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MODELLING OF SUBSTITUTIONAL AND ORIENTATIONAL DISORDER IN MOLECULAR CRYSTALS

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Abstract The mixed crystal, A_xP_{1-x}-TCNB, of the charge-transfer complex with mixed-stack architecture is used to learn how to model numerically the substitutional (concentration x) and orientational (two orientations of the P molecules) disorder. The calculated free energy indicates a pronounced minimum for x = 0.75, critical concentration found experimentally.

1. INTRODUCTION

Family of two component (1:1) organic crystals with tetracyanobenzene (TCNB) as acceptor and naphtalene (N), anthracene (A) and phenanthrene (P) as donors are model systems to study details and different kinds of an orientational disorder.[1] The TCNB molecules form a rigid network for the donors and different orientational disorder follows: dynamical in A-TCNB, static in N-TCNB and statistically static in P-TCNB.

In case of N-TCNB and A-TCNB systems, the disorder drives phase transitions from monoclinic C - centered lattice into primitive lattice, at 70K and 210K, respectively. The disorder and the phase transitions have been successfuly modelled, using so called "split" molecule approach.[2]

In the paper we address the problem of modelling of orientational and substitutional disorder in mixed A_xP_{1-x}-TCNB crystal. The P molecules as non-centrosymmetric, occupy centro-symmetric sites in two statistically distributed orientations.

2. CALCULATIONS

The mixed-crystal, A_xP_{1-x}-TCNB, is modelled in following manner. The sites of C - centered lattice are occupied in the alternating pattern (the mixed-stack architecture) by TCNB molecules and A and/or P molecules according to concentration x. The donor (A, P) sublattice is modelled as, so called, virtual lattice e.g. every site is constructed according to the chemical formulae, A_xP_{1-x}-TCNB. The P molecule contribution in this formulae is, however, due to an object which is centrosymmmetric. This means that a "split" molecule has to be formed by introducing on every site two P molecules with different orientations. Now the average molecules constructed from one molecule A and a "split" (two P molecules!) molecule interacts with surroundings according to assumed concentration x. The concentration decides on a weight with which the intermolecular interactions are counted. The interactions are calculated using atom-atom, 6-exp, potential function[3,4]. The lattice energy, calculated for the whole range of the concentration, x, has been minimized with respect to lattice parameters, a, b, c and β. Results are shown in Table 1. and compared with experimental ones.[5]

TABLE 1. Comparision of experimental[5] and calculated (this work) lattice parameters for few concentrations in A_xP_{1-x}-TCNB

Concentration x	a [Å]		b [Å]		c [Å]		β [Å]	
	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.
0.000	9.41	9.46	13.10	13.27	7.25	7.22	87.1	85.1
0.230	9.45	10.22	13.02	12.99	7.29	7.06	88.4	79.3
0.614	9.50	10.18	12.90	12.80	7.36	7.09	90.3	82.4
0.747	9.50	9.97	12.84	12.76	7.37	7.16	91.0	85.6
1.000	9.52	9.89	12.77	12.71	7.43	7.22	92.4	87.5

The minimized lattice energy, E, together with configurational entropy

$$S_{conf} = R\cdot\left\{ (1-x)\cdot\ln(2) - x\cdot\ln(x) - (1-x)\cdot\ln(1-x) \right\}$$

forms simplest estimation of free energy, A = E - T·S. Figure 1. presents results of calculations.

For x = 1 (pure A-TCNB), the energy does not depend on temperature

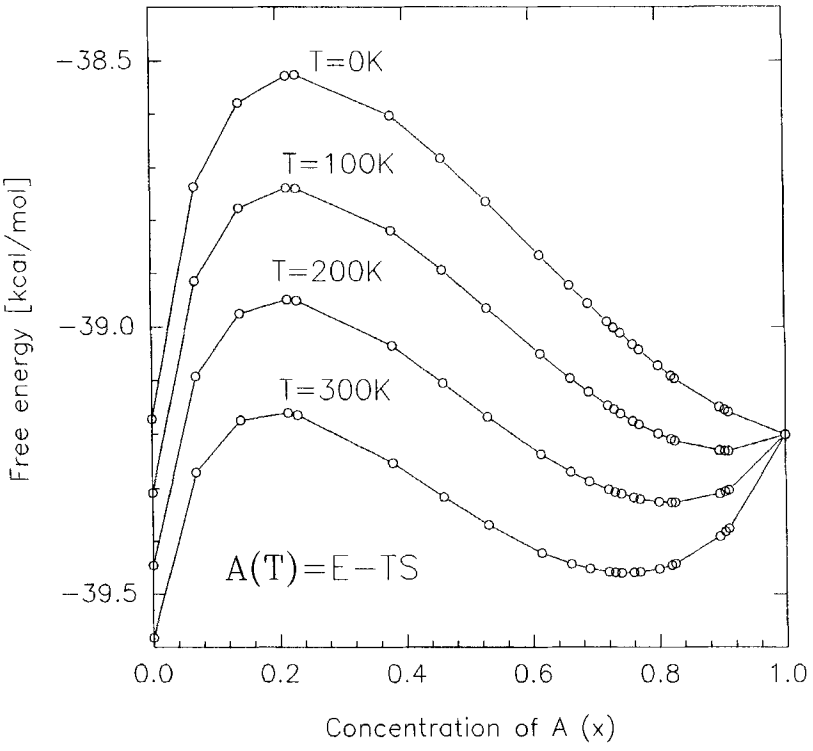

FIGURE 1 Results of free energy calculations as a concentration and temperature function

as it is only configurational entropy included. On the other hand the degeneracy (equal 2) of the orientational state of P molecules gives the temperature dependence for x = 0 (pure P-TCNB). It is striking that the internal lattice energies are almost equal for both, pure compounds. The degeneracy of P sites decreases the free energy and makes pure P-TCNB system most stable for higher temperatures. At about 300K, the crystals of P-TCNB and mixed one with $x \approx 0.75$ are equally stable. This indicates that the mixed system with $x < 0.75$ will trend to decom-

pose on pure P-TCNB and the mixed crystal with concentration $x \approx 0.75$. With increasing temperature, the critical concentration varies slowly towards smaller values.

2. CONCLUSIONS

We have performed, for the first time, modelling of both, orientational and substitutional disorder in the mixed charge-transfer crystals, A_xP_{1-x}-TCNB. The orientational disorder has been modelled by "split" molecule and the free energy, including configurational entropy, has been calculated as a function of concentration. The calculations do suggest that $x \approx 0.75$ seems to be critical concentration for the system to be considered as solid solution and that below this concentration of A molecules, the system tends to decompose on mixed crystals with $x \approx 0.75$ and pure P-TCNB. This tendency is due to the double orientational degeneracy of the lattice sites occupied by P molecules. This conclusion, coherent with experimental investigations, where concentration $x = 0.75$ has been found as a critical one for the C lattice of the mixed crystal.[5] It is worth to stress that, in fact, the calculations help to understand the experimental results. The modelling of the mixed crystals will be continued towards more sophisticated calculations of the free energy.

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