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"DISORDER - DISORDER" PHASE TRANSITION IN SEMI-PLASTIC CRYSTALS

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Abstract The 2-Chloronaphthalene and 2-Bromonaphthalene present two types of disordered structures (form II and form I). The passage II ⇆ I corresponds to a second order transition,the premonitory effects of which extend over a large temperature range (50 K). The disorders is induced by molecular motions (reorientation or/and diffusion).

INTRODUCTION

An exhaustive study of the behaviour of the polymorphism in the β-R naphthalene series[1-4] has pointed out that all the compounds may be considered as "semi-plastic" crystals in their high temperature forms. The chloro and bromo derivatives are particularly attractive owing to the fact that they present two types of disordered structures respectively called II and I.

STRUCTURAL RELATIONS BETWEEN FORMS I AND II

The structural determinations of forms I and II show, in both cases, a statistical molecular entity :

- form I is isostructural with naphthalene* ($P2_1/a$, $Z = 2$) (see Table I). The statistical molecular entity is centrosymmetrical.

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* At 293 K, its cell parameters are[4] : $a = 8.262(3)$, $b = 5.984(3)$, $c = 8.678(5)$ Å , $\beta = 122.80(2)°$.

TABLE I Crystal data

Form	2-Chloronaphthalene	2-Bromonaphthalene
I	T = 315 K	T = 323 K
	a = 7.733 (3) Å	a = 7.773 (4) Å
	b = 5.963 (5) Å	b = 5.960 (4) Å
	c = 21.331 (9) Å	c = 10.835 (8) Å
	β = 120.00 (6)°	β = 118.22 (3)°
II	T = 293 K	T = 293 K
	a = 7.660 (2) Å	a = 7.682 (4) Å
	b = 5.954 (2) Å	b = 5.921 (4) Å
	c = 21.311 (8) Å	c = 21.680 (15)Å
	β = 120.32 (3)°	β = 119.15 (3)°
II	T = 223 K	T = 263 K
	a = 7.571 (3) Å	a = 7.682 (4) Å
	b = 5.910 (3) Å	b = 5.911 (4) Å
	c = 21.257 (10)Å	c = 21.660 (15)Å
	β = 120.35 (3)°	β = 119.24 (3)°

- form II corresponds to an unidirectional substructure of form I along the c axis (see Table I). They are isomorphous ($P2_1/n$, Z = 4). The statistical molecular entity is non centrosymmetrical ; one of the four molecular orientations is clearly predominant.

The values of the characteristical occupancy factors relative to the different statistical molecular entities of 2-chloronaphthalene are given in Table II.

TABLE II 2-Chloronaphthalene statistical molecular entity : occupancy factors of the four β sites

Forms	T(K)	f_1	f_2	f_3	f_4
I	315	0.33	0.17	0.33	0.17
II	293	0.58	0.14	0.12	0.16
II	223	0.64	0.11	0.09	0.16

CHARACTERIZATION OF THE II ⇄ I TRANSITION AND NATURE OF THE DISORDER

The passage II ⇄ I corresponds to a reversible second order transition which occurs at 313 K for the chlorine derivative and 319 K for the bromine one. The actual transition is preceded by premonitory effects which extend over a large temperature range (about 50 K). The phase transition does not destroy the single crystals.

The crystal data given in table I correspond to the 3 different states of the structure : before, during and after the premonitory zone.

In the premonitory temperature range, anomalies are observed in both energetical and structural observations versus T :

- The Cp curves show a large anomaly with two maxima respectively at 285 and 313 K for the 2-chloronaphthalene and at 296 and 319 K for the 2-bromonaphthalene.

- The variations of the principal components of the

thermal expansion tensors and the variations of the intensity of the substructure diffraction lines also show anomalies at the same temperatures.

These facts suggest that their are two competitive temperature dependent molecular motions. The most probable hypothesis according to N M R analysis[5,6] , interdiffusion measurements[7] , calculation[8,9] and diffuse scattering phenomenons is :

- in form I exists both molecular jumps between lattice sites and in-plane reorientational motions of the molecules.

- in form II, the disorder is also dynamical in the high temperature range but, when the temperature decreases, the molecular motions are progressively frozen and the residual disorder is then quasi-static.

REFERENCES

1. N.B.Chanh, Y.Haget, L.Bonpunt, A.Meresse et J.Housty Analytical Calorimetry (Plenum publ.corp.New York,1977) p.233.
2. N.B.Chanh, Y.Haget, A.Meresse and J.Housty, Mol.Cryst. Liq.Cryst., 45, 307 (1978).
3. N.B.Chanh, Y.Haget, A.Meresse, D.Louer et R.Shirley, J.Phys.Chem.Sol., 42, 217 (1981).
4. A.Meresse, Thèse Bordeaux (1981).
5. C.Cazaux, Thèse Bordeaux (1972).
6. N.B.Chanh, Y.Haget, J.Dufourcq and B.Lemanceau, First European Crystallographic Meeting, Bordeaux (1973).
7. Y.Haget, N.B.Chanh et A.Meresse, Mol.Cryst.Liq.Cryst. 32, 49 (1976).
8. A.Gavezotti and M.Simonetta, Acta Cryst.A31, 645(1975).
9. A.Gavezotti and M.Simonetta, Acta Cryst.A32, 997(1976).