

**05.1-41** POLYMORPHIC TRANSITION IN SUCCINIC ACID CRYSTALS. By N.N. Petropavlov, S.B. Yarantsev, Institute of Biological Physics of the USSR Acad.Sci., Pushchino, Moscow Region, USSR.

The polymorphic transition (PT)  $\beta \rightarrow \alpha$  in  $C_4H_6O_4$  crystals was studied by experimental methods. Though the fact of PT in succinic acid (F. Dupré La Tour, Ann.Phys. (1932) 18, 199) and the phase structures have long been established with different degree of accuracy ( $\beta$ -phase J.S. Broadley et al. Proc.Roy.Soc. (1959) A251, N 1267, 441;  $\alpha$ -phase G.D. Rieck, Rec.Trav.Chim. (1944) 63, n 4, 170), little is known about the transition itself. As objects served perfect monocrystals in  $\beta$ -phase grown from different solvents. A substantial hysteresis reaching tens of degrees was found. The reversibility of the process was first registered. The temperature of phase equilibrium was close to 116°C. The PT represents growth of daughter crystals (D) of the  $\alpha$ -phase inside the matrix crystal (M) which is analogous to growth of crystals from ordinary media. The morphology of growth of D inside M was studied. The anisotropy of the crystalline medium, steric hindrance arising from abrupt increase in specific volumes of the phases and due to strong hydrogen bonding highly diversify the course of the PT. Orientation of the phase lattices received primary emphasis. Measurements of 200 dim out directions of D in crossed nicols with respect to direction of cleavage [001] in M gave statistical distribution in a sector between 0° and 90° close to an isotropic one. The diagram of the angles formed by straight-line boundaries of D inside M with respect to the same direction [001] is constructed. Optical evidence is found to correlate well with the diagram, thus indicating the orienting effect of M. While intersecting the twinning planes (001) and (101) of M, the straight-line boundary retains the initial direction without "taking notice" of changes in orientation of the "building material". Using an extremely high hysteresis of PT  $\alpha \rightarrow \beta$ , we managed to indicate the boundaries in both lattices on the "hybrid" crystal at room temperature (Fig.1 a,b). Indicating was performed by the X-ray technique for monocrystals. It was found that the boundaries represent faces with low indices in the lattice of D and high indices in the lattice of M (except for the plane of cleavage). Based on the obtained evidence and the structural data, a molecular model of the boundary in (010) of M is constructed.

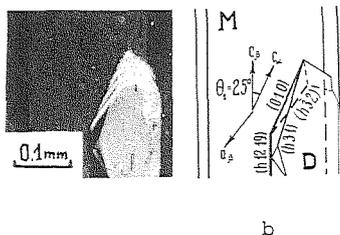


FIG.1 Micrograph of the PT in succinic acid (a) and the scheme of indicating of boundaries in the lattice of D (b).

**05.1-42** THE ORDER-DISORDER TRANSFORMATION IN THE  $\pi$ -MOLECULAR COMPOUND PYRENE:PYROMELLITIC DIANHYDRIDE. By F. H. Herbststein, R. E. Marsh and S. Samson, Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, CA 91125, U. S. A.

The crystal structure of pyrene:pyromellitic dianhydride (PMDA) has been determined at temperatures of 295, 240, 183, 149, 100 and 19 K using the low-temperature accessory designed by Samson, Goldish & Dick (J. Appl. Cryst. 13, 425 (1980)) for a four-circle diffractometer. Earlier results for the ordered and disordered structures (Herbstein & Snyman, Phil. Trans. Roy. Soc. London A264, 635 (1969)) are confirmed and extended. At 295 K  $a = 13.94(1) \text{ \AA}$ ,  $b = 9.34(1)$ ,  $c = 7.31(1)$ ,  $\beta = 93.65(9)^\circ$ , space group  $P2_1/a$ ,  $Z = 2$ ; at 19 K  $a = 13.664(3) \text{ \AA}$ ,  $b = 9.281(2)$ ,  $c = 14.420(3)$ ,  $\beta = 91.80(2)^\circ$ , space group  $P2_1/n$ ,  $Z = 4$ , there being 2 sets of pyrenes at independent centres of symmetry and 4 PMDA molecules in general positions. There are no discontinuities in the variation of the cell dimensions with temperature (measurements at  $\sim 10$  K intervals, down to 19 K) but  $db/dT$  has a discontinuity at 175 K and  $db/dT$  a point of inflexion in the same temperature region. Below 175 K superlattice reflections appear, corresponding to the doubling of  $c$  and the change of space group; their intensities increase as the temperature is lowered, approaching maximal values asymptotically as  $T \rightarrow 0$  K. These results confirm that the transition is second-order, in accordance with the form of  $C_p - T$  curves (Boerio-Goates & Westrum, Mol. Cryst. Liq. Cryst. 60, 249 (1980)). Below the transition temperature the two independent pyrenes are separated by a rotation about the normal to the molecular plane. At 19 K this angle is  $12.6^\circ$  and it decreases slowly with rising temperature. Above the transition temperature the pyrene molecules have a single azimuthal orientation, analysis of the Debye-Waller factors suggesting appreciable libration but no static disorder.

**05.1-43** X-RAY AND NEUTRON INVESTIGATION OF ORDER-DISORDER TRANSITIONS IN UREA INCLUSION COMPOUNDS. By H. Boysen, R. Forst and H. Jagodzinski, Institut für Kristallographie und Mineralogie der Universität München, München, BRD. C. Zeyen, ILL, Grenoble, France.

The different states of order of hexadecane ( $C_{16}H_{34}$ ) included in channels formed by urea along the hexagonal  $c$ -axis have been investigated. At 150 K a continuous transition from a hexagonal high-temperature phase to an orthorhombic (distorted pseudo-hexagonal) structure takes place preceded by a sharpening of diffuse intensity (streaks) at the locations of the rhombic superstructure reflections. This diffuse intensity was shown to be mainly of elastic or quasi-elastic origin by a measurement on the 5-axis neutron diffractometer D10 at ILL in "elastic" and energy-integrated configuration. The transition is connected with a lateral ordering of the adducts, the superstructure being referred to an interaction between chain and channel.

Hexadecane, which has a length close to but not equal to  $2c$  of urea shows sharp reflections with  $c^* = c^*/2$  and  $a^* = a^*$  of urea as well as diffuse layers perpendicular to  $c^*$  corresponding to its own chain-length. Below 119 K new reflections on these layers occur belonging to a lattice which has  $a$  and  $b$  of urea and is commensurate with higher order in  $c$ . With decreasing temperature these new reflections grow at the expense of the " $c^*/2$ " ones until they finally prevail indicating an ordering of the chains according to their length. There is a hysteresis of about 15 K. At the same time first and higher order satellites are found due to a longitudinal modulation of the structure along  $c$  caused by a "resonance" between guest and host.