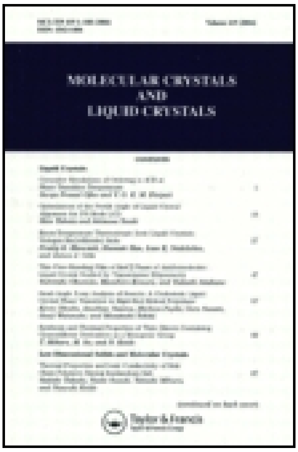

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

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Tadeusz Luty [a] & Krzysztof Rohleder [a]

[a] Institute of Organic and Physical Chemistry, Technical University, Wroclaw, Poland

Version of record first published: 04 Jun 2010.

To cite this article: Tadeusz Luty & Krzysztof Rohleder (1993): Lattice-Dynamical Aspects of Neutral-Ionic Transition in TTF-Chloranil Charge-Transfer Crystal, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 229:1, 141-146

To link to this article: http://dx.doi.org/10.1080/10587259308032188

Mol. Cryst. Liq. Cryst. 1993, Vol. 229, pp. 141–146
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Printed in the United States of America

LATTICE-DYNAMICAL ASPECTS OF NEUTRAL-IONIC TRANSITION IN TTF-CHLORANIL CHARGE-TRANSFER CRYSTAL.

Tadeusz Luty and Krzysztof Rohleder

Institute of Organic and Physical Chemistry, Technical University, Wroclaw, Poland.

Abstract The paper presents results of numerical calculations of the statics (crystal structure minimisation) and lattice dynamics for the neutral (higher temperature) phase of the TTF-Chloranil crystal. The results, in particular the low frequency phonons are discussed in relation to neutral-ionic phase transition, which takes place in the system at around 80 K.

INTRODUCTION

Some of the charge-transfer crystals with so called mixed-stack architecture, which show reasonable low energy of the first charge-transfer state (close to neutral-ionic boundary[1]), exhibit temperature, pressure or photo-induced structural transition from neutral into ionic ground state.[2] The TTF-Chloranil (TTF-CA) crystal, the first which has shown the temperature induced transition[2] and thus have been intensively studied during last ten years[3], is considered as model system for the transition. Mechanism of the nuetral-ionic phase transition is not completely understood yet. The main question is what is a role of lattice vibrations in the mechanism. It is understandable, that the coupling between electron transfer and the lattice phonons is important, but it is not clear which phonons are most important and how structural instability takes place (locally or in the bulk of crystal).[4] Those questions became even more important in the context of recent structural investigations,[5] where interesting symmetry changes and metastability have been observed.

Here, we present results of lattice dynamics calculations for the TTF-CA crystal in its high symmetry (high temperature, low pressure) phase,[6] compare the results with this done by Bonadeo[7] and conclude on a possible role of phonons in mechansim of the phase transition.

CALCULATIONS

The lattice dynamics calculations have been done in two steps: minimisation of lattice energy with respect to all degrees of freedom (assigned for the symmetry of $P2_1/n$ space group[6]) and than calculation of eigenfrequencies of the lattice within the assumption of the rigid molecules. In the calculations, we have used the same set of parameters for the "6-exp" atom-atom potential function, as have been used by Bonadeo.[7] It is believed that the electrostatic interactions in TTF-CA crystal (and similar ones) are important and one should try to include them in the calculations. The essential point is to know charge distribution for the molecules in the crystal. Bonadeo[7] have used charge distributions, presented as point atomic charges, calculated for <u>ionized</u> molecules TTF and CA[8]. In the high symmetry phase the molecules are predominantly in the neutral state, thus calculations for this phase have to be done with another charge distribution. In our calculations, we have used point charges calculated in self-consistent procedure[9] for TTF and CA molecules in the crystal environment of the high symmetry phase. It has to be stressed that the calculations indicated that the molecules are completely neutral (!) in the phase of $P2_1/n$ symmetry with mixed-stack architecture. This result is significant, because it

TABLE 1 Structural parameters for $P2_1/n$ phase of TTF-CA crystal

Parameter	EXP.	CALCULATIONS			
		without Culomb int.		including Culomb int.	
		(1)	(2)	(1)	(2)
a	7.41	7.36	7.21	7.41	6.94
b	7.62	7.88	7.83	7.66	8.18
c	14.57	13.63	14.71	14.19	14.22
β	99.20	96.68	99.69	101.90	98.89
Latt. en. [kcal/mol]		-55.15	-52.75	-56.79	-51.35

(1) - this work
(2) - according to ref. 7

indicates that ionization of molecules (the valence instability) does not follow only(!) from an influence of electrostatic interactions.

Table 1 presents results of structure minimisation for high symmetry phase and compares the results with experimental[6] and previously calculated.[7] It has to be stressed that the results depends on the numerical method used for the lattice energy minimistation. In our calculations, the package MINUIT has been used.[10] We have to notice an effect of including in the calculations the electrostatic interactions.

For the minimised structure, the harmonic lattice dynamical calculations have been done, following the procedure already employed for the charge-transfer crystals.[11] In the context of the phase transition in the TTF-CA system, which takes place at around 80 K from $P2_1/n$ space group into P1 symmetry, without a change in translational symmetry,[5]

TABLE 2 Lattice modes at the center of Brillouin zone of TTF-CA crystal

Mode symmetry (main component CA, TTF)	Frequencies in [cm^{-1}]		
	(1)	(2)	(3)
Bg (Ry,Ry)	27.8	30.5	30.8 (Ry,Ry)
Bu (Ty,Tz)	32.8	36.5	32.5 (Ty,Ty)
Au (Ty,Tz)	33.3	40.1	28.8 (Tx,Tz)
Bg (Rx,Rx)	36.5	37.4	38.1 (Rx,Rx)
Ag (Ry,Rx)	38.2	43.7	42.8 (Rz,Rx)
Bu (Ty,Ty)	42.3	47.6	45.1 (Tz,Tz)
Au (Tx,Tx)	47.1	49.4	46.3 (Tz,Ty)
Au (Tz,Tz)	53.0	55.1	59.0 (Tz,Ty)
Bu (Tz,Ty)	56.1	54.0	69.7 (Ty,Ty)
Ag (Ry,Rx)	56.4	65.0	54.1 (Rz,Ry)
Bg (Rz,Rx)	57.5	62.4	56.1 (Rx,Rz)
Ag (Rz,Rz)	67.0	72.0	58.8 (Ry,Ry)
Au (Tz,Tz)	67.1	67.3	69.5 (Ty,Tz)
Bg (Rz,Rz)	70.4	76.7	66.6 (Rz,Rx)
Ag (Ry,Ry)	73.0	75.8	64.7 (Rx,Rx)
Ag (Ry,Rz)	93.8	92.9	89.7 (Rx,Rz)
Au (Tx,Tx)	109.3	107.7	110.6 (Tx,Tx)
Bg (Rz,Ry)	109.3	98.8	92.6 (Rz,Rz)
Bg (Rz,Rz)	117.9	116.6	116.9 (Ry,Ry)
Bu (Tx,Tx)	118.7	112.8	115.3 (Tx,Tx)
Ag (Rz,Rz)	122.0	118.0	115.2 (Ry,Ry)

(1) - atom-atom potential without Coulomb interaction
(2) - atom-atom potential with Coulomb interaction (atomic charges calculated for quasineutral molecule).
(3) - according to ref. 7 (without Coulomb interaction)

the most interesting are phonons of the Brillouin zone center. Table 2 presents the frequencies of the phonons, their symmetries, main components of eigenvectors and comparison with results of Bonadeo.[7] The differencies are not very significant indicating that the lattice dynamics is not very sensitive on both the electrostatic interactions and, in fact, on procedures of crystal structure minimisations. As long as the main feature of the structure, e.g., the mixed-stack architecture, is preserved the lattice dynamics is essentially the same. This is clearly an indication that even in the charge-transfer complexes of this type the mechanics of the lattice is determined by close packing of the molecules and the empirical potentials are used to measure this effect quantitatively.

According to the recent structural studies,[5] the change in symmetry from $P2_1/n$ to $P1$, require lattice deformations (rather small) of B_g and B_u symmetries. The results presented in Table 2, do indicate that the expected deformations would follow the paterrns movest phonons of this symmetries. In that sense, the calculations can be helpful for further structure refinement of the low-symmetry (low temperature) phase of TTF-CA crystal. The calculations of the lattice dynamics also indicate that the lattice phonons of translational character, with mo-

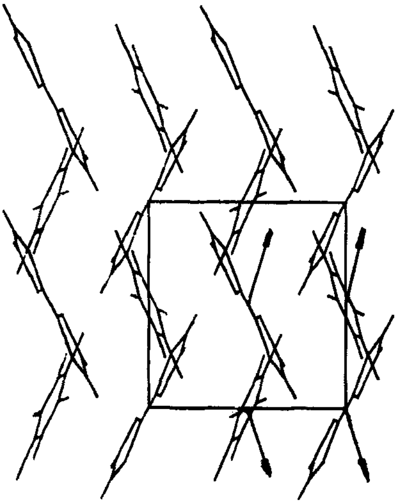

Figure 1. The pattern of lowest translational phonon mode of Bu symmetry (projection on ab plane)

lecular displacements predominantly along the molecular stacks (T_x, T_x), have rather high frequencies (above 100 cm^{-1}) and cannot be responsible for symmetry breaking (dimerization) and the phase transition mechanism. In fact this is quite understandable, because the translational motions of molecules along the stacks are most difficult due to "sandwich-like" structure along that direction. Figure 1 show the structure of the TTF-CA crystal in its high symmetry phase with indicated displacement pattern for lowest B_u phonon mode. Most likely, this is the lattice deformation (together with deformation of B_g type according to pattern of the lowest phonon of this symmetry), which will be observed in the low symmetry phase of P1 symmetry.

CONCLUSIONS

From the harmonic lattice dynamical calculations for the high symmetry phase of TTF-CA crystal we can conclude as follows.

- The electrostatic calculations do not play an essential role in the structure and lattice dynamics determination,
- Translational phonons with molecular displacements along the molecular stacks are, most probable, not responsible for symmetry breaking at the transition from $P2_1/n$ to P1 space groups. This result implies that the electron phonon coupling via the modulation of transfer integral (commonly assumed in theories of the neutral-ionic transition) is not an effective mechanism for the discussed phase transition.
- The calculated patterns of the lowest frequency phonons, most likely, indicate lattice distortions expected in the low symmetry phase and, we hope, will be useful for the structure refinement.

We plan to extent the calculations by including in the calculations an effect of molecular deformation due to valence change, the effect which is important in the phase transition.[12] The TTF-CA will be modelled by a composition of molecules deformed according to its state of ionicity.

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