)_2NH)_x$. However, owing to the fibrillar morphology of the samples, simple dc techniques may reflect the electrical characteristics of the contact between fibrils and hence not genuine conduction properties of the polymeric chain. We report on 35 GHz conductivity measurements and compare them to earlier obtained, specially adapted dc techniques.

STUDIES ON ELECTROCHEMICALLY DOPED POLYPYRROLES

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Electrochemical polymerization of pyrrole in aqueous solution as first reported by Dall'Olio et al. has been studied using H_2SO_4, $HClO_4$ and KPF_6 as supporting electrolytes. The doped polypyrroles (PPy) obtained showed good conductivities. However, the morphology and apparent density were found to be quite different. For example, HSO_4^- doped PPy from aq. solution had an apparent density of 1.50 as compared to those of BF_4^- and PF_6^- doped PPy from CH_3CN solution being 0.260 and 0.368 resp. HSO_4^- doped PPy from aq. solution showed good stoichiometry in regard to the atomic ratios C:H:N. Metallic temperature dependence of the conductivity of doped PPy from RT to 77K has been demonstrated by voltage shorted compaction (VSC) measurements. BF^- doped PPy from CH_3CN solution when partially reduced showed a metal semi-conductor transition at ca. 100 K on VSC measurements. The morphology of BF_4^- doped PPy from CH_3CN solution was in the form of spherical bowls of a few μm dia. When a Au-plated Cu net of 27x27 μm square holes was used as the anode, the nucleation of the doped polymer growth was found to be always initiated at the middle of the four sides of the square holes so that a regular array of hollow bowls resulted. The morphology of HSO_4^- doped PPy from aq. solution was in the form of flat blocks.

CONDUCTING CARBON-NITROGEN PYROPOLYMERS DERIVED FROM CYANOGEN

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Electropolymerization of cyanogen in acetonitrile containing an electrolyte yields a poly(cyanogen). Its structure involves an open-structured dimer derived from the heterocyclic anion $C_7N_7^-$ mixed with a sequence of nitrile substituted carbon-nitrogen bonds. Anionic initiators also cause polymerization of cyanogen in solution but yield primarily open-structured dimers and $C_7N_7^-$. The poly(cyanogen) is an insulating solid, but pyrolysis in vacuo to 700° leads to highly conducting carbon-nitrogen pyropolymers via cross-linking and nitrogen elimination. The 700° pyropolymer has a carbon-nitrogen ratio of 5:1, a room temperature conductivity of 1 Ω^{-1} cm^{-1} and a very small activation energy for conduction (< .03 eV) when measured as a compacted disk.

Supported by NSF - Solid State Chemistry Grant DMR83-02329.

COPOLYMERS AND BLEND OF CARBAZOLE TYPE CONDUCTING POLYMERS

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In an attempt to increase the molecular weight, solubility, and mechanical strength of the polycarbazole conducting polymers more flexible linkages have been copolymerized with stiffer carbazole oligomers. One example is the copolymer formed by linking the dimer, 3,3'-N'N dimethyl dicarbazolyl, with methylenes through the 6,6' positions (PDMCZM). This polymer is more soluble than the corresponding poly 3,3' N-methyl carbazolyl (PMCZ) and of higher molecular weight. Upon oxidation with I_2 or $NOBF_4$ the positive charges are delocalized through doubly bonded methine linkages formed by loss of hydrogen during oxidation. Consequently the room temperature conductivity of the complexes is surprisingly high $\sim 10^{-3}$ ohm^{-1}cm^{-1}. Another advantage of this material is its ability to form solid solutions with up to 60% of PMCZ that have high fracture resistance in thin film forms suitable for microelectronics. Another strategy we have employed to increase mechanical strength while maintaining processability and environmental stability is to copolymerize carbazole oligomers with more flexible aniline type oligomers as for instance, N,N' diphenyl paraaminobenzene. Iodine complexes of these copolymers have air stable, room temperature conductivities in the 1 ohm^{-1}cm^{-1} range and fracture strengths of several thousand psi.

A NEW TECHNIQUE FOR SYNTHESIZING POLYTHIAZYL

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A new technique has been developed for the synthesis of Polythiazyl on alkali halide substrates (eg. KI). The new technique allows the formation of a stable red monomer species due to rapid thermal quenching of the gas phase products from the catalytic degradation of S_4N_4. Annealing of the red monomer above 0^oC produces a deeply blue-colored polymer. Previous workers have proposed that Polythiazyl, produced from a red monomer species, should yield a more perfect crystal than is normally obtained. We have observed this from electron diffraction obtained from our samples. FTIR spectra showed only weak peaks above 1090 cm^{-1} which indicates little hydrolytic degradation of the chain. Optical microscopy indicates that the polymer probably is a new phase, with a different band structure in reflection, since thick films of the material are blue in reflection. The electron diffraction patterns from these rod-like crystals (observable in both electron and optical microscopy) oriented in the substrates'(100) directions, indicate the epitaxial growth of a new phase of Polythiazyl has occurred.

AN AB INITIO HARTREE-FOCK APPROACH TO THE STUDY OF ONE-DIMENSIONAL PERIODIC SYSTEMS.

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An ab initio Hartree-Fock computational scheme for the study of polymers is presented; the techniques used for the treatment of the Coulomb and exchange series ensure a very rapid convergence of the energy and of the wavefunction with respect to the number of neighbours considered.
Results for cis and trans polyacetylenes, metallic and "broken symmetry" polysulphur nitride $(SN)_x$ and for metallic polyacene are presented and compared with previous ab initio results.

EXTENDED HÜCKEL CALCULATIONS FOR THE INTERCHAIN VS. INTRA-CHAIN COUPLING OF ONE-DIMENSIONAL CONDUCTORS

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The strong anisotropy of electrical conductivity of 1-D-conductors results from the much stronger coupling of electrons within the same chain compared to the coupling of electrons of different chains. Nevertheless, since all real chains have a finite length the interchain coupling is important for the mechanism of conductivity, too. The effect is expressed by the broadening of the energy bands of the crystal compared to the sharp levels in an isolated molecule and can be studied by the dependence of $E(k_z)$ relative to $E(k_x)$ of $E(k_y)$. A transient consideration that is executed here is the comparison of the energy bands of a single chain with those of a double chain. The samples treated by the extended Hückel approximation are: bis(dimethyl-glyoximato)-pyrazin-Co(II), whose exact crystal structure is well known, but which has only a poor conductivity, and tetrazaporphinato-Co(III)-cyanide with a guessed lateral arrangement of the chains, instead of the larger phthalocyanine-Co(III)-cyanide that shows even undoped a considerable conductivity. The computer program was newly developed and utilizes crystal symmetries as widely as possible. The results show that the former treatment of single chains was reasonable for the comparison of different materials. Calculations on full 3-D-structures are underway.

QUANTUM MECHANICAL THEORY OF CARRIER MOBILITY

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Although carrier mobility is usually considered to be a phenomenological variable or a theoretical concept of Solid State Physics, it is actually a fundamental quantum mechanical concept. Starting with a set of atoms and an electric field and using second order perturbation theory, we derive mobility as a function of interatomic geometry (including overlap integrals) and 'effective mass'. The application of the theory to inter- and intramolecular mobilities for conductive polymers will be discussed.

ELECTROACTIVE SPECIES COVALENTLY BONDED TO ELECTRONICALLY CONDUCTIVE POLYMERS : POLYPYRROLE SUBSTITUTED WITH PQ^{2+}

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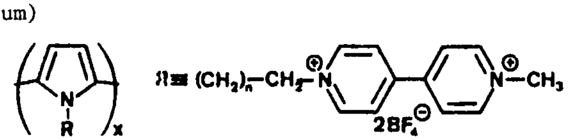
Polymer-modified electrodes has been synthesized by electropolymerization of pyrrole N-substituted with aliphatic chain bearing the redox mediator PQ^{2+} : (PQ^{2+} = 1,1'-dimethyl-4,4' bipyridilium)



n = 1, 2, 5, 10

Electrolysis at controlled potential (in CH_3CN, 0.1 M $N(Et)_4BF_4$, 1 V vs Ag/Ag^+ 10^{-2} M) produced a continuous increase in the well-behaved peaks due to the two successive reversible one-electron reductions of the PQ^{2+} group. Moreover, the simultaneous appearance of a redox couple in the anodic region shows the formation of electroactive polypyrrole chains. The formation of an electronically conducting matrix insure the growing of the film without the use of a redox mediator which is usually need as in the case of electropolymerization of vinyl derivatives. The chemical binding between the conducting polymer and the redox group seems an improvement in the stability of such electrode compared with ionic incorporation. The electropolymerization of adequately substituted pyrrole open a new field in the coating of electrode containing electroactive and photosensitive centers.

CHEMICAL POLYPYRROLE AS ELECTRODE MATERIAL FOR RECHARGEABLE BATTERIES

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Polypyrrole is prepared in chemical way by oxidation of pyrrole monomer by iron perchlorate in water. The conducting powder is then mixed with carbon black and teflon emulsion, dried and compacted in pellets. The batteries are formed by associating the polypyrrole pellets with $LiClO_4$ in propylene carbonate electrolyte and Li or Al-Li as counter electrode. Charging and discharging cycles show that polypyrrole can be oxidized and reduced many times without degradation of the batteries. The measured coulombic capacity is higher than the capacity calculated in assuming one ClO_4^- ion doping for three pyrrole rings. Ionic diffusion coefficients as high as 10^{-8} cm^2/sec, have been measured and are responsible of the good performance of these rechargeable batteries.

ELECTROCHEMICAL p-DOPING PROCESS OF POLYACETILENE IN LITHIUM ORGANIC ELECTROLYTE CELLS.

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The electrochemical p-doping process of polyacetylene has been investigated in lithium cells using lithium perchlorate in propylene carbonate as the electrolytic solution. The kinetics and the ciclability of this process have been examined by cyclic voltammetry, charge-discharge curves and EPR analyses.
The results show that the kinetics of the process are controlled by the diffusion of the dopant species throughout the polymer. Therefore the cyclability characteristics of the lithium-polyacetylene cells (such as coulombic efficiency, charge-discharge rates) are greatly influenced by the morphology of the polymer. Indeed, foam-type polyacetylene electrodes, where the intrinsic high porosity induces large surface area, show much better performance than typical Shirakawa-type, polyacetylene film electrodes.

NEW CATALYST FOR THE POLYMERIZATION OF ACETYLENE: SYNTHESIS OF BLOCK COPOLYMERS

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We have investigated the kinetic of the polymerization of acetylene with a new catalyst based on lithium. The polymers obtained were studied by I.R. (F.T.) spectroscopy, 13-C in the solid state, and scanning electron microscope.
This new catalyst has allowed the synthesis of block copolymers, like [isoprene-block acetylene], poly[styrene-block acetylene].
These problems will be given further consideration.

THE ELECTRONIC CONDUCTIVITY OF OXIDIZED $(CH^{+y})_x$ OVER A WIDE RANGE OF ELECTROCHEMICAL DOPING

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Under anodic load two different reactions are indicated by two different peaks in the cyclovoltamogramm of $(CH^{+y}A_y)_x$ electrodes ($A = ClO_4^-$ or AsF_6^-). The first reaction that occurs in a potential range of $2{,}5\ V < U < 3{,}8\ V$ vs. Li/Li^+ results in a doping level of about 9% CH units. In the second reaction ($3{,}8\ V < U < 6\ V$) an additional amount of charge ends up to "doping levels" of more than 50% CH units. During the first reaction the electronic conductivity of the $(CH^{+y})_x$ electrode increases monotonically while the second reaction results in a decreasing conductivity. The electronic conductivity as a function of the whole range of doping will be discussed in terms of the tunneling effect.

CHARACTERIZATION OF CHEMICALLY MODIFIED POLYPYRROLE

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The electronic conductivity of the electrochemically prepared conducting polymer polypyrrole can be reversibly switched over four orders of magnitude by treatment with alkali and acids (1). We have extended previous investigations of this effect and report transport measurements of the chemically modified material (conductivity and thermopower as a function of temperature). These results indicate a major rearrangement of the conjugated system. We also present studies of the modified material using magic angle spinning ^{13}C NMR, showing that the oxidation level of the polymer is reversibly changed by exposure to alkali and acids. ESR studies also show a reversible change of the line width and number of paramagnetic centra.

(1)O. Inganäs, R. Erlandsson, C. Nylander and I. Lundström, to appear in J. Phys. Chem. Solids.

SYNERGETIC EFFECT OF O_2 AND H_2O ON THE CONDUCTIVITY OF BF_4^- DOPED POLYPYRROLE

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Electrochemically made polypyrrole in its "as prepared", BF_4^- doped state has been considered to be relatively stable to atmospheric exposure, compared with many other conducting polymers. This does, however, not imply that the system is inert with respect to atmosphere, and the material does in fact exhibit quite strong degradation effects. We have followed the conductivity by four point probe measurements of electrochemically made PPy films during storage in Ar, O_2, O_2 + H_2O, Ar + H_2O and laboratory atmosphere. The films were made galvanostatically in an electrolyte consisting of 0.1 M Et_4NBF_4 and 0.1 M pyrrole in acetonitrile, and they were exposed to atmosphere before insertion in the test chambers. The results show that the conductivity is very stable in the case of Ar and Ar + H_2O exposures while O_2 and O_2 + H_2O have a degrading effect. The effect of O_2 + H_2O is, however, much stronger than that of O_2 alone, indicating a synergetic effect of O_2 and H_2O. XPS measurements also show that the BF_4^- anion is completely removed after a year's storage in atmosphere and that this anion depletion takes place all through the film (film thickness < 1μm). We have also investigated the influence of liquid water on the properties of PPy films, and it is shown that the conductivity is strongly affected by dissolved O_2. It is shown by XPS measurements that the chemistry induced by O_2 saturated liquid water is very similar to the effects previously reported when PPy is subjected to NaOH. In both cases the data can be interpreted in terms of a deprotonation of the heteroatom, an effect that is reversed when the film is exposed to HCl.

HOPPING CONDUCTIVITY IN ONE DIMENSION

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The characteristic temperature dependence of dc hopping conductivity σ_o in a disordered system, ln $\sigma \propto (T/T)^{1/d+1}$ in d dimensions, is a consequence of the application of percolation theory to a system of sites randomly distributed in space and energy. The relationship is obtained by a simple scaling argument. However, in one dimension the $T^{-\frac{1}{2}}$ law is not a genuine prediction because no non-trivial percolation surface exists. The $T^{-\frac{1}{2}}$ law is instead obtained by considering sites on a lattice in one dimension with random energies and long range coupling. This model is solved in the extended pair approximation for σ_0 and the frequency dependent complex conductivity $\sigma(\omega)$. The results are used to analyse experimental data on candidates for quasi one-dimensional conductors including the TCNQ compounds and polyacetylene.

CRITICAL FACTORS IN DETERMINING THE EXCITONIC INTERACTION IN MOLECULAR CONDUCTORS.

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We report our latest results on estimating the net on-site Coulomb interaction or attractive excitonic interaction resulting from molecular polarizability in molecular conductors. The critical importance of both a near degeneracy in the energy of two components of the system and the weakness of the overlap integral between them is stressed if a strong excitonic interaction is to result. Some examples are considered where this interaction could be strong.

LOCALIZATION AND INTERACTION IN QUASI-ONE-DIMENSIONAL SYSTEMS

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Abstract In a strictly one-dimensional disordered electron system, interactions between the electron lead to an insulator-metal transition. This can be shown using several approaches, in particular using an extension of the scaling theory of localization.[1] A more intuitive approach[2] considers the elastic and inelastic scattering lengths. The ratio of the lengths varies critically with the interaction parameter. One range of values leads to an essentially classical series resistance form which vanishes at zero temperature while in the other range quantum localization effects dominate and the resistance diverges at zero temperature.

A generalization of our method[3] gives a two step scaling approach for a system of chains which are weakly coupled by an interchain hopping t. For noninteracting electrons we determine the critical value t_c which separates insulating and conducting behavior. The inclusion of interaction is a difficult problem and only a simple generalization using the one-dimensional conductance of interacting electrons has been worked out.

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LONG-RANGE COULOMB INTERACTIONS IN QUASI-ONE DIMENSIONAL CONDUCTORS

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Instabilities and phase transitions in quasi-1D conductors are often discussed in terms of the so-called "g-ology" Hamiltonian. Here, I introduce the long-range Coulomb interaction ($V(r) = e^2/r$) in a system of coupled chains with intrachain backward-(g_1) forward-(g_2), and umklapp (g_3-) scattering. The long-range part of the Coulomb interactions gives rise to small momentum transfer interactions and, within the bosonization formalism, only affects the charge density degrees of freedom. In the absence of umklapp scattering, the problem can be solved exactly : the Coulomb interaction favours CDW and SDW instabilities with respect to superconductivity, and in addition, for $g_1 > 0$ there appears a "metallic" region in the g_1-g_2 diagram, with no instability at all. If $g_3 \neq 0$, these results are not changed qualitatively. The general origin of the metallic regions as well as implications for $(TMTSF)_2X$ superconductors are discussed. Finally, the crossover to three-dimensional order, induced by interchain backward scattering or tunneling, will be considered.

QUANTUM HALL EFFECT IN ORGANIC CONDUCTORS

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A theory of organic conductors in very strong magnetic fields is presented. In particular the conditions for integral and fractional quantization of the Hall effect are assessed, and the implications for recent experiments on organic superconductors are discussed.

ELECTRONIC STRUCTURE OF SUPERCONDUCTING CHARGE TRANSFER SALTS: COMPARISON OF TMTSF AND BEDT-TTF COMPOUNDS

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We explore the application of single-particle band theory to the electronic structure and static physical properties of the Bechgaard salts of TMTSF and the 2:1 compounds of BEDT-TTF. Especially striking is the similarity between the $k = (0,1/2,0)$ ordered structure of $(\mathrm{TMTSF})\mathrm{ClO}_4$ and the high pressure behavior of the BEDT-TTF compounds. We have estimated the important transfer integrals for several (BEDT-TTF) compounds from dimer splittings computed in the Mulliken-Wolfsberg-Helmholtz approximation. For the 2:1 salt containing ReO_4, which is superconducting at high pressure, we find an average anisotropy $t_{\parallel}/t_{\perp} \simeq 5$, with $\langle t_{\parallel} \rangle \simeq 250$ meV. Thus this compound has the lowest anisotropy of any known superconducting charge transfer salt, a result of the optimization of a key interchain interaction predicted earlier for the 2:1 salts of TMTSF.[1]

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[1] P.M. Grant, J. Physique 44 (Colloque C3), 847 (1983).

VARIATION VERSUS PRESSURE OF THE SUPERCONDUCTING STATE OF $(TMTSF)_2ClO_4$

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We have studied versus pressure, down to 0.1 K, the variation of both the magnetization and the electrical resistivity of $(TMTSF)_2ClO_4$. As measured by magnetization the initial variation of T_c is $(dT_c/dp)_{p=0} = 0.3$ K/kbar. Above 2 kar the transition to a superconducting ground state (S.C.) cannot be detected by magnetic properties. In the C^* direction H_{c1} decreases very rapidly $|(d(\mathrm{Log}\ H_{c1})/dp| = 80\%$/kbar. The resistivity measurements show that the anion ordering temperature does not decrease with pressure and the quenching effect on T_c can be obtained. We review the possible explanations for such a sensitivity to pressure of S.C.

ZERO MAGNETIC FIELD GROUND STATE INVESTIGATION IN $(TMTSF)_2ClO_4$

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The superconducting ground state in $(TMTSF)_2ClO_4$ is very sensitive to the anion ordering which can be controlled by a cooling rate. We report the investigation of the low temperature specific heat as a function of the anion disorder. As T_c is reduced we observe a decrease of the superconducting entropy and corresponding specific heat jump. A thermodynamical analysis of the data reveals that the pair-breaking effect associated with anion disorder is similar to the magnetic field one on type II superconductors: mixed state. T_c rounding is interpreted in term of a crossover between the superconducting coherence length and the size of the anion ordered regions. These results are compared with predictions of a singlet ground state model.

EVIDENCE FOR PARTIAL DIAMAGNETISM IN $(TMTSF)_2FSO_3$

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We have searched for and have found superconducting diamagnetic screening currents as well as Meissner effects in $(TMTSF)_2FSO_3$ at different pressures above ∿5 kbar. The largest signals, however, amount to only 2% of those expected for a perfect superconductor and are observed when the field is oriented transverse to the sample a-axis. The fact that the Meissner signals are not much smaller than the shielding signals suggests that superconductivity is well developped in isolated regions in the crystal which occupy only 2% of the sample volume. Possible correlations with the proposed "glassy" state of the FSO_3-anions are discussed.

THERMAL CONDUCTIVITY OF IRRADIATED SAMPLES $(TMTSF)_2X$

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We have measured the temperature dependence of thermal conductivity of samples $(TMTSF)_2X$ ($X = PF_6^-$, ClO_4^-, AsF_6^-) irradiated by X-rays. For small concentration of deffects (less than 0.1 %) there is no correlation of decrease of thermal conductivity with increasing electrical resistance of the sample. The thermal conductivity starts to decrease at higher doses when the phonon mean free path is comparable to the mean distance between the deffects. At low temperatures (10 K) the samples exhibit a deep minimum in thermal conductivity due to the resonant scattering of phonons on localized modes introduced by irradiation.

SPIN DENSITY WAVE RESPONSE IN $(TMTSF)_2PF_6$ AND ITS ALLOYS

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Frequency and electric field dependent transport studies below the metal-insulator transition are reported in $(TMTSF)_2PF_6$ and its alloys with $(TMDTDSF)_2PF_6$. While the low field dc nonlinearity is due to spurious effects (heating and microscopic breaks) the frequency dependent conductivity at microwave frequencies shows clear evidence for the first time for collective response due to a spin density wave mode. Impurities in the alloys strongly depress the frequency dependent response, indicative of pinning. The characteristic frequencies (microwave) are 2 orders of magnitude higher than for typical CDW materials. Further comparisons with transport due to collective charge density wave response will be given.

CRYSTAL STRUCTURES OF $TMTTF_2$-(As_x, Sb_{1-x})F_6 SOLID SOLUTIONS

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Electrical and magnetic properties of $TMTTF_2(As_xSb_{1-x})F_6$ solid solutions have a particular behaviour according to the value of x. In order to get a better understanding of the evolution of these properties we have determined the crystal structures of $TMTTF_2$-SbF_6 and of three solid solutions (x = 0,2; 0,5; 0,8) and analyzed in a comparative way the main structural parameters such as interplanar distances, interstack interactions and the disorder of the anions. We have also studied the variation of the cell parameters versus concentration and established a "concentration tensor".

NEUTRON DIFFRACTION STUDY OF MAGNETIC ORDERING IN $(TMTTF)_2SCN$

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$(TMTTF)_2SCN$ has been shown to have an antiferromagnetic ground state at low temperatures. The magnetic ordering appears at $T_N \sim 7K$. Neutron diffraction experiments were carried out on a 1g polycrystalline sample in order to specify the magnetic ordering. Diffraction data were collected on the D1B neutron diffractometer at the ILL, Grenoble (wavelength: 2.518 Å). Spectra were obtained at 1.5 K and 20 K with a counting period of 18 hours at each temperature. From the difference diagram and previous magnetic experiments, a magnetic structure is proposed, in which the spins are aligned antiferromagnetically along b^* and coupled ferromagnetically along c^* and a-axis.

LOW TEMPERATURE STRUCTURES ($T<10$ K) OF THE $(TMTTF)_2PF_6$ AND $(TMTSF)_2ClO_4$ COMPOUNDS.

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The low temperature structures of $(TMTTF)_2PF_6$, $(TMTSF)_2PF_6$ and $(TMTSF)_2ClO_4$ have been investigated below $T \simeq 10$ K by neutron diffraction for the PF_6 compounds, by neutron and X ray diffraction for $(TMTSF)_2ClO_4$. All refinements were performed in a $P\bar{1}$ space group.

At room temperature, $(TMTSF)_2PF_6$ or ClO_4 compounds show specific Se-Se interchain distances and a diadic character which is less pronounced than in $(TMTTF)_2PF_6$. The evolution of these interactions will be given for all compounds as a function of temperature and a comparative study will be presented below T = 10 K.

If the PF_6 anions are disordered near 300 K, the F atoms appear ordered at 4 K with a well defined position for each F atom in difference electron density maps. In $(TMTSF)_2ClO_4$, the ordering in the b direction, involves only weak translations of the Cl atoms, without any translation of the (TMTSF) molecules.

VIBRATIONAL PROPERTIES OF TMTSF AND TMTTF MOLECULES AND THEIR RADICAL CATIONS

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Infrared and Raman studies of organic conductors and superconductors have proven to be quite useful in characterizing their electronic and structural properties like e.g. CDW formation, electron-molecular vibration coupling, degree of band filling. The necessary prerequisite of these studies is a sound knowledge of the vibrational behaviour of the molecular constituents. We have carried out an extensive vibrational analysis of TMTSF, TMTTF and their radical cations as the (1:1) Br^- and ClO_4^- salts. The main steps of the procedure will be outlined with reference to TMTSF. They involve the recording of a wide body of Raman and infrared data including the polarized absorption spectra of the neutral molecule crystals which have been of special importance for the symmetry assignments of the observed frequencies. In addition, the normal mode frequencies and eigenvectors have been calculated using an empirical modified valence force field. The atomic displacement vectors in each totally symmetric mode will be displayed. The frequency changes following ionization observed for the present case and those reported for TTF will be compared and discussed. Vibronic absorptions are observed in the infrared spectra of the (1:1) salts and their frequency and intensity will be related to the strength of the electron-molecular vibration coupling.

Appeared in J. Chem. Phys. 80, 6210 (1984).

MAGNETIC ANIONS IN TMTTF AND TMTSF SALTS

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We prepared TMTTF and TMTSF salts of the MCl_4^{x-} anions, M=Fe, x = 1; M=Mn, Zn, x = 2. The materials have been structurally characterized and their stoichiometries and solid state properties depend on the charge of the anion. Preliminary results will be discussed on the effect of the anion on the properties of the wide variety of salts prepared.

IONICITY AND VIBRATIONAL SPECTRA OF MIXED STACK CT SYSTEMS: M_2P-TCNQ and M_2P-TCNQF_4.

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The results of a thorough vibrational analysis of the title compounds (M_2P = 5,10-dihydro-5,10-dimethylphenazine) are presented and allow the determination of the degree of ionicity (ρ) which is an important parameter in the interpretation of the physical properties of CT systems. Polarized infrared absorption spectra of an oriented film of M_2P-TCNQ let one: (i) to sort out the vibronic features due to the electron-molecular vibration interactions and (ii) to assign the IR active modes. From the frequency of the latter modes a value of $\rho = 0.4_9 \pm 0.1$ is obtained. The vibronic part of the spectrum has been successfully reproduced adopting the dimeric model for mixed stack systems introduced by A. Girlando et al., Phys. Rev., B26, 2306 (1982). For M_2P-TCNQF_4, which at room temperature has a regular mixed stack motif, an almost fully ionic ground state is found.
By lowering the temperature the IR spectrum displays a phase transition (T = 110 K) to distorted stacks as revealed by the rise of the vibronic absorptions and in agreement with the reported magnetic susceptibility data (Z.G. Soos et al., J. Chem. Phys., 74, 5287 (1981)).

TCNE AS PARTNER OF TTF: UNUSUAL STACKING PATTERN AND IONICITY IN CRYSTALLINE TTF-TCNE

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TCNE, one of the strongest electron acceptors, is well known as partner of CT complexes with a neutral electronic ground state and a typical ...DADA... stack motif. The only known structure where TCNE is present in partially ionic form seems hexamethylphenazine (M_6P)-TCNE (1). We have prepared TTF-TCNE by using various solvents and obtained two different crystal forms displaying different vibrational spectra. The interest in exploiting these data for determining the ionicity and the electron-molecular vibration coupling constants prompted us to investigate firstly the two crystal structures. Both polymorphs are monoclinic ($P2_1|n$) with four DA units in the cell, and correlated cell parameters. The stacking for polymorph I and II (hereafter PI and PII) is very similar consisting of a TTF-TTF-TCNE-TCNE motif with alternating pairs of TTF and TCNE. Within each pair the molecules are related by a crystallographic center of symmetry. The distance between the two planar TTF moieties in the pair is 3.58 Å, while that of nearly planar TCNE pair is 3.39 Å. The distance between TTF and the nearest TCNE is much more short: 3.15 Å indicating a strong CT interaction. PI presents perpendicularly to the stacking direction nearly planar sheets (dihedral angle 1.26° between TTF and TCNE planes) tightened by relevant C-H...N contacts. In PII the sheets are noticeably warped (dihedral angle 36.17°). The ionicity estimated by a bond length vs. degree of charge transfer diagram for similar compounds gives a value of about 0.5 for TTF-TCNE.

(1) S. Flandrois et al., Mol. Cryst. Liq. Cryst. 95, 149 (1983).

ESR- NMR- AND CONDUCTIVITY MEASUREMENTS ON RADICALCATION-SALTS (RKS) OF AROMATIC HYDROCARBONS.

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The RKS of aromatic hydrocarbons grown by anodic oxidation exhibit most of the electrical properties of the so called organic metals, but differ considerably in the magnetic properties of the highly delocalized spins. Lacking strong spin orbit coupling, the ESR-line widths are orders of magnitudes smaller as usual. The crystallization in separated stacks of cations and anions PF_6^-, AsF_6^- SbF_6^- favorizes onedimensional behaviour with the consequence of metal to isolator phase transitions. The transition temperatures depend strongly on the crystal growing conditions, i.e. temperature and solvent. We present ESR, NMR (Proton- and Fluorine) and conductivity measurements in the temperature region 300 K = T = 1,2 K on salts containing fluoranthene, naphthalene and pyrene as cations in order to determine the dynamical properties of the spin and charge carriers and their mutual correspondence.

CONDUCTING SOLIDS DERIVED FROM 1,6-DICHALCOGENO-PYRENS

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We present results for a new series of donors: 1,6-dichalcogeno-pyrens. The new materials are rather one dimensional, but anyway a metallic state is stable to low temperature in at least one of the new solids. In light of these results we discuss the apparent effects of increasing the dimensionality in organic conducting solids in general.

SALTS OF METAL DITHIOLATES WITH BEDT-TTF AND TMTSF

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The organic cations $TMTSF^+$ and $BEDT\text{-}TTF^+$ form low-dimensional metallic conductors with a variety of simple anions. Salts of metal dithiolene anions with small cations have also been shown to possess metallic properties at room temperature. The combination of these anions and cations within the same crystal structure affords the potential for a new type of conductor. Electrocrystallisation techniques previously used for the growth of single crystals of $(BEDT\text{-}TTF)_2X^-$ ($X = ClO_4^-$, PF_6^-, ReO_4^-, TaF_6^-) using BEDT-TTF and $Bu_4N^+X^-$ in THF or 1,1,2-trichloroethane proved unsuccessful when using the metal dithiolene anions $M[S_2C_2(R)_2]_2^-$ (when M = Ni or Pt, R = CN or CF_3) due to the competition at the electrode of the second electroactive species. Preparation of salts of this type has, however, been successfully achieved using a two compartment cell in which the anode compartment contained BEDT-TTF and $|Bu_4N||M(S_2C_2(CN)_2)_2|$ (M = Ni or Pt) and the cathode compartment TCNQ and $Bu_4N^+Br^-$ in THF. Preliminary electrical conduction studies indicated that the adducts have a room temperature conductivity of 10^{-6} Ω^{-1} cm^{-1} on compressed pellet samples and behave as semiconductors.

FIRST STEREOSELECTIVE SYNTHESIS OF DISSYMETRICALLY SUBSTITUTED TTF. NEW MATERIALS.

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The stereoselective access in high yields from mesoionic dithioles to new dissymetrical TTF derivatives is described. $NaBH_4$ reduction of mesoionic 2-amino 4-thioxo, 1,3-dithioles in the presence of an alkyl halide is a new route to 4-alkylthio-2--amino-1,3-dithioles which are easily converted into 2-alkyloxy-4-alkylthio 1,3-dithioles. In acidic media these compounds give new dissimetrically trans-substituted tetrathiafulvalenes. New single-chain charge transfer salts have been prepared and characterized.

SYNTHESIS OF TETRASELENANAPHTHALENE AND RELATED DONOR MOLECULES

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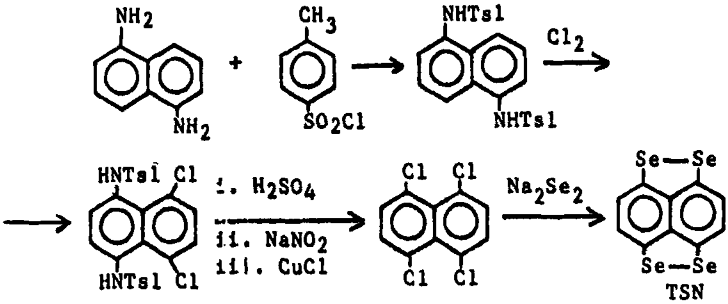
Tetrathiatetracene and its analogues are attractive donor molecules for the preparation of low-dimensional organic conductors. We have synthesized a new donor molecule, tetraselenanaphthalene (TSN), from the following scheme:[1]



Charge-transfer complexes of TSN were obtained by a diffusion method and electrochemical crystallization. The electrical conductivities of the crystal were low (S cm^{-1}): TSN•I$_{0.99}$ 1.6x10^{-5} TSN•TCNQ 5.97x10^{-7}; TSN(PF$_6$)$_x$ 4.5x10^{-6}. Other related donor molecules, such as ditelluratetracene, ditelluraanthracene, ditelluranaphthalene, and diselenanaphthalene, were also obtained. Several attempts to the synthesis of condensed aromatic molecules possessing polychalcogenides will be reported.

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[1] A. Yamahira, T. Nogami, and H. Mikawa, J. Chem. Soc., Chem. Commun., 904 (1983).

ELECTRONIC PROPERTIES OF LIQUID CRYSTALLINE ORGANIC CHARGE TRANSFER SALTS.

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We discuss criteria for the stability of new fluid charge-transfer salts in the liquid crystalline state, using theoretical concepts and the first synchrotron x-ray studies of discotic single liquid crystals. We find that the compounds can exist either as one-dimensional conductors or Mott insulators. Experimental transport and magnetic measurements are discussed.

ERASABLE OPTICAL SWITCHING IN ORGANIC CHARGE-TRANSFER COMPLEXES

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Materials capable of undergoing a change of state when subjected to optical radiation have been widely studied for potential applications in optical communications and optical storage media. We have previously reported reproducible bistable electrical switching between two resistance states in polycrystalline organometallic semiconductor films. More recently, we have been able to induce erasable optical and optoelectronic switching using a variety of laser sources in this same class of materials. The observation of optical switching between two states in these films has been made by electrical resistance and spectroscopic methods. Line or pattern generation has been observed for exposure above certain optical threshold levels. The spectral response and power density dependence on the optical switching threshold have also been measured; they provide significant evidence to support the electric field induced redox reaction mechanism of bistable switching. Finally, we wish to report the first demonstration of an erasable switching media capable of storing and processing multiple bits of information at each elemental region using a single laser source.

EVIDENCE OF INCOMMENSURATE PHASES IN KTCNQ CRYSTALS AS STUDIED IN THE SOLITON MODEL BY 14-N NUCLEAR QUADRUPOLE RESONANCE

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Measurements have been accomplished between room temperature and 300°C in order to study the phase transition previously reported at 122°C. A very peculiar trend as a function of the temperature of the ν^+ and ν^- 14-N NQR resonances has been obtained. The trend is indicative of the softening of two symmetric phonons at 142°C. Just above 122°C incommensurate lineshapes show up and increase in amplitude up to 142°C where the normal commensurate lines disappear. Above 142°C the incommensurate lines persist but modify their shape. A very large istheresis of the lineamplitude has been detected when the temperature goes up and down across the phase-transition temperature which should be better fixed, on the basis of our measurements, to 142°C. The results have been rationalized by using the time-independent sine-Gordon equation in the narrow-soliton limit.

ACCURATE ELECTRON-MOLECULAR VIBRATION COUPLING CONSTANTS FROM POWDERS OPTICAL SPECTRA: TCNQ AND TTF

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Several years ago it was shown how the electron-molecular vibration (e-mv) coupling constants (g) can be experimentally determined by analysing infrared reflectance spectra of dimerized segregated stack semiconductors (M.J. Rice et al., Phys. Rev. Lett. 39, 1359 (1977)). However only a few systems, all based on TCNQ, have been investigated so far, and the e-mv constants obtained are scattered in a relatively large range of values. The problem is that the proposed method is a difficult one, requiring single crystal spectra; furthermore, a non-linear curve fitting procedure has to be performed, in which the e-mv coupling constants are only part of the adjustable parameters. In the present communication we show that the above difficulties can be avoided by determining the e-mv coupling constants from the oscillator strength of the charge transfer transition and from the Raman and infrared frequencies of the vibrational modes coupled to the electron. The required data can be obtained by a careful examination of the Raman, infrared and near-infrared absorption spectra of powdered samples; the solution of a set of linear equations directly gives the g's. The simplified procedure has been tested on KTCNQ, obtaining results comparable to those achieved by the reflectance method. The previous determination of the TCNQ e-mv coupling constants are critically reviewed, sorting out a reasonably accurate and transferable set of g values for this molecular structure. Analogously, the spectra of the (1:1) bromide salt of TTF give e-mv coupling constants which nicely compare with those determined from the mixed stack complex of TTF with chloranyl (A. Girlando et al., J. Chem. Phys., 79, 1075 (1983)).

Appeared in Solid State Commun., 52, 801 (1984).

ANISOTROPY OF THERMOPOWER IN MEM(TCNQ)$_2$

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Measurements of the thermoelectric power along the three crystallographic axes of MEM(TCNQ)$_2$ are reported. The first order metal-insulator phase transition at 338 K is observed as a discontinuous change between the temperature independent values $S_a = -50$ $S_b = -35$ and $S_c = -65\mu\,\mathrm{VK}^{-1}$ in the metallic phase (T 338 K) and the values $S_a = -7$ $S_b = -48$ and $S_c = +35\mu\,\mathrm{VK}^{-1}$. In the semiconducting phase S_b is almost temperature independent, but both S_a and S_c increase upon cooling. At 314 K, a strong anomaly is made evident as a drastic change in the slope of S_a and S_c versus temperature. The electrical conductivity accurately measured along the three crystallographic axis, also shows an anomalous decrease for $T < 314$ K. The thermopower and conductivity anomalies at 314 K, are consistent with a second order phase transition originated in a change of cation motion, and associated mainly with a decrease in the mobility of the charge carriers, the role of a possible increase in the gap being secondary.
For $T < 314$ K there is a predominant decrease of the electron mobility mainly along c but also along the a axis, while, along b, both the electron and hole mobilities decrease, remaining with equal values.

ANISOTROPY OF ELECTRON TRANSPORT IN MTPP$(TCNQ)_2$ NEAR THE 311 K PHASE TRANSITION

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The first order phase transition of methyltriphenylphosphonium $(TCNQ)_2$ at 311 K is studied. Measurements of thermopower (TEP) and electrical conductivity were made along the three different crystallographic axes. The TEP measurements along the three crystallographic axes show a strong anisotropic behaviour. In the high temperature phase the TEP is almost temperature independent with a nearly isotropic value $-60\ \mu VK^{-1}$. In the low temperature phase the TEP shows a strong anisotropy; the value parallel to the TCNQ chains increases slightly upon cooling becoming positive, while the values in the directions perpendicular to the TCNQ chains remain negative and almost temperature independent. These results show that the increase of the order in the phenyl groups and the slight change in the TCNQ overlaps during the phase transition lead to a large and anisotropic decrease of the charge carriers mobility, the electron becoming significantly less mobile than the holes along the TCNQ chains.

CONDUCTING TCNQ SALTS OF THE IRON SANDWICHES $|C_5H_5Fe(II)C_6(CH_3)_6|^+$ AND $|C_6(CH_3)_6|_2$ Fe(I, II)$^{1,2+}$

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Exchange with KI on resin give the iodides of the title cations, isolated and characterized. The usual redox reaction starting from TCNQ generate the corresponding tetracyanoquinodimethanides salts. Characterization and properties of a variety of new semi-conducting complexes will be presented.

ELECTRONIC STRUCTURE OF THE INCOMMENSURATE QUASI-ONE-DIMENSIONAL METAL $Hg_{3-\delta}AsF_6$

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The synthetic compound $Hg_{3-\delta}AsF_6$ has two interpenetrating families of linear chains of mercury atoms. These chains give rise to one-dimensional metallic properties. This material has been of interest lately because of its unusual lattice properties and unusual superconductivity, as found by the Pennsylvania group. The coupling between the chains in the x- and y- directions is strong, yet the Fermi surface contains planar sections, as determined from dHvA measurements by Razavi et al., and very sharp corners between these planar sections as determined from a logarithmic divergence of the magnetoresistance. In addition, the incommensurate nature of this compound is of considerable interest, because $\vec{k}$ is not a good quantum number in incommensurate systems. A mathematical theory imbedding these structures in multidimensional spaces has been proposed by Janner and Janssen. Nevertheless, the material is found experimentally to be an excellent metal with an extremely long mean-free-path at low temperatures. We carried out a calculation of the electronic band structure, including the effect of the incommensurate potential. We found the existence of novel selection rules which severely limit the effect of incommensurate potential, as well as the effect of the strong interchain coupling. We calculated the matrix elements of the incommensurate potential and measured them by measuring the magnetic breakdown effect in a dHvA experiment.

CHARGE DENSITY WAVE DYNAMICS IN LINEAR CHAIN COMPOUNDS

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Recent experiments concerning the dynamics of charge density waves in materials $NbSe_3$, TaS_3, $(TaSe_4)_2I$ and $K_{0.3}MoO_3$ will be summarized. The frequency dependent response points to the importance of disorder, associated with random impurity pinning of the phase of the condensate. This leads to a low frequency behaviour $\sigma(\omega) = A(i\omega)^{\alpha}$ with $\alpha<1$, similar to that observed in disordered materials and glasses. At high frequencies, the conductivities saturate at values close to those which could be observed in the absence of the Peierls transitions. In the current carrying state both coherent and incoherent effects are observed. The former manifest themselves in current oscillations and sharp interference phenomena when both ac and dc fields are applied, the latter in broad band noise, finite widths of the Fourier transformed current oscillations and volume dependent oscillation amplitude. These phenomena indicate finite length scales associated with the phase correlations. These are further studied by employing a temperature gradient method which strongly suggest that phase-phase correlation effects (Fukuyama, Lee-Rice correlation) and current-current correlations are determined by different characteristic lengths.

ELECTRIC FIELD DEPENDENCE OF ELASTIC STIFFNESS IN LINEAR CDW SYSTEMS.

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Using the vibrating reed technique, the low frequency (< 20 KHz) Young's modulus E of TaS_3,$(TaSe_4)_2I$, and $NbSe_3$ was measured vs. temperature and electric field. We have established that (1) $E = E_o$ for $V < V_T$ but $E < E_o$ for $V > V_T$. (2) E approaches a limit E_∞ for $V >> V_T$. (3) $\Delta E = E_o - E_\infty$ well below the transition has the same order of magnitude as the dips in E_o near T_p. (4) $\Delta E/E_o$ increases strongly with T_p. These observations indicate decoupling of the CDW from the lattice. Possible mechanisms for the effect of the decoupling will be presented.

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THERMOELECTRIC ASPECTS OF CHARGE DENSITY WAVE TRANSPORT

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We measure the field-dependent thermoelectric power of TaS_3 and other charge density wave conductors, and apply a general analysis of thermoelectricity in non-ohmic conductors. The Peltier heat coefficient of the nonlinear electric current is zero at high temperatures and independent of applied voltage at all temperatures. Our results are consistent with a moving condensate accompanied by low-temperature phonon drag, but not with certain alternative nonlinear conduction mechanisms.

THE HIGH FREQUENCY LIMIT OF CHARGE DENSITY CONDUCTION

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The high frequency (micro and millimeter wave) response of the collective charge density wave (CDW) mode was measured in the linear chain compounds TaS_3, $(TaSe_4)_2I$ and $K_{0.3}MoO_3$. In all of the nominally pure materials the conductivity saturates at these frequencies at values close to the "metallic" value which would be obtained in the basence of Peierls transitions. Impurities strongly depress the high frequency conductivity. These results indicate that the high frequency limit is sensitive to details of CDW motion. Furthermore the conductivity in this frequency is essential to evaluating the frequency dependent response at (optical) frequencies comparable to the single particle gap. Comparisons with the results of optical studies and the relation to the high field ($E \to \infty$) limit will be discussed.

PRESSURE AND TEMPERATURE DEPENDENCE OF THE CONDUCTIVITY AND CHARGE DENSITY WAVE THRESHOLD FIELDS IN $NbSe_3$ AND TaS_3

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The temperature and pressure dependences of the conductivity and threshold field have been studied for the CDW systems TaS_3 and $NbSe_3$. We have found a depression of the Peierls transition temperature and a depression of the threshold field for onset of sliding CDW conductivity with increasing the applied pressure. These observations will be discussed in context of the pinning mechanism of the CDW domains in these systems.

DISCRETIZED VOLTAGE JUMPS IN THE CHARGE-DENSITY-WAVE NOISE OF TaS_3

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Using a transient digitizer we have captured the voltage oscillations (narrow-band noise) in the charge-density-wave (CDW) conduction state. For fields E near threshold E_T (frequency f below 1 kHz) the periodic voltage structure decomposes into stochastic jumps which are bidirectional, and quantised in multiples of $\Delta V(E)$. As $E-E_T$ increases the number and magnitude of the jumps increases until a stable periodic pattern develops, comprised of voltage spikes all pointing in one direction.
We analyze the data in terms of the vortex array model recently proposed by Ong, Verma and Maki (Phys. Rev. Lett. 52, 663 (1984).) The jumps are interpreted in terms of a vortex entry or exit with $\Delta V \sim$ a phase slip of π. The value of ΔV provides a value for the vortex drift velocity v_D which is consistent with time-scales of the experiment.

A MODEL FOR THE $ZrTe_5$ TRANSPORT PROPERTIES BASED ON AN EXPERIMENTALLY DETERMINED ELECTRONIC STRUCTURE

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A theoretical model for the transport properties of $ZrTe_5$ has been developed based on a complete de Haas-Shubnikov determination of its electronic structure. We observe three accurately elipsoidal Fermi surfaces with the sum of the volumes of the two smaller surfaces equaling the larger to within experimental error. We have also determined the effective masses and Dingle temperatures. All of the data is consistent with parabolic energy dependencies for the three elipsoidal volumes. Using this information a model of the electronic structure can be constructed and used to explain features of the unusual and heretofore unexplained transport properties reported in this system. We construct three Fermi spheres (2 electron one hole) which mirror the properties of the three elipsoids important to electronic transport such as number of carriers, effective mass, etc.
We then use Thomas-Fermi theory and Boltzman equation transport theory to calculate the temperature dependence of the transport properties. No recourse is made to the onset of charge density waves or other phase transformations which have been suggested by earlier work but have so far eluded detection.