05.1–73 POLYMORPHIC TRANSITIONS IN ORGANIC CRYSTALS. By N.N.Petropavlov, I.G.Tsygankova, Institute of Biological Physics of the USSR Acad.Sci., Pushchino, Moscow Region, USSR

Experimental study of the mechanism of temperature polymorphic transitions (P.T.) in organic crystals involves several stages: 1) obtaining perfect single crystal samples; 2) study of the phase behaviour and morphology of growth of a new phase; 3) microcalorimetric study; 4) determination of orientational phase interrelations; 5) structural interface studies; 6) estimation of thermodynamic parameters; 7) modelling of the mechanism of P.T. Studies of the polymorphic transitions carried out along these lines on a number of substances indicate that P.T. belong to the first order phase transitions and represent a growth of crystals of a new phase inside the matrix phase. The defects of the initial crystal are the centers of nucleation. All P.T. are characterized by hysteresis, the actual value of which depends on macroscopic parameters as well as on specificity of the structure of the substance under study. Orientation of crystals of a new phase inside the matrix phase may be different depending mainly on the geometric form of the molecule. Specific intermolecular forces (H-bonds), conformational mobility of molecules etc. complicate the picture of the process and the possibility of modelling the mechanism of P.T. A number of phenomena accompanying P.T. are investigated, their emergence is explained. Microcalorimetric studies and calculations of characteristic temperatures describe, to a rather high accuracy, the type of polymorphic transitions and help in understanding the general idea of the phenomenon. The revealed factors allow semiempirical prediction of some main features of P.T. in majority of molecular crystals. To elucidate whether there is a direct relation between morphological, structural and energetic characteristics on the one hand and molecular mechanism of the phenomenon on the other, one should have at least by one order of magnitude more statistic data on P.T. than available. The significance of the revealed factors for modelling structural transitions in heteromolecular complexes is discussed.

05.1–74 STRUCTURAL INTERPRETATION OF PHASE TRANSITIONS IN SODIUM CARBONATE. By P.M. de Wolff and F. Tuinstra, Delft University of Technology, Department of Applied Physics, P.O. Box 5046, 2600 GA Delft, The Netherlands.

The two second-order transitions α-β (489°C) and β-γ (361°C) of sodium carbonate can be interpreted in terms of a columnar structure model. This view is based on detailed structure analyses at various temperatures and it is supported by analogous phase changes in rubidium- and potassium carbonate. In the three isomorphous α phases, space group $P6_3mmc$, face-sharing $A'O_6$ octahedra form parallel columns in a hexagonal array, with C and the remaining alkali atoms A" alternating in a row on each axis between three adjoining columns. So the latter are connected by the anions through oxygen sharing; in the α form the anions are perpendicular to the columns. The oxygens act as flexible joints allowing huge shear distortions in the sheaf of undistorted columns. This is what happens when thermal motion of the weakly bound A" ions becomes insufficient to stabilize the α form. For Na_2CO_3 a the α-β softening mode is one component of E_{1g} (rotation of anions about an O-O edge); it couples at q ≈ 0 with the a-polarized shear belonging to E_{1u} (axes: b ≈ a√3). In the γ phase the complementary modes of E_{1g} and E_{1u} (wiggle of anions about C-O and b-polarized periodic shear) are condensed with an incommensurate q. The columnar model allows an interpretation of the anomalous thermal expansion and of the fact that q is normal to the average plane of the anions. Diffuse scattering shows persistance of the softening throughout the β-phase. The thermal behaviour of birefringence and IR spectra is readily interpreted in terms of the known structural changes.

05.1–75 LATTICE PARAMETERS AND THERMAL EXPANSION OF V_3O_5 NEAR PHASE TRANSITION. By S. Åsbrink* and M. Wołcyrz**, Arrhenius Laboratory, University of Stockholm, Sweden* and Institute for Low Temperature and Structure Research, Polish Academy of Sciences, Wrocław, Poland**.

V_3O_5 undergoes a first order phase transition at T_t = 427.9 K of the semiconductor-to-metal type. Both low- and high-temperature phases are monoclinic with Z = 4 and the space groups P2/c and I2/c, respectively. According to the accurate structure determination (Åsbrink, Acta Cryst. (1980) B36,1332; Hong & Åsbrink, Acta Cryst. (1982) B38,713), an ordered distribution of tri- and tetravalent vanadium atoms in low-V_3O_5 is replaced by the only partially ordered one in high-V_3O_5, but the shifts in the atomic positions are less than 0.1 Å.

A dependence of the lattice parameters vs. temperature was precisely investigated using Bond-type diffractometer with high-temperature attachment (Łukaszewicz et al., Krist. Tech. (1978) 13,561). The measurements were performed in the temperature range 298-480 K with the stability better than ± 0.02 K. The results for the temperatures just below and just above T_t are following:

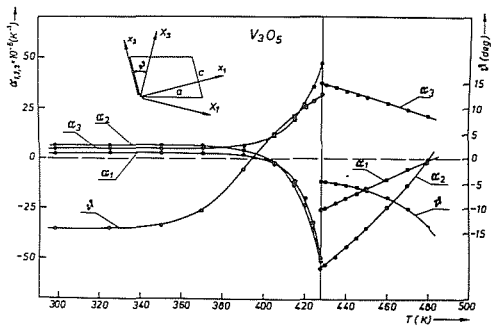
	298.16 K	427.85 K	427.90 K
a (Å)	9.85727(4)	9.85623(4)	9.84816(4)
b (Å)	5.04057(2)	5.04135(2)	5.03457(2)
c (Å)	6.98882(5)	6.99646(5)	7.00225(5)
β (°)	109.4742(6)	109.4815(6)	109.4947(6)
V (Å³)	327.383(6)	327.742(6)	327.278(6)

The linear Lagrangian strain tensor at the transition was calculated and diagonalized (Schlenker et al., Acta Cryst. (1978) A34,52). Its principal components are following:

$l_1 = -9.18\cdot10^{-4}$, $l_2 = -13.42\cdot10^{-4}$, $l_3 = 8.45\cdot10^{-4}$

$\upsilon = 5.77°$ (axes description - see scheme in fig.)

The thermal expansion tensor was applied in the limit of infinitesimal displacements. Its coefficients α_i and angle υ are plotted below as the functions of temperature.



One can conclude that the crystal structure starts to change continuously at the temperature of about 360 K. Above T_t in the range of 50 K the thermal parameters tend to return to their previous values from the low-temperature phase. The analysis of the strain as well as the thermal expansion tensor leads to the conclusion that the directions of the structure instabilities lie closely to the direction parallel to the c-axis (i.e. along the diagonal of the basis of the VO_6 octahedra) and to the direction perpendicular to it. Referring to the structural results one may suggest that from 360 K upwards the difference between the two unequivalent vanadium positions regarding the valencies starts to disappear. At T_t the valency-mixing reaches a level where a symmetry change is needed for the energetical reasons and with further temperature increase results in the statistical distribution of the vanadium atoms of different valencies.