

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 (τ_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.

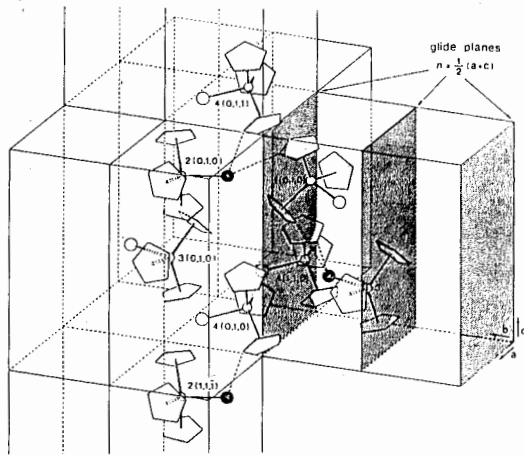


Figure. Representation of the structure of UCp_3Cl at 120K as determined by a crystallographic refinement of the neutron intensities from a single crystal. The large circles are the chlorine atoms. The dashed lines from these to the H atoms at the corners of the Cp rings indicate the short Cl-H distances 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.Hamaya¹⁾ and Y.Fujii²⁾. The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-01, Japan. Ochanomizu Univ.¹⁾. ISSP, Univ. of Tokyo²⁾.

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

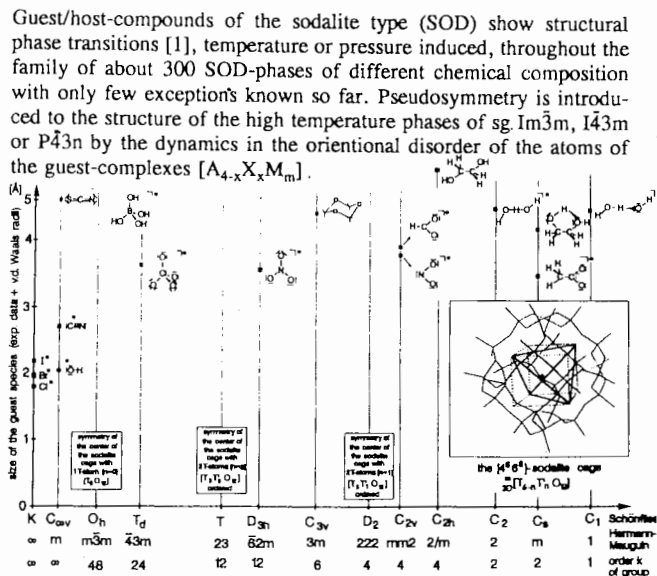
competing interactions such as ANNNI model. These systems exhibit infinite number of C-phases and the periodicity as a function of temperature or pressure has an infinity of steps, i.e., "the devil's staircase."

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.

PS-21.03.20

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



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The true symmetry of the anions A or template molecules M is of lower grade than cubic symmetry, predominately in the various SOD-compounds under scope. With increasing temperatures the guest/host symmetry misfit is diminished by dynamics of the guest atoms. They approach spherical character by hopping between equivalent positions with hopping frequencies up to 10^{15} Hz close to T_{dec} , the temperature of peritectical decomposition of the host structure. T_{dec} is the temperature critical to the guest/host interaction. In the given SOD-compounds the values of T_{dec} vary between 900 and 1500K for the same type of host composition [$T_{6-n}T'_nO_{12}$]. Thus a given host structure of lattice energy U_h might serve to test the real v.d.WAALS and COULOMB forces given by the atoms of the guest complexes encapsulated in the 4^66^8 -SOD-cage. There is some evidence for a *dot gas* character of the guest complexes close to T_{dec} , from the high chemical potential provided by the dynamics of the atoms intra-cage rotation, the translational movement being forbidden by the periodic $\frac{3}{a}$ matrix of cages. Upon cooling structural phase transitions occur through cooperation of the guest atoms with the host structure on a certain level of hopping frequencies, thus lowering the symmetry of the host structure[2]. Phase transitions present critical phenomena in the individual type of interactions between the chemical species of the guest- and of the host structure as revealed in the peak shapes by DSC-microcalorimetry. Some SOD-phases show no structural phase transitions, surprisingly, but irregularities in the trace of regular DSC-experiments run with a 5K/min cooling rate. The shift in the c_p -curves, the value of 0.20 J/gK is observed in the hydrosodalite type $[Na_3\Box(OD_2)_4]_2[Si_3Al_3O_{12}]_2$ at $T_g = 150K$, resemble the glass transition of polymers and inorganic glasses. Contrary to the findings in *orientational glasses* we like to introduce the term *dot glass* to this group of new materials, which differ by the periodic $\frac{3}{a}$ matrix of cages as in zeolite like materials.

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PS-21.03.21 MECHANISMS OF PHASE TRANSITIONS IN HEXAGONAL MODEL WITH 1q AND 3q INCOMMENSURATE PHASES

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A hexagonal two-dimensional model of particles with displacive degree of freedom and interacting via potential energy with harmonic and anharmonic third and fourth order terms has been studied by the molecular-dynamics technique. The phase diagram of the model exhibits normal, $k=0$ commensurate, one-dimensional (1q) and three-dimensional (3q) incommensurate phases. The 3q phase can be visualised as a sequence of columns, oriented along the hexagonal axis. The columns form a hexagonal discommensuration lattice. At higher temperature, the 3q incommensurate phase is more stable than the 1q phase.

The simulation shows that: (i) The $1q \rightarrow k=0$ phase transition is driven by the antistripes, which are topological defects of the stripe discommensuration lattice. (ii) In the $3q \rightarrow k=0$ phase transition, the columns are suppressed. The first eliminations occur at random, the following ones rather close to already annihilated columns. (iii) The $1q \rightarrow 3q$ phase transition which preserves the modulation wavelength, is driven by anisotropic antistripes nucleated equidistantly on the discommensuration planes of the 1q phase. The appearing 3q phase may contain deperiodization (dislocation) loops at the sites of a hexagonal discommensuration lattice. (iv) In the $3q \rightarrow 1q$ phase transition with constant modulation wavelength, the columns of phase 3q merge into each other to form a stripe of discommensuration plane. (v) The mechanism of the $3q \rightarrow 3q'$ phase transition associated with a change of the modulation wavelength, exhibits three types of deperiodization loops.

PS-21.03.22 STRUCTURAL TRANSITIONS AND MAGNETIC PROPERTIES IN $LaFe_{13-x}Al_x$ SYSTEM. By W.H. Tang*, J.K.Liang, X.H.Yan, G.H.Rao, and S.S.Xie. Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China.

The excellent magnetic properties of the $LaCo_{13}$ intermetallic compound raised the interest of many researchers. For exploring new rare-earth 3d transition-metal permanent magnet, it is important to investigate intermetallic compounds related to the $NaZn_{13}$ type structure. As is well known, those materials which have cubic structure are impossible to be used as permanent magnets because of their high symmetry. From the point of view of crystal structure, we attempt to lower the symmetry of cubic $NaZn_{13}$ by proper heat treatment or elemental substitution, in order to improve magnetic anisotropy.

After annealing at 773K for about two months, structural transitions from cubic to orthorhombic have been observed for $LaFe_{13-x}Al_x$ ($x=6,7$). The results of X-ray diffraction and magnetic measurements show that under the given heat treatment procedure, only those cubic $NaZn_{13}$ phase samples with mictomagnetic character change their structures. Selected-area electron diffraction patterns confirm that, after annealing at 773K, $LaFe_{13-x}Al_x$ have a body centered orthorhombic structure with a structural modulation along the a-axis. For $LaFe_6Al_7$, the modulated period is $0.068a^*$ ($a = 8.21\text{\AA}$). The structural transitions result in the change of magnetic properties from mictomagnetism to ferromagnetism.

PS-21.03.23 INVESTIGATION OF THE FERROELECTRIC TRANSITION IN POTASSIUM IODATE. By J.G. Zhang, Institute of Crystal Materials, Shandong University, Jinan, China

Potassium iodate crystals are ferroelectric and belong to the triclinic system with space group P1. They possess piezoelectric properties in the range from -195°C to $+300^\circ\text{C}$. Irreversible spontaneous polarization along the pseudo three-fold axis is observed. Four phases exist in this temperature range: the first one exists above 212°C , the second one between 72 and 212°C , the third one between -15 and 72°C , and the last one below -15°C .

Monodomain and multidomain crystals with good optical characteristics were selected. Observations were performed on 2-mm thick (001) ground and polished plates. An investigation of the ferroelectric transition was carried out using an OPTON polarizing microscope, a Leitz heating stage, a long-focus objective lens and a thermocouple temperature measurement device with automatic compensation.

In the hexagonal structure of KIO_3 , potassium ions are at the vertices, oxygens at face centers and iodine ions at body centers. The crystals are paraelectric in phase I. In phase II, iodine ions move along the body diagonal, and spontaneous polarization takes place with formation of 120° domains. In phase III, iodine atoms move perpendicular to the oxygen ions in on {100} planes, and crystals become triclinic. Below 212°C , potassium iodide crystals are mostly 120 and 60° multi-domain crystals.

PS-21.03.24 CHANGE OF LATTICE PARAMETERS AS EVIDENCE OF AUSTENITE THERMAL INSTABILITY IN MANGANESE STEELS. By V.E. Danilchenko, A.V. Nedolya* and V.M. Nadutov, Metal Physics Institute and Department of Physics, Zaporozhye State University, Ukraine.