05. PHYSICAL PROPERTIES AND STRUCTURE

05.1-41 POLYMORPHIC TRANSITION IN SUCCINIC ACID CRYSTALS. By N.N. Petrovskov, S.B. Varshavsky, Institute of Molecular Biology of the USSR Acad.Sci., Pushchino, Moscow Region, USSR.

The polymorphic transition (PT) α→β in \( \text{C}_4\text{H}_6\text{O}_4 \) 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 (α-phase J.S. Broadley et al. Proc.Roy.Soc. (1959) A251, N 1267, 441; α-phase G.D. Rieck, Rec.Trav.Chim. (1964) 83, n 4, 170), little is known about the transition itself. As objects served perfect monocrystals in α-phase grown from different solvents. A substantial hysteresis reaching tens of degrees was found. The reversibility of the process was first registered. The reversibility arising from abrupt increase in specific volumes of the phases and due to hindrance arising from abrupt increase in specific volumes of the phases and due to

05.1-42 THE ORDER-DISORDER TRANSFORMATION IN THE α-MOLECULAR COMPOUND PYRENE:PYROMELLITIC DIHYDRIDE. By H. Krath, B. Mayer and K. Samson, Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, CA 91125, U. S. A.

The crystal structure of pyrene:pyromellitic dianhydride (FPDA) has been determined at temperatures of 295, 240, 183, 209, 100 and 19 K using the low-temperature accessory designed by D. Broadley (J. Phys. Chem. 61, 425 (1958)) for a four-circle diffractometer. Earlier results for the ordered and disordered structures (Herbst et al., Acta Cryst. 27, 1001-1004 (1971)) are consistent. At 295 K α - 15.96(1) A, b = 9.34(1), c = 7.51(1), \( \beta = 93.65(7) \)\( ^\circ \), space group P2₁/a, \( Z = 2 \). At 19 K α - 13.66(4) A, \( \beta = 91.80(7) \), space group P2₁/a, \( Z = 2 \), thare being 2 sets of pyrene molecules in independent centres of symmetriy and 4 FPDA molecules in general positions. There are no discontinuities in the variation of the cell dimensions with temperature (measurements to 10 K intervals, down to 19 K) but db/dT has a discontinuity at 173 K and db/dT a point of inflexion in the same temperature region. Below 175 K superlattice reflections appear, corresponding to the doubling of α and the change of space group; their intensities increase as the temperature is lowered, approaching maximal values asymptotically as T→0 K. These results confirm that the transition is second-order, in accordance with the form of \( C_2^f \) curves (Boerio-Goates & Westrum, Mol. Cryst. Liq. Cryst. 65, 29 (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° and it decreases slowly with rising temperature. Above the transition temperature the pyrene molecules have a "clathrate structure". A transmission electron microscopy analysis of the Debye-Waller factors suggesting appreciable libnation but no static disorder.


The different states of order of hexadecane (C₁₀₆₃₄) 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 rhombohedral superstructure reflections. This diffuse intensity was shown to be mainly of elastic or quasi-elastic origin by a measurement on the 3-axis neutron diffractometer R10 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 chains and channels. Hexadecane, which has a length close to but not equal to 4c 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 115 K some 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 "\( c/2 \)" 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.