

HIGHLIGHT OF THE MONTH

Mixed-stack organic charge-transfer compounds

(A few steps in the jungle)

C. Koenig and C. Hoerner

GMCM - University Rennes-1, France

1 Introduction

Charge-transfer (CT) molecular compounds are composed of two types of nearly flat organic molecules: closed-shell- π -electron donors (D) and acceptors (A). In the crystalline state, the tendency for these molecules is to pile up along linear and often parallel chains, like hands put one above the other one, thus forming either segregated stacks: $\dots D - D - D - D \dots$ and $\dots A - A - A - A \dots$, or mixed-stacks: $\dots D - A - D - A \dots$. The electron transfer from D to A is at the origin of the very interesting electronic, magnetic and optical properties of these compounds. For example, it is responsible for the one-dimensional conductivity in segregated stack compounds such as TTF-TCNQ; but this high conductivity is relatively rare. In the mixed-stack D-A (1:1) CT-compounds, such as TTF-CA, TTF-BA, TMB-TCNQ, TMPD-CA, DMTTF-CA, etc. (see [1] for a zoological description), the charge transfer occurs within the chains and all these compounds are small-gap semiconductors.

Some of those mixed-stack compounds exhibit uncommon electronic instabilities, which give rise to different types of reversible structural transitions under pressure, temperature or photo-irradiation. A common feature of all these transitions is the loss of symmetry-inversion in the crystal below a critical temperature T_c or above a critical pressure P_c .

This symmetry breaking is accompanied by a more or less abrupt variation of the charge transfer. In the vicinity of the transition, very interesting and puzzling phenomena are observed: colour variation, precursor effects, phase-coexistence and thermal hysteresis, disorder, etc., and also non linear excitations.

The aim of this highlight is to review the essential aspects of the observed instabilities. For the sake of "simplicity", it will be focused on the 1:1 mixed-stack compounds, disregarding more complex structures such as the D_2A packings, which generally do not form well defined stacking chains.

2 Structural properties

What is striking when considering the structural data at room temperature is the great diversity of possible crystalline structures for compounds constituted with very similar molecules.

Some of them exist in different structures at room temperature and atmospheric pressure: for example monoclinic and triclinic TMB-TCNQ [2, 3], or green (mixed-stack) and black (segregated) phases for TTF-CA [4].

Also, it seems hopeless to try and find any systematics in the structural properties of whole families such as the tetrathiafulvalene-tetrahalo-p-benzoquinones, or TTF-A (A = FA: Fluoranil, CA: Chloranil, BA: Bromanil, IA: Iodanil), of general formula $C_6S_4H_4-C_6X_4O_2$. These four compounds form indeed mixed-stacks, but in different structures: TTF-FA and TTF-IA are triclinic with one TTF and one FA or IA entity per unit cell, pertaining to one chain [5, 6]. Green TTF-CA is monoclinic $P2_1/n$ with two TTF and two CA per cell (two equivalent chains) [5], whereas TTF-BA forms two non-equivalent and non-parallel chains in a triclinic structure [7]. The situation is far more complex than in "standard" metallic and semi-conducting compounds, and in those conditions, no obvious trends can be deduced from simple considerations such as the increasing electronegativity in the halogen series: at room temperature TTF-FA, TTF-CA and TTF-IA are nearly neutral, whereas TTF-BA is ionic.

3 What is known concerning the two phases

The structural and dynamical effects associated with the phase transitions in the 1:1 CT complexes have been studied for many years, mainly in US, Japan, Italy and France. For some of these materials, especially TTF-CA, an ensemble of fundamental physical properties has been analysed, which can be used as a guide and control for theoretical investigations:

- The variations of the intra- and inter-molecular vibration modes have been measured by infra-red and Raman spectroscopies [4, 8]. The appearance of new IR lines of a_g symmetry below T_c or above P_c is the clear signature of the loss of the center of inversion. These experiments are therefore among the most important tools for analysing the transitions.
- The exact positions of the atoms in the high symmetry phase have often been obtained by X-ray measurements [5, 7]. For TTF-CA, an analysis of the structural changes at the transition (which symmetry-elements are lost?) has been performed by neutron diffraction [9] and NQR [10]. A distortion of the molecules has been observed in the low symmetry phase, accompanied by a weak "dimerization" along the stack (weak D-A pairing by a reduction of $\simeq 0.1\text{\AA}$ (2%) of their intermolecular distance). In other compounds, the loss of centrosymmetry has also been interpreted as a dimerization (as the most probable way by which it can happen), though the corresponding molecular displacements have not been estimated.
- The width of the electronic gap is estimated from the position of the "charge transfer excitation band" in the polarized reflection spectra [11, 12]. It is of about 0.8 to 1 eV in TTF-CA.
- The value of the charge transfer in each crystalline phase is deduced in an indirect way (which will be discussed hereafter) from Raman, infra-red and reflectivity measurements [12, 2].
- The magnetic state of the compounds is obtained from susceptibilities deduced from ESR experiments [8, 13].
- An estimate of the entropic contribution to the free energy at the transition has been deduced from specific heat measurements [14].

4 Which kind of transition?

The common characteristic of the structural transitions observed in these compounds is the appearance of an electric polarization along the chains below T_c or above P_c . However, there is an important qualitative difference with respect to the standard ferroelectric transitions occurring in ionic compounds such as $BaTiO_3$:

Instead of single ions, the sites here are large deformable molecules and the molecular

orbitals involved in the charge transfer and the polarization are constructed by linear combinations of a dozen of atomic wave-functions. This allows more complex electronic configurations and several original phenomena accompanying these transitions have been observed.

The two phases have been *a priori* characterized by two parameters: the **charge transfer** ρ between D and A , and the **dimerization parameter** η , which represents the displacements of the molecules in the low symmetry phase, with respect to equidistant positions along the chains. There exists experimental evidence that the coupling between these two parameters is complex, since very different behaviours are observed at the transition for compounds presenting only small structural or chemical differences:

-TTF-CA [12] is the prototype for the "neutral to ionic" transition. The "neutral" phase, at high temperature or low pressure, is non-dimerized, with a weak charge transfer ($\rho \simeq 0.3e^-$) from TTF to CA. This charge transfer undergoes a sudden jump at $T_c \simeq 80K$, and reaches a value of about $0.7e^-$ in the low temperature dimerized phase ("ionic" phase).

- In TTF-BA [7], in which the four chlorine atoms of CA are replaced by four bromine atoms, a "dimerization" (i.e. a loss of centrosymmetry) occurs at the transition temperature ($50K$), without any noticeable change in the degree of ionicity ($\rho \simeq 0.8e^-$ in both phases).

It must be noted here that this charge transfer and its variation have to be shared among all the atoms of each molecule, so that the corresponding value for each atom is very small ($\simeq 0.1e^-$ or less), and could be accounted for by small deformations of the molecular orbitals.

Magnetism plays also a great part in the nature of the transition. Most of the compounds considered here are diamagnetic in the dimerized phase, apart from a weak paramagnetic susceptibility attributed to intrinsic defects (see below). The standard explanation for this is the formation of $S=0$ electronic states due to the pairing of the D^+ and A^- molecules. Their magnetic behaviour at high temperature together with the charge transfer variation and the structural data have been used in the literature to classified the mixed-stack compounds in several categories, according to the principal characteristics of their transitions:

1 - Some compounds remain diamagnetic in the non-dimerized phase. This is quite understandable in the case of TTF-CA, where the molecules become suddenly nearly neutral above T_c . This is a typical **neutral to ionic** transition. Due to its similar magnetic behaviour, monoclinic TMB-TCNQ has also been classified in that category [3] though in this compound the charge transfer discontinuity is much smaller ($\Delta\rho \simeq 0.1e^-$) [2]. By extension, its high temperature phase is also called "neutral" phase, despite its non-negligible ionicity ($\rho \simeq 0.6e^-$).

2 - In TTF-BA, the charge transfer is relatively high in both phases, without discontinuity at the transition. The high temperature phase is paramagnetic (and not neutral!), with probably an antiferro- or ferri-magnetic coupling between adjacent D and A molecules. The similarity of its susceptibility with what is obtained in an Heisenberg linear chain of spins $1/2$ [7] suggests here a **spin-Peierls** mechanism for the transition.

3 - For triclinic TMB-TCNQ, where ρ keeps an intermediate value of about $0.6e^-$, the magnetic susceptibility remains weak in both phases [3]. The only noticeable anomaly is in the dielectric constant, so that the transition is only characterized by the **ferroelectric** ordering along the chains, induced by the dimerization.

4 - TMPD-CA has to be considered separately [8]. The estimated degree of ionicity is also of about $0.6e^-$ in both phases. But the vibrational spectra show that the stack is dimerized even at room temperature, and that the high temperature phase is characterized by a non-negligible disorder due to tilting and distortion of the molecules. In that case, the transition is supposed to be of an **order-disorder** (orientational) type.

The transition itself is often a first order one, but its characteristics vary in the different compounds and for different experimental conditions: for example, the charge transfer discontinuity is weaker and the thermal hysteresis larger in monoclinic TMB-TCNQ than in TTF-CA. Under increasing pressure, this discontinuity decreases [15, 16] suggesting possible existence of a critical point beyond which it would be of second order. On the other hand, a large domain of coexistence of the two phases can be observed in some compounds (e.g. DMTTF-CA [17]).

5 Charge transfer and vibration modes

A fundamental parameter characterizing the high and low symmetry phases is the charge transfer ρ from D to A . Therefore, its precise experimental determination is of foremost importance. The value of ρ is principally extracted from the IR and Raman spectra, by assuming a linear variation of the frequency of specific intramolecular modes with ionicity, which are assumed to be otherwise unperturbed by environmental effects. Extensive work [18] on TTF-X-p-benzoquinones has shown that two categories of intra-molecular modes are particularly interesting:

- The a_g totally symmetric modes (with respect to the isolated molecule point group), which are Raman active and are observable in the IR spectra only in the absence of

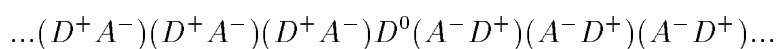
the center of inversion. They are coupled by symmetry with the electrons, so that their frequency variation versus ρ may be highly nonlinear. In the literature, this coupling with the electrons is often called e-mv (i.e. electron-molecular-vibration) coupling, or vibronic interaction.

- The b_u non-symmetric modes, which are only observable in the IR spectra and whose frequencies can be used as ρ probes by interpolating between the corresponding frequencies of the fully neutral and fully ionic species. The step-like curve of ρ versus temperature presented in the literature for compounds undergoing a neutral to ionic transition [2, 12] is in fact a direct translation of the step-like variations of their intramolecular modes versus temperature.

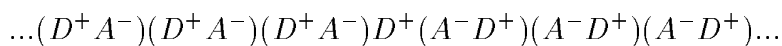
However, experimental tests on the linear variation of these b_u modes in TTF derivatives have revealed some anomalies, and no such check can be made for the CA molecule, in the absence of synthesized compounds where a partial degree of ionicity could be supposed to be fixed by stoichiometry [4]. The charge transfer in those compounds is nevertheless extracted from the "most reliable" intramolecular vibrations, for example the b_{1u} C=O stretching mode of CA in TTF-CA. It is obvious that due to the importance of this parameter in the analysis and modelization of the transition, the assumption of linearity has to be somehow verified, at least by theoretical simulations when no direct experimental control seems possible.

6 Domain walls and dynamical properties

One of the most interesting originalities in the series of mixed-stack compounds is that a wide range of dynamical properties: non-linear conductivity, magnetic susceptibility, ESR motional narrowing [19], dielectric response [21], spin-lattice relaxation time [20], etc., is connected to the existence of localized defects, which are mobile along the chains near the transition. In the low temperature phase, their concentration (estimated from susceptibility measurements) is about 10^{-5} per unit cell. They are identified with intrinsic phase mismatch defects in the lattice, such as soliton-like defects in polyacetylene [22] or in halogen-bridged Pt or Pd complexes (often called MX chains) [23]. They correspond to domain walls between ionic states of opposite polarizations in the ionic phase, carrying a charge or a spin:



or



In the neutral phase, they correspond to fluctuating ionic domains just above T_c :

$$\dots D^0 A^0 D^0 A^0 (D^+ A^-) (D^+ A^-) (D^+ A^-) D^0 A^0 D^0 A^0 \dots$$

The detailed study of the dynamics associated to these domains is of course a key for the understanding of these systems.

7 Models

It seems obvious that these transitions result from a delicate interplay between electronic, magnetic and dynamical interactions in the crystal. The first empirical attempts to explain these phenomena relied on a competition between the energy cost of the transfer of one electron from D to A (which can be estimated from the difference between the ionisation energy of D and the affinity of A) and the Madelung energy gained in this transfer [11, 24]. However, several other parameters have to be taken into account to obtain a quantitative description of these transitions: electronic charge transfer integrals, on-site Coulomb repulsion, coupling with the phonons, etc.

Later on, theoretical studies of these phase transitions have been developed, principally based on expansions of the free energy of the crystal [25, 26], or on one dimensional model-Hamiltonians of Su-Schrieffer-Heeger or extended-Hubbard type [27]. These Hamiltonians are similar to those which were devised to study the elementary excitations (solitons, polarons) in polymeric chains such as polyacetylene [22].

In these models, each molecule is represented by one orbital on a fictitious particle in a one-dimensional chain. The most complete Hamiltonian that has been considered can be written as:

$$\begin{aligned} H = & \sum_{l,\sigma} T_{l,l+1} (C_{l,\sigma}^+ C_{l+1,\sigma} + C_{l+1,\sigma}^+ C_{l,\sigma}) + \frac{\Delta}{2} \sum_l (-1)^l n_l \\ & + U \sum_l n_{l,\uparrow} n_{l,\downarrow} + V \sum_l n_l n_{l+1} + K \sum_l (u_l - u_{l+1})^2 \end{aligned}$$

The orbitals with even and odd l represent respectively the LUMO (lowest unoccupied molecular orbital) of A and the HOMO (highest occupied molecular orbital) of D . $C_{l,\sigma}$ ($C_{l,\sigma}^+$) is the annihilation (creation) operator of an electron at site l with spin σ , and $n_{l,\sigma}$ the corresponding number of electrons. Here $T_{l,l+1}$ is the electron transfer, Δ is the site energy difference between D and A molecules, U is the on-site Coulomb repulsion, and V is the Coulomb interaction between nearest neighbours. Finally, K represents the

electron-lattice interaction, u_l is the particle displacement along the stacking axis. $T_{l,l+1}$ is supposed to vary linearly with $u_l - u_{l+1}$.

Obviously, simulations lead to various kinds of transitions (with or without charge transfer variation, with or without dimerization) depending upon the choice of the values of the parameters T , Δ , U , V and K . In the most explicit calculations, the transition has been studied as a function of Δ for fixed values of T , U and V . The introduction of the electron-phonon coupling K was necessary to reproduce the right values for ρ in both phases of TTF-CA, but it smoothed out its variation at the transition.

These schematic models give a general description of the sensitivity of a class of materials to the magnitude of the different interactions. However, they have no direct relation to the experimental results for one precise compound, due to the impossibility of fixing a set of parameters which would be really specific to this compound. Moreover, they cannot analyse the interplay between electronic distribution and dynamics at the atomic level.

8 Are they as low-dimensional as that?

The anisotropic character of these crystals has been observed in their polarized light optical properties, parallel or perpendicular to the chains. On the other hand, the strong anisotropies obtained in the dynamical properties near the transition (dielectric constant, conductivity) are due to intrinsic defects mobile along the chains. There are however some indications that the three-dimensional aspects may be important in the interpretation of the experimental data.

In most of these compounds, the particularly flat character of the molecules is enhanced by the fact that they are tilted with respect to their stacking axis and often form in two other directions, very well defined planes containing molecules of both species, pertaining to different stacking chains. For someone who is not concerned with the "linear chain" aspect, the resulting structure can be described in a more precise way by a stack of interacting parallel molecular planes. Those planes are conspicuous in structures already published such as TMB-TCNQ [2], or TTF-p-QC1₂ [30], which is a fifth member of the family of TTF-X-p-benzoquinones, obtained by replacing two equivalent Cl atoms of CA by two hydrogen atoms (triclinic, 1 chain/cell). They are also visible in green TTF-CA [9] but form in that case two intersecting stacks of planes due to the existence of a gliding mirror connecting the two equivalent chains in the unit cell.

The fact that the molecules are arranged in such a peculiar way shows that the "inter-chain" interactions, which are in great part "intra-plane" interactions, are of foremost importance in the stability of the structure. In particular, the interactions between the hydrogen atoms of TTF and the halogen and oxygen ones of the neighbouring X-p-benzoquinone should be

considered with special care. Moreover, it would also be interesting to understand the very different crystalline structure of TTF-BA, with two crossed linear chains and no obvious molecular planes, which is certainly connected to its different behaviour.

The intra-chain interaction is probably the strongest interaction in the crystal. From a pure geometrical point of view, it couples the successive above-mentioned molecular planes. Its analysis helps to clarify the analogies which have been made between those CT complexes and polyacetylene or MX chains.

It has been known for a long time (and it is easy to show by ab-initio calculations [28]) that the molecular orbitals involved in the crystalline structure: the LUMO of the acceptor A and the HOMO of TTF in TTF-p-benzoquinones, are formed from linear combinations of p-atomic orbitals pointing perpendicularly to the molecular planes and coupled by π interactions. Due to the tilt of the molecules with respect to the chain, the interaction between the molecular orbitals occurs in a zig-zag way rather than exactly along the stacking axis: a given A molecule interacts more strongly with the right part of the TTF molecule situated just below, and the left part of the one just above [5, 8].

Nevertheless, this inter-molecular interaction is much more of σ than of π type, which makes an essential difference with polyacetylene, apart from the fact that the two partners of the pair here are of different chemical species. It resembles more the type of interactions occurring between the d_{z^2} orbitals of the metal and the p_z orbitals of the halogen atom in the MX chains. Therefore, the recent ab-initio theoretical studies performed by Alouani et al. [29] on the dimerization in these mixed-valence halogen-bridged CT complexes are particularly interesting. These calculations were able to explain the origin of the charge density waves (CDW) observed in the Pt and Pd based compounds, as well as the spin density waves (SDW) in Ni based compounds. Especially, they have shown that the inter-chain interactions, propagated through ligands surrounding the metal atoms, are necessary to generate the insulating ground state and the lattice distortion observed in the Pt based compounds.

However, the analogy with the organic complexes should be considered with some caution: instead of a "dimerization": $\dots XM - XM - XM\dots$, the transition in the Pt and Pd based MX chains induces a doubling of the unit cell by creating an alternation of isolated M atoms and triplets XMX along the chains: $\dots M - XMX - M - XMX\dots$, with non-negligible atomic displacements ($\simeq 10\%$).

A point which is worth noticing in these comparisons concerns the non-linear excitations. The large enhancement of σ or ϵ in the vicinity of T_c [19, 21] is attributed to the increased mobility of intrinsic defects of soliton-type, associated with the domain walls. This type of excitations exists also in polyacetylene and some MX chains, inducing the appearance of an absorption peak in the middle of the gap. It is very interesting to remark that

this extra-peak does not appear in MX-materials with strong inter-chain interactions [23]. Such an analysis of the absorption spectra below the charge-transfer peak in the 1:1 CT complexes (which is lacking) would give valuable information on the strength of the inter-chain coupling in these compounds.

Finally, it must be noted that, when going beyond the usual picture of solitons moving along linear chains, it is difficult to visualize in 3-dimensions those domain-walls and their displacements. Due to the very weak dimerization observed in some of these CT complexes, they may correspond to weak displacements of the above mentioned molecular planes, accompanied by distortions of the molecules in these planes. Pending new crystallographic studies in the low temperature or high pressure phases for most of these compounds, this is still an open question.

It will most probably be necessary to take properly into account those 3-dimensional interactions to reproduce correctly the subtle transitions occurring in the 1:1 CT organic compounds. This is confirmed experimentally by the fact that, in TTF-CA, the unit cell undergoes a small discontinuous contraction just at the transition temperature, in the directions \vec{b} ($\simeq 0.5\%$) and \vec{c} ($\simeq 0.1\%$) i.e. roughly perpendicularly to the direction \vec{a} of the chains [9]. This implies a discontinuity in the inter-chain interactions at the transition.

The lattice contraction, coupled with the charge-transfer discontinuity, induces also a sudden variation of the Madelung energy of the crystal. This Madelung energy is an important factor of stabilization of the ionic phase. Nevertheless, it is usually reduced in the model Hamiltonians to the nearest neighbour Coulomb interaction *along* the chains, which completely neglects the implications of its 3-dimensional character.

9 Perspectives

It is now possible to tackle these problems by ab-initio self-consistent numerical techniques. These calculations should give a really local description of the crystal on both sides of the transition: variation of the ionicity of each atom, charge transfer between the molecules and Madelung energy in the crystal, total energy, forces and relaxations, etc., i.e. quantities which are related to the experimental results obtained for these materials. The direct calculation of the charge transfer can be compared to its indirect experimental determination deduced from vibration spectra; the self-consistent determination of the potential on each atom may help to interpret local measurements such as the NQR on the Cl atoms in CA [10]; these calculations could also be useful for a less ambiguous determination of the parameters entering the Hubbard-like Hamiltonian describing the actual transitions.

The aim of these studies is to build a general theoretical scheme in the frame of which all

the different mixed-stack compounds and their different behaviours could be described, on the same footing, in a quantitative way.

Several numerical codes based on similar techniques are now available. These techniques rely on different basis-sets for the description of the electronic structure within the Local Density Approximation (LDA) or on more sophisticated treatments of electronic exchange and correlations: Linear Muffin-Tin Orbitals (LMTO), plane waves (LAPW), Projected Augmented Waves (PAW) [31], etc. The latter is coupled to molecular dynamics calculations, so that it allows straightforward relaxations, finite temperature simulations and ab-initio determinations of the eigenfrequencies and eigenvectors of the molecular vibrations [32].

Our preliminary results in this domain seem promising. The nature of the intra-chain interactions can be analysed [28] with the help of a full-potential LMTO code which has been devised to study the dimerization along linear polymeric chains [33]. The importance of the inter-chain interactions can be studied with the use of a faster LMTO-ASA 3-dimensional code [34]. For example, we have obtained with this code a small gap and a reasonable value of the charge transfer in TTF-p-QC l_2 [35]. With the PAW program, it has been possible to prove numerically that for an isolated charged CA molecule, the C=O stretching mode indeed varies linearly with the charge [36]. This provides the necessary confirmation of the empirical rule from which the experimental value of the charge transfer is extracted.

The difficult points in those calculations are the large number of atoms and the molecular character of the crystal, i.e. the importance of the interstitial region. In these weakly interacting systems, the exchange and correlation interactions have to be treated carefully, which requires to go beyond the possibilities of the LDA (self-interaction, non-local corrections, etc.).

References

- [1] - TTF = tetrathiafulvalene ($C_6 S_4 H_4$)
- DMTTF = 2,6-dimethyltetrathiafulvalene ($C_8 S_4 H_8$)
- TMPD = tetramethyl-p-phenylene ($C_{10} N_2 H_6$)
- TMB = 3,3',5,5'-tetramethylbenzidine ($C_{12} N_2 H_{16}$)
- TCNQ = tetracyanoquinodimethane ($C_{12} N_4$)
- CA = tetrachloro-p-benzoquinone or chloranil ($C_6 Cl_4 O_2$)
- BA = bromanil ($C_6 Br_4 O_2$)
- etc...

- [2] Y. Iwasa, T. Koda, Y. Tokura, A. Kobayashi, N. Iwasawa and G. Saito, *Phys. Rev. B* **42**, 2374 (1990)
- [3] Y. Iwasa, "Busseti Kenkyu (research on Properties of Matter)" **58-5** (1992)
- [4] A. Girlando, F. Marzola and C. Pecile, *J. Chem. Phys.* **79**, 1075 (1983)
- [5] J.J. Mayerle, J. B. Torrance and J.I. Crowley, *Acta Cryst. B* **35**, 2988(1979)
- [6] S. Matsuzaki, T. Hiejima and M. Sano, *Bull. Chem. Soc. Jpn.* **64**, 2052 (1991)
- [7] A. Girlando, C. Pecile and J.B. Torrance, *Sol. St. Comm.* **54**, 753 (1985)
- [8] A. Girlando, A. Painelli and C. Pecile, *J. Chem. Phys.* **89**, 494 (1988)
- [9] M. Le Cointe, M.H. Lemée-Cailleau, H. Cailleau, B. Toudic, L. Toupet, G. Heger, F. Moussa, P. Schweiss, K.H. Kraft and N. Karl, *Phys. Rev. B* **51**, 3374 (1995)
- [10] J. Gallier, B. Toudic, Y. Delugeard, H. Cailleau, M. Gourdji, A. Péneau and L. Guibé, *Phys. Rev B* **47**, 11688 (1993)
- [11] J. B. Torrance, J. E. Vasquez, J.J. Mayerle and V.Y. Lee, *Phys. Rev. Lett* **46**, 253 (1980)
- [12] C.S. Jacobsen and J.B. Torrance *J. Chem. Phys.* **78**, 112 (1983)
- [13] J.B. Torrance, in "Low Dimensional Conductors and Superconductors", edited by D. Jérôme and L.G. Caron, Plenum (1987)
- [14] C. Ayache and J.B. Torrance, *Sol. St. Comm.* **47**, 789 (1983)
- [15] K. Takaoka, Y. Kaneto, H. Okamoto, Y. Tokura, T. Koda, T. Mitani and G. Saito *Phys. Rev B* **36**, 3884 (1987)
- [16] M.H. Lemée-Cailleau, B. Toudic, H. Cailleau, F. Moussa, M. Le Cointe, G. Silly and N. Karl, *Ferroelectrics* **127**, 19 (1992)
- [17] S. Aoki, T. Nakayama and A. Miura, *Phys. Rev B* **48**, 626 (1993)
- [18] C. Pecile, A. Painelli and A. Girlando, *Mol. Cryst. Liq. Cryst.* **171**, 69 (1989)
- [19] T. Mitani, G. Saito, Y. Tokura and T. Koda *Phys. Rev. Lett* **53**, 842 (1984)
- [20] B. Toudic, J. Gallier, M. Bouzama and H. Cailleau, *J. Phys. France* **51**, 1671 (1990)
- [21] H. Okamoto, T. Mitani, Y. Tokura, S. Koshihara, K. Komatsu, Y. Iwasa and T. Koda, *Phys. Rev. B* **43**, 8224 (1991)
- [22] A.J. Heeger, S. Kivelson, J.R. Schrieffer and W.P. Su, *Rev. Mod. Phys.* **60**, 781 (1988)

- [23] H. Okamoto, T. Mitani, K. Toriumi and M. Yamashita, Phys. Rev. Lett **69**, 2248 (1992)
- [24] M. Metzger and J.B. Torrance, J. Am. Chem. Soc. **107**, 117 (1985)
- [25] N. Nagaosa, J. Phys. Soc. Jpn. **55**, 3488 (1986)
- [26] N. Kojyo and Y. Onodera, J. Phys. Soc. Jpn. **56**, 3228 (1987)
- [27] N. Nagaosa, J. Phys. Soc. Jpn. **55**, 2754 (1986)
- [28] C. Hoerner, M. Springborg and C. Koenig, (1994) unpublished
- [29] M. Alouani, J.W. Wilkins, R.C. Albers and J.M. Wills, Phys. Rev. Lett. **71**,1415 (1993)
- [30] A. Girlando, A. Painelli, C. Pecile, G. Calestani, C. Rizzoli and R.M. Metzger, J. Chem. Phys. **98**,7692 (1988)
- [31] P. Blöchl, Phys. Rev B **50**, 17953 (1994)
- [32] P. Margl, K. Schwarz and P. Blöchl, J. Chem. Phys. **100**, 8194 (1994)
- [33] M. Springborg, Phys. Rev. B **33**, 8475 (1986)
- [34] G. Krier, M. van Schilfgaarde, A.T. Paxton, O. Jepsen and O.K. Andersen, Tight-binding LMTO, version 4.6 (1994), Max-Planck Institut Stuttgart
- [35] S. Simak, unpublished
- [36] C. Hoerner, P. Blöchl, P. Margl and C. Koenig to be published