

21-Crystallography at Non-Ambient Temperatures and/or Pressures; Phase Transitions

At 120K, it appears two short distances Cl-H which can induce special behavior of two Cp rings among the six to be considered. We consider also the possibility that a Cp ring may oscillate about its mean position - thus librating with a certain magnitude. This model confirms libration is not equivalent for two Cp rings due probably to the appearance of some Cl-H bonding.

Inelastic neutron scattering experiments have been performed on polycrystalline samples of  $U(C_5H_5)_3Cl$ , from 5K to 300K, to examine the quasielastic scattering that occurs from the hydrogen atoms in the cyclopentadienyl rings. The analysis of the scattering shows that a reorientational mode consistent with a  $2\pi/5$  process is present. At 300K, the proton correlation time ( $\tau_c$ ) is  $4.2 \cdot 10^{-12}$  s and is associated with an activation energy ( $E_A$ ) of 4.9KJ/mole. Major differences in the dynamic behavior of the rings have been observed in the following regions :  $300K > T > 245K >$  ;  $245K > T > 78K$  ;  $78K > T$ . This is consistent with the observation of structural phase transitions at 78 and 245K as deduced from the diffraction studies. Below 245K, the activation energy, which represents the potential barrier between sites, increases from 4.9KJ/mole to 9 KJ/mole. At the same time 1/3 of the rings are blocked by intermolecular hydrogen bonds that arise during this first transition. At 78K the second structural phase transition induces a triclinic symmetry (coupled with a twinning), and generates a "freezing" of the rings. This review confirms the great interest to carry out both elastic and inelastic experiments in this kind of studies.

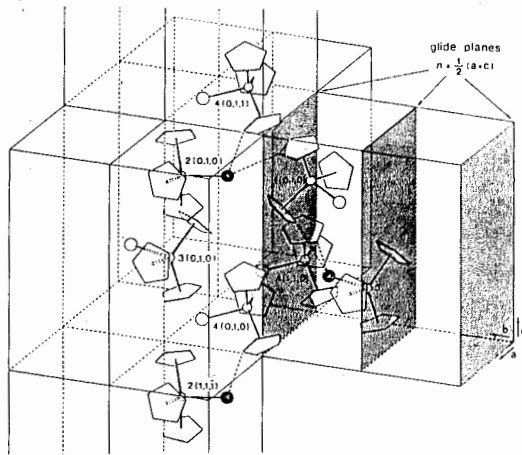


Figure. Representation of the structure of  $UCp_3Cl$  at 120K as determined by a crystallographic refinement of the neutron intensities from a single crystal. The large circles are the chlorine atoms. The dashed lines from these to the H atoms at the corners of the Cp rings indicate the short Cl-H distances that develop at low temperature and cause a hindering of the dynamical rotation of the relevant Cp rings. This is the process that causes 1/3 of the Cp rings to stop rotating below the 245K phase transition.

PS-21.03.19 PRESSURE-INDUCED MODULATED PHASES OF  $(N(CH_3)_4)_2MCl_4$  (M=Mn,Zn). By S.Shimomura\*, N.Hamaya<sup>1)</sup> and Y.Fujii<sup>2)</sup>. The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-01, Japan. Ochanomizu Univ.<sup>1)</sup>. ISSP, Univ. of Tokyo<sup>2)</sup>.

It is well known that  $(N(CH_3)_4)_2MCl_4$  (TMATC-M) compounds, where M is a transition metal such as Mn, Fe, Co, Ni, Cu and Zn, undergo commensurate(C)-incommensurate(IC) phase transitions, and their pressure-temperature(P-T) phase diagrams have the geometrical similarity. Theoretically C-IC phase transitions can be explained by Ising models with

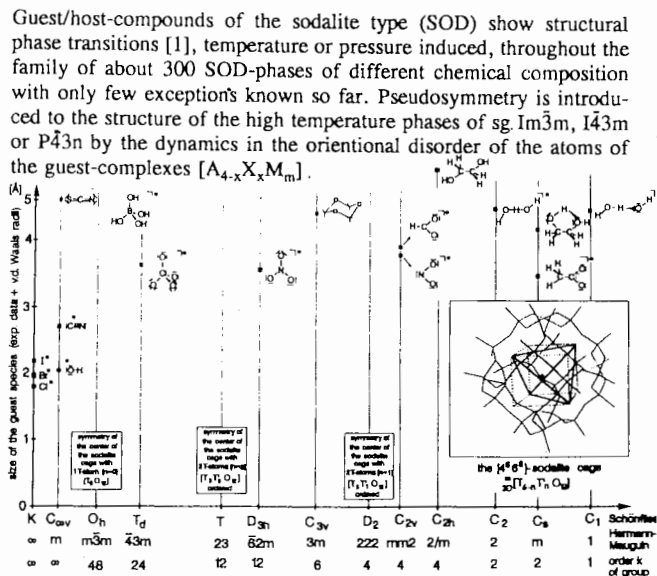
competing interactions such as ANNNI model. These systems exhibit infinite number of C-phases and the periodicity as a function of temperature or pressure has an infinity of steps, i.e., "the devil's staircase."

In order to study the C-IC phase transitions of TMATC-Mn, we have carried out high precision x-ray diffraction experiments under hydrostatic pressure at several fixed temperatures. It has been revealed that the existence of several new C-phases with long period. The wave number of these C-phases constitutes the Farey-tree series. The pressure dependence of the wave number and the observed P-T phase diagram are in good agreement with those calculated by the ANNNI model (Hamaya, Shimomura & Fujii, 1991). To search for the higher order C-phases in other compounds, we are under way to investigate the modulation of TMATC-Zn by using the same method.

One of the present authors (SS) would like to thank Special Researchers' Basic Science Program, RIKEN. Hamaya, N., Shimomura, S. & Fujii, Y. (1991). J.Phys.: Condens.Matter3, 3387-3391.

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BLOCKED STRUCTURAL PHASE TRANSITIONS IN SODALITE COMPOUNDS  $[A_{4-x}X_xM_m]_2[T_{6-n}T'_nO_{12}]_2$ ; DOT GASES OR DOT GLASSES FROM FROZEN IN ORIENTATIONAL DISORDER OF THE GUEST COMPLEXES  $[A_{4-x}X_xM_m]$ , A:  $Na^+, Ag^+, \dots$  X:  $OH, B(OH)_4^-, \dots$  M:  $H_2O, \dots$ ,  $0 < x < 1$ ,  $0 < m < 4$ , WHICH SHOW SOFT COULOMB COUPLING WITH THE HOST STRUCTURE  $[T_{6-n}T'_nO_{12}]$ , T: Si, Ge; T': Al, Ga;  $0 < n < 3$  St. Assmann, P. Behrens, J. Felsche\*, G. vdGOOR, P. Sieger, G. Wildermuth Dept. of Chemistry, University of Konstanz, D-7750-Konstanz, Germany



Guest/host-compounds of the sodalite type (SOD) show structural phase transitions [1], temperature or pressure induced, throughout the family of about 300 SOD-phases of different chemical composition with only few exceptions known so far. Pseudosymmetry is introduced to the structure of the high temperature phases of sg. Im3m, I43m or P43n by the dynamics in the orientational disorder of the atoms of the guest-complexes  $[A_{4-x}X_xM_m]$ .