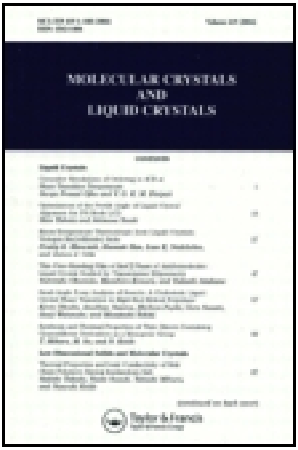

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Phase Transition Versus Chemical Reaction Approach to Transformations in Mixed-Stack Organic Crystals

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To cite this article: Tadeusz Luty (1992): Phase Transition Versus Chemical Reaction Approach to Transformations in Mixed-Stack Organic Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 216:1, 85-89

To link to this article: http://dx.doi.org/10.1080/10587259208028754

Mol. Cryst. Liq. Cryst. 1992, Vol. 216, pp. 85–89
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Printed in the United States of America

PHASE TRANSITION VERSUS CHEMICAL REACTION APPROACH TO TRANSFORMATIONS IN MIXED-STACK ORGANIC CRYSTALS.

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Abstract The paper presents a view that the neutral-ionic transformation in mixed-stack organic solids, which involves both structural (dimerization) and molecular (ionization) changes, can be analysed either as a phase transition or a chemical reaction. A coupling between molecular and lattice deformations, due to molecular compressibility, determines a reaction path or equation of state if the transformation is treated as a phase transition.

INTRODUCTION

Several compounds with mixed-stack architecture of donor (D) and acceptor (A) molecules are known to show thermally or pressure induced neutral-ionic transformation,[1] accompanied by lattice distortion as in case of TTF-Chloranil.[2,3] The system and the transformation serves as a model to learn more about differencies and similarities between solid state chemical reactions and phase transitions in organic solids.

CONSIDERATIONS

The electronic structure of the stack and its ground state energy is determined by: on-site potential, α, being a difference of energy of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and overlap integral between the orbitals, t. The stack is characterized by charge-density wave (CDW) centered on sites and its amplitude is modulated due to modulation of the on-site potential by totally symmetric molecular modes. In terms of normal coordinates, Q_i,

$$\alpha = \alpha_o + \sum_D g_D Q_D + \sum_A g_A Q_A , \qquad (1)$$

The anti-symmetric phonons of intermolecular character induce bond charge-density wave (BOW), due to modification of the overlap integral,

$$t = t_o + \sum_n \beta_n q_n \quad , \tag{2}$$

where q_n stands for normal coordinates of the phonons. If δQ_i and δq_n are expectation values of the coordinates, quantities:

$$\Delta_s = \sum_i \Delta_s^i \quad , \text{ where } \quad \Delta_s^i = \frac{1}{\sqrt{N}} g_i \delta Q_i \tag{3}$$

and

$$\Delta_b = \sum_n \Delta_b^n \quad , \text{ where } \quad \Delta_b^n = \frac{1}{\sqrt{N}} \beta_n \delta q_n \tag{4}$$

measure amplitudes of molecular and lattice distorsions. The distorsions induce changes in amplitudes of the CDW ($\delta\rho$) and BOW (δp),

$$\begin{pmatrix} \delta\rho \\ \delta p \end{pmatrix} = - N \begin{pmatrix} \chi_{CDW} & \chi \\ \chi & \chi_{BOW} \end{pmatrix} \begin{pmatrix} \Delta_s \\ \Delta_b \end{pmatrix} \tag{5}$$

The electronic susceptibility can be evaluated when electronic ground state energy is known.

The total energy of the stack is,[4]

$$\frac{1}{N} \Delta F = \frac{1}{2} \left\{ \sum_i \frac{\omega_i}{g_i^2} (\Delta_s^i)^2 - \chi_{CDW}(\Delta_s, \Delta_b)\, \Delta_s^2 \right\} - \chi(\Delta_s, \Delta_b)\, \Delta_s \Delta_b +$$

$$+ \frac{1}{2} \left\{ \sum_n \frac{\omega_n}{\beta_n^2} (\Delta_b^n)^2 - \chi_{BOW}(\Delta_s, \Delta_b)\, \Delta_b^2 \right\} \quad , \tag{6}$$

where ω_i and ω_n are bare phonon frequencies of intramolecular (symmetric A_g) and intermolecular (antisymmetric A_u) modes in the absence of electron-phonon couplings. Limit of molecular stability, e.g. condition for the molecular transformation is,

$$\chi_{CDW}^{-1} = \sum_i \frac{g_i^2}{\omega_i} = \sum_i \lambda_i = \lambda_s . \tag{7}$$

An expansion of the stack-energy around high-symmetry point ($\Delta_s, \Delta_b = 0$)

gives,

$$\frac{1}{N}\,\Delta F = \frac{1}{2}\left\{ \sum_i \lambda_i^{-1}(\Delta_s^i)^2 - \chi_{CDW}(0,0)\,\Delta_s^2 \right\} +$$
$$+\ \frac{1}{2}\left\{ \sum_n \lambda_n^{-1}(\Delta_b^n)^2 - \chi_{BOW}(0,0)\,\Delta_b^2 - \left[\frac{\partial\chi_{BOW}(\Delta_s,\Delta_b)}{\partial\Delta_s}\right]_{\Delta_b} \Delta_s\Delta_b^2 \right\}. \qquad (8)$$

This equation forms essentially the Landau free energy expansion. The condition for equilibrium gives the important relation between parameters

$$\Delta_s = \chi'_{BOW}\,\lambda_s\,(1 - \chi_{CDW}\,\lambda_s)^{-1}\,\Delta_b^2. \qquad (9)$$

This relation (Fig. 1) determines a path for reaction:

$$\begin{array}{lcl} & \longrightarrow & \cdots\ \underline{D^+A^-}\ \underline{D^+A^-}\ \underline{D^+A^-}\ \underline{D^+A^-}\ \cdots\ (IA) \\ \cdots D^\circ A^\circ D^\circ A^\circ D^\circ A^\circ D^\circ A^\circ D^\circ A^\circ \cdots & & \\ (N) & \longrightarrow & \cdots\ \underline{D^+}\ \underline{A^-D^+}\ \underline{A^-D^+}\ \underline{A^-D^+}\ \underline{A^-}\ \cdots\ (IB) \end{array}$$

χ'_{BOW} stands for the derivative of the BOW susceptibility with respect to molecular deformation. The energy of the stack along the reaction path can be expressed as a function of one (order) parameter,

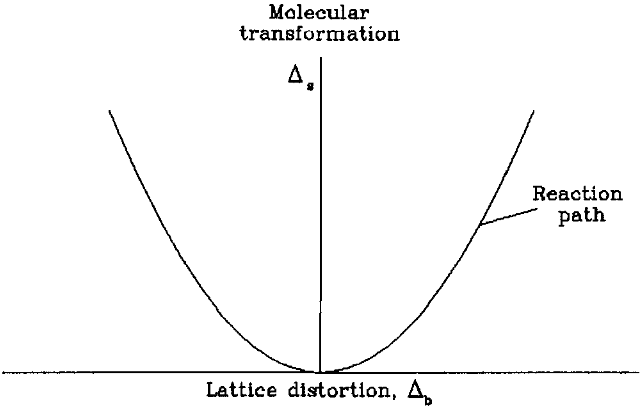

FIGURE 1 Schematic representation of the reaction path, eg. (9).

$$\frac{1}{N}\,\Delta F = \frac{1}{2}\left\{ \sum_n \lambda_n^{-1}(\Delta_b^n)^2 - \chi_{BOW}\,\Delta_b^2 \right\} + b\,\Delta_b^4 + \ldots\ldots\ , \qquad (10)$$

where

$$b = -\frac{1}{2}(\chi'_{BOW})^2 \lambda_s (1 - \chi_{CDW} \lambda_s)^{-1} , \qquad (11)$$

is negative as long as molecules are stable ($\lambda_s^{-1} > \chi_{CDW}$). The term,

$$\lambda_s (1 - \chi_{CDW} \lambda_s)^{-1} = (\lambda_s^{-1} - \chi_{CDW})^{-1} \qquad (12)$$

is a measure of molecular compressibility and determines charge-transfer or CDW instability.

CONCLUSIONS

The energy function represented by expansion (10) shows three minima (Fig.2) which (as postulated by Nagaosa[5]) correspond to three states. If the transformation is treated as a phase transition than the curve describes discontinueous phase transition and allows one to consider metastability. It is the molecular compressibility, which plays essential role in the mechanism of the transformation. We have defined the compressibility as more general property than just mechanical one by

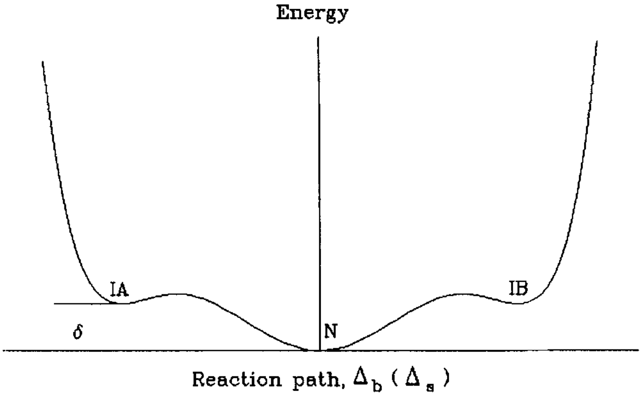

FIGURE 2 Energy curve of mixed-stack along reaction path (order parameter) for neutral-ionic chemical reaction (phase transition).

taking into account coupling between the molecular deformation and electron transfer to neighboring molecules. Let us stress that the molecular compressibility in case of the phase transition in mixed-stack structures acts as lattice compressibility in structural phase transitions making the transitions, in most cases, discontinuous. The effect of lattice compressibility can give an additional contribution to the discontinuity. Larger the molecular compressibility, smaller the energy barrier created for a transition from one state to the other. The energy of the barrier is related to the energy of the lattice-relaxed neutral-ionic domain wall, the excitation postulated by Nagaosa.[5] A limit, when molecular compressibility becomes infinite, corresponds to molecular charge-transfer (valence) instability, and drives the transition as continuous, without an activation energy. Obviously, the transformation can be treated as a solid state chemical reaction, where the reactant (N) and products (IA, IB) are characterized by the minima in Fig.2. As an extreme, the curve can be seen as a set of three parabolas, where their intersections determine transition states. Assuming the curvatures are the same the activation energy for N ——> IA, IB transition is,

$$\Delta f_a = \delta + \frac{(\delta + \Delta E_{CT})^2}{4\Delta E_{CT}} , \qquad (13)$$

where ΔE_{CT} is energy of charge-transfer between D and A molecules in neutral (N) state, which involves molecular deformation, Δ_s, only. The relation (12) is known for electron transfer reactions in solutions[6], where the reaction path is along solvent polarization coordinate (insted of $\Delta_b(\Delta_s)$ as in case of considered solids). It is belived that the considerations will be useful for other solid state transformations like methyl-transfer reaction in p-dimethylaminobenzene.[7]

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