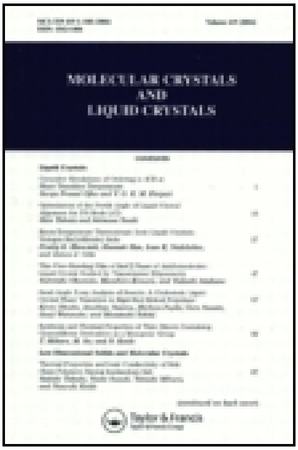

Molecular Crystals and Liquid Crystals

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

Mixed Stack Compounds, Phonons and Solitons

Baruch Horovitz [a]

[a] Department of Physics, Ben-Gurion University, Beer-Sheva, 84105, Israel

Version of record first published: 17 Oct 2011.

To cite this article: Baruch Horovitz (1985): Mixed Stack Compounds, Phonons and Solitons, Molecular Crystals and Liquid Crystals, 120:1, 1-8

To link to this article: http://dx.doi.org/10.1080/00268948508075752

Mol. Cryst. Liq. Cryst. 1985, Vol. 120, pp. 1-8
0026-8941/85/1204-0001/$15.00/0

Printed in the United States of America

MIXED STACK COMPOUNDS, PHONONS AND SOLITONS

BARUCH HOROVITZ†
Department of Physics, Ben-Gurion University, Beer-Sheva 84105
Israel

Abstract Phase transitions in organic mixed-stack compounds, known as "neutral-ionic" transitions, are reinterpreted as the onset of bond dimerization. The phase diagram is derived and the effects of temperature, pressure and the difference of donor-acceptor potentials are correlated. Electron-multi phonon couplings lead to renormalization effects both above and below the transition. A soft mode at the transition is predicted. Analysis of the phonon spectra is an efficient test for any quantitative theory of these compounds. Solitons are possible excitations below the transition and may account for conductivity and ESR data. The incommensurate situation is described by a soliton lattice.

INTRODUCTION

Most organic charge transfer solids are composed of donor (D) and acceptor (A) molecules which stack alternately on top of each other. The overlap between molecules along the stack could lead to conductivity, however in the mixed stack configuration the DA pair forms a filled band and the system is a semiconductor.

The discovery of phase transitions in many of these compounds(1,2) has stimulated a renewed interest in them. The transitions are induced by pressure and in some cases also by temperature; the latter case corresponds to the most studied compound TTF-CA.(1-3) The transitions are usually accompanied by a strong shift of the absorption in the 3-5 eV range. Above the transition, this high energy absorption is similar to that of D°, A° molecules in solution, while below the transition it corresponds to that of D^+A^- in solution. The transition was termed therefore a "neutral to ionic" transition.(1,2) Other features of this transition are strong changes in intensities of Raman scattering and of some phonon absorptions,(2,3) changes in lattice parameters(2) and sharp changes in ESR and conductivity.(4)

In the neutral-ionic approach the amount of D to A charge transfer is considered as the order parameter for the transition.(1,2) This approach leads to a number of difficulties: a) Theories for the neutral ionic transition usually predict a first order transition.(1,5) Experimentally however the transition seems to be continuous and none of the data(1-4) shows hysteresis. This is in fact a basic difficulty -- change in the charge transfer does not change a symmetry and therefore it cannot describe a continuous phase transition.(6) b) The second difficulty is that some compounds undergo a similar transition as seen from ESR and phonon spectroscopy; however the high energy absorptions are only weakly affected. This is demonstrated by extensive early studies on TMPD-CA(7) and by recent spectroscopic studies on TTF-BA.(8)

In view of these difficulties, we have proposed(9) that the order parameter for these transitions is bond dimerization, i.e. D-A transfer integrals have alternating values below the transition. This order does not change translation symmetry since the unit cell contains D-A pairs in both phases. Instead inversion symmetry at the center of a donor (or acceptor) molecule is broken. The existence of this inversion above the transition guarantees equal D-A transfer integrals.

The physical reasoning for such a transition is as follows: The electrons from the donor molecules see a difference of 2α in the D-A on site potential. This leads to a charge density wave (CDW) centered on the sites. Imagine now the limit $\alpha = 0$ -- this is the polyacetylene $(CH)_X$-type problem(10) which is well known to have bond dimerization, i.e. a CDW centered on bonds. The driving force for bond dimerization in $(CH)_X$ is an electron-phonon coupling λ^b; the dimerization opens a gap at the electron

Fermi level and the gain in electronic energy overcomes the loss in elastic (phonon) energy. This so-called Peierls transition is then a metal-insulator transition and leads to a change in translation symmetry.

For $\alpha \neq 0$ but small the Peierls mechanism is still valid just by continuity. The condition is that α is small and that λ^b is sufficiently strong. The transition is then a Peierls insulator to insulator transition and inversion symmetry is broken.

The loss of inversion symmetry explains naturally why some normal modes are active both in Raman scattering and in absorption.(2,3) In fact an extreme limit of the dimerized chain -- that of isolated dimers -- was used to explain the spectroscopic data.(3) Furthermore, very recent x-ray data have directly confirmed the onset of dimerization at the transition,(10) as indeed previously proposed.(9)

The proposed (T,α) phase diagram is shown in Fig.1. T is temperature and Δ_0 is the gap in the $\alpha=0$ limit at $T=0$; it is an increasing function of λ^b. (A specific model is given in Section II.)

Under pressure Δ_0 can increase (by increasing λ^b or the transfer integral) and the phase transition is induced as shown by the arrow in Fig. 1. As α increases the required pressure is expected to increase, in agreement with data on 10 compounds.(1) For compounds with low α the transition can also be induced by lowering the temperature as known for TMPD-CA(7) (compound D) and TTF-CA(2) (compound F).

II. THE PHASE TRANSITION

In this section the general theory for mixed stack compounds is presented. Of particular importance is the coupling of electrons to many phonons. A weak coupling theory is also presented as a more specific example.

Two types of phonons are important: phonons which modulate the on-site potential α and couple to $\sum_m (-)^m C_m^\dagger C_m$; $C_m^\dagger$ is an electron

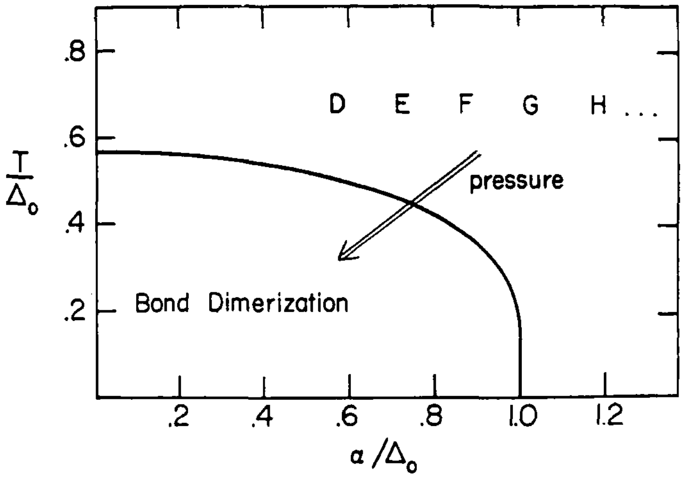

FIGURE 1 Phase diagram for mixed stack compounds. Compounds A-Z are defined in Table I of Ref.1. They are placed at their expected positions at room temperature. A phase transition is induced by either temperature change in compounds D (Ref.7) and F (Ref.2) or by pressure in compounds E-L, N and Q (Ref.1).

creation operator on site m; spin index is implicit. The Hamiltonian is symmetric under inversion so that these phonons must be symmetric.(Phonons here and below refer to those at the zone center.) The second type of phonons modulate the transfer integral and allow for bond dimerization; these phonons couple to $\sum_m(-)^m C_m^\dagger C_{m+1}$ + H.C. and must be antisymmetric. The amplitude of these phonons times their electron-phonon coupling is denoted by Δ_n^s (n=1,2,...,N) for the symmetric modes (inducing site CDW) and Δ_n^b (n=1,2,...N') for the antisymmetric modes (inducing bond CDW); N and N' are the number of corresponding normal modes. The electrons respond to the combinations

$$\Delta^s = \sum_n \Delta^s_n \qquad\qquad \Delta^b = \sum_n \Delta^b_n \tag{1}$$

The single assumption in the following theory is that of the adiabatic limit, i.e. the bare phonon frequencies $\omega_n^{so},\omega_n^{bo}$ of the site and bond phonons are much smaller than the gap in the electron spectrum. This gap is $\sim$1 eV both below and above the transition$^{(2,7)}$ while the phonon frequencies are $\lesssim$ 0.2eV. Thus the adiabatic limit is justified in these compounds. The electrons then respond to the instantaneous values of $\alpha+\Delta^s$ and Δ^b and their total free energy (including electron-electron interactions!) is of the form

$$\langle H_{e\ell} + H_{e\ell-e\ell} + H_{e\ell-ph}\rangle = -N(0)F_i(\alpha+\Delta^s,\Delta^b). \tag{2}$$

Temperature is an implicit variable and $N(0)=(\pi t_o a)^{-1}$ (t_o is the D-A transfer integral and a is the D-A distance) is convenient for defining dimensionless electron-phonon couplings λ_n^s,λ_n^b. The effective Lagrangian for Δ_n^s,Δ_n^b and their time derivatives $\dot{\Delta}_n^s,\dot{\Delta}_n^b$ is

$$L=N(o)\left\{\sum_n\frac{1}{4\lambda_n^b}\left[-(\Delta_n^s)^2+\left(\frac{\dot{\Delta}_n^s}{\omega_n^{so}}\right)^2\right]+\sum_n\frac{1}{4\lambda_n^b}\left[-(\Delta_n^b)^2+\left(\frac{\dot{\Delta}_n^b}{\omega_n^{bo}}\right)^2\right]+F_i(\alpha+\Delta^s,\Delta^b)\right\} \tag{3}$$

The equation of state is obtained by minimizing (3),

$$\Delta^s=2\lambda^s\frac{\partial}{\partial\alpha}F_i(\alpha+\Delta^s,\Delta^b);\quad \Delta^b=2\lambda^b\frac{\partial}{\partial\Delta^b}F_i(\alpha+\Delta^s,\Delta^b) \tag{4}$$

where $\lambda^s=\sum_n\lambda_n^s$ and $\lambda^b=\sum_n\lambda_n^b$. Since F_i is symmetric under $\Delta^b\to-\Delta^b$ (inversion symmetry) Eq.(4) has always a $\Delta^b\neq0$ solution. A stable $\Delta^b\neq0$ solution may appear below a temperature T_c. On the other hand Eq.(4) in general does not have a $\Delta^s=0$ solution. In fact Δ^s does not break a symmetry so that $\Delta^s\neq0$ is induced at all T.

As a more explicit example consider a weak coupling situation where gap << bandwidth. Define $C=\sum_{k\simeq-\pi/2a}C_k^\dagger C_{k+\pi/a}$ so that only states with momentum near $k=\pm\pi/2a$ are important. Hence

$$2(\alpha+\Delta^s)\Sigma(-)^m C_m^\dagger C_m+\Delta^b[\Sigma(-)^m C^\dagger C_{m+1}+H.C.]\simeq 2(\alpha+\Delta^s+i\Delta^b)C+H.C. \tag{5}$$

The CDW amplitude and phase are then

$$\Delta = [(\alpha+\Delta^s)^2 + (\Delta^b)^2]^{1/2}; \quad \theta = \tan^{-1}[\Delta^b/(\alpha+\Delta^s)] \tag{6}$$

These results are also obvious from a site CDW as function of space x $(\alpha+\Delta^s)\cos(\pi x/a)$ combined with a bond CDW $\Delta^b\sin(\pi x/a)$. Assume now that the electron-electron interaction is independent of θ; this is valid if the interaction varies slowly in space or if the description with spinless fermions is valid.(5) (This assumption corresponds to no electronic umklap scattering.) The electron free energy is then $F_i=F_i(\Delta)$ and $F_i(\Delta)$ describes also the $(CH)_X$ type problem(10) $(\alpha=0)$. When $\alpha=0$ $\Delta^b=\Delta$ solves the equation $\Delta=2\lambda^b F_i'(\Delta)$ with a solution $\Delta_o(T)$ (assuming $\lambda^s=0$ for simplicity). Eq.(4) yields $\Delta=(\alpha^2+\Delta^{b2})^{1/2} = 2\lambda^b F_i'(\Delta)$ and therefore $\alpha^2+(\Delta^b(T))^2 = \Delta_o^2(T)$. A transition is possible if $\alpha<\Delta_o(0)$ and T_c is determined by $\alpha=\Delta_o(T_c)$. For TTF-CA $\alpha \simeq 0.5$ eV while $T_c=84$°K.(1) This implies that α and $\Delta_o(0)$ are comparable and that a delicate balance between them leads to a rather low T_c.

Eqs.5,6 involve the assumptions of weak coupling and no electronic umklapp. This example serves to a) illustrate the possibility of the phase transition, and b) provide a quantitative result which may be valid for some compounds.

III. PHONONS

In this section the general formulation as defined by the Lagrangian Eq.(3) is used to study the oscillation around the minimum of Eq. (4). The analysis leads to significant information on the electron system.

The second order derivatives of F_i define 3 parameters:

$$a^s = 2\lambda^s\left[\frac{\partial^2}{\partial\alpha^2} F_i(\alpha+\Delta^s,\Delta^b)\right]_{min}; \quad a^b = 2\lambda^b\left[\frac{\partial^2}{\partial\Delta^{b2}} F_i(\alpha+\Delta^s,\Delta^b)\right]_{min}$$

$$a^* = (4\lambda^s\lambda^b)^{1/2}\left[\frac{\partial}{\partial\alpha}\frac{\partial}{\partial\Delta^b} F_i(\alpha+\Delta^s,\Delta^b)\right]_{min} \tag{7}$$

The linearized equations of motion for Eq.(3) yield the equation for the eigenfrequencies

$$[1+a^sD_o^s(\omega)][1+a^bD_o^b(\omega)] = a^*D_o^s(\omega)D_o^b(\omega) \tag{8}$$

where $D^s_{\cdot}(\omega) = {}_n(\lambda^s_n/\lambda^s)/[(\omega/\omega^{so}_n)^2-1]$ and similarly $D^b_o(\omega)$ with b replacing s.

Note first that for $T>T_c$ ($\Delta^b=0$) the $\pm\Delta^b$ symmetry determines $a^*=0$. Hence the site and bond phonons in Eq. (8) decouple. The Raman active modes then satisfy $1+a^sD^s_o(\omega)=0$ while those active in IR absorption satisfy $1+a^bD^b_o(\omega)=0$. The data was in fact analyzed in this form with the symmetric modes and a^s was determined by the isolated dimer model.(3) However for $T<T_c$ Eq. (8) shows that the antisymmetric modes modify this analysis.

At $T=T_c$ the restoring force in the Δ^b direction vanishes, i.e. $a^b(T_c)=1$ and $\omega=0$ is a solution. Thus the antisymmetric mode with the lowest frequency becomes a "soft mode" with $\omega\to 0$ as $T\to T_c$. Finally for $T<T_c$ the bond and site phonons are coupled and each is active in both Raman scattering and IR absorption.

IV. SOLITONS AND CONCLUSIONS

The Δ^b degeneracy allows for soliton excitations. These correspond to the sequence D-A···D-A···D···A-D···A-D where - and ··· are short and long bonds respectively.

As an explicit model consider the weak coupling theory in the absence of electron-electron interaction. Solitons in this model are known(12,13) and were suggested to appear in $(AB)_X$ type polymers.(13) The unusual feature of these solitons is their irrational charge. Since the ground states have phases $\pm\theta$ (Eq.) the counting rule(14) yields for the soliton charge $\pm 2\theta/\pi$ -- an irrational number in general. Finally, soliton lattice solutions were found.(9) These represent the incommensurate system where a finite charge density ρ is added to the system (e.g. by doping). The interesting feature here is that the soliton lattice exists even if $\alpha>\Delta_o$, i.e.

no phase transition in the ρ=0 system (see Fig.1).

In conclusion, it was shown that phonon spectroscopy is an effective tool for obtaining information on an interacting electron system as demonstrated by studies on $(CH)_X$.(15) Here the situation is even more interesting due to nontrivial changes of a^s,a^b and a^* with temperature. The analysis, as done for $(CH)_X$,(15) then yields the functions $a^s(T)$,$a^b(T)$ and $a^*(T)$ which are a critical test for any detailed theory of interacting electrons.

An additional fascination of these compounds is their unusual solitons. A recent conductivity experiment on TTF-CA(16) indicates thermally excited charged solitons, while the strong ESR signal(7,16) may be related to spin carrying soliton defects.

REFERENCES

1. J.B. Torrance, J.E. Vazquez, J.J. Mayerle and V.Y. Lee, Phys. Rev. Lett. 46, 253 (1981).
2. J.B. Torrance et al., Phys. Rev. Lett. 47, 1747 (1981).
3. A. Girlando, F. Marzola, C. Pecile and J.B. Torrance, J. Chem. Phys. 79, 1075 (1983).
4. T. Mitani, G. Saito, Y. Tokura and T. Koda (to be published).
5. R. Bruinsma, P. Bak and J.B. Torrance, Phys. Rev. B27, 456 (1983).
6. L.D. Landau and E.M. Lifshitz, Statistical Physics (Pergamon Press, 1969).
7. G.T. Pott and J. Kommandeur, Mol. Phys. 13, 373 (1967).
8. A. Girlando, A. Painelli and C. Pecile, in proceedings of this conference.
9. B. Horovitz and B. Schaub, Phys. Rev. Lett. 50, 1942 (1983).
10. For a review see S. Kivelson in Solitons, edited by S.E. Trullinger and V. Zakharov (North Holland, to appear).
11. S. Kagoshima, Y. Kanai, M. Tani, Y. Tokura and T. Koda, in proceedings of this conference.
12. S.A. Brazovski and N.N. Kirova, JETP Lett. 33, 4 (1981); S.A. Brazovski, Soviet Scientific Reviews, Physics Vol. 6 (1983).
13. M.J. Rice and E.J. Mele, Phys. Rev. Lett. 49, 1455 (1982).
14. Y. Frishman and B. Horovitz, Phys. Rev. B27, 2565 (1983).
15. Z. Vardeny, E. Ehrenfreund, O. Brafman and B. Horovitz, Phys. Rev. Lett. 51, 2326 (1983); Syn. Met. 9, 215 (1984).
16. T. Mitani, G. Saito, Y. Tokura and T. Koda (to be published).

† On leave from the Weizmann Institute, Rehovot, Israel.