

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

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PS-21.03.15 THE FERROELECTRIC PHASE TRANSITION IN LIGHTLY DOPED BARIUM TITANATE. By C.N.W. Darlington, School of Physics, University of Birmingham, Birmingham, U K, and R.J. Cernik, Daresbury Laboratory, Warrington, U K.

The ferroelectric phase transition in lightly-doped barium titanate at 130°C has been studied using the diffractometer on line 9.1, SRS, Daresbury in high-resolution mode. The concentration of dopant was typically 0.3 mole % with both barium and titanium being replaced. In all cases the transition was smeared out, with the discontinuity unobservable. We find that, when the valency of the dopant is different from that of the ion it replaces, the value of a critical exponent indicates that the system behaves as "host" i.e. pure barium titanate, plus point-like impurity. Impurities with a higher valency than the replaced ion are electrically screened, while those with lower valency are not. However no difference in behaviour between them was detectable. All impurities studied caused the low-temperature phase to form locally at temperatures above the transition temperature of the pure material, yet lowered the temperature at which the overall symmetry became tetragonal. This is interpreted as inhibition of phonon softening of the low-temperature form by small clusters. Solid solutions e.g. (barium, strontium) titanate behave differently: clearly one cannot consider strontium as an impurity in a barium-rich solid solution.

PS-21.03.16 THE PHASE SEQUENCE OF $\text{Ca}_8[\text{Al}_{12}\text{O}_{24}](\text{CrO}_4)_2$. By R. Melzer*, W. Depmeier¹, S. Doyle². Hahn-Meitner-Institut, Glienicke Str.100, D-1000 Berlin 39. ¹Mineralogisch-Petrographisches Institut, Universität Kiel, D-2300 Kiel. ²HasyLab, DESY, Notkestr. 85, D -2000 Hamburg 52.

$\text{Ca}_8[\text{Al}_{12}\text{O}_{24}](\text{CrO}_4)_2$, in short notation CACr, is a member of the aluminatite sodalite family (Depmeier, Phys. Chem. Min. 15, 419, 1988). According to complex host-guest interactions in this cage structure, all end members show one or more, in general, ferroic phase transition. Three of them were found for CACr at high temperatures. The only structural information available for CACr was that the room-temperature phase shows a 3:2:1 modulation. Therefore, we focussed our attention on CACr and started investigations such as temperature-dependent X-ray powder and single crystal diffraction.

In order to follow the lattice parameters of CACr with increasing temperature, an X-ray powder experiment was performed on the diffractometer at beamline B2 at HasyLab using the furnace described by Arnold (Materials Sc. For. 79-82, 445, 1991). All three known phase transitions could be identified by anomalies in the variation of lattice parameters. We found an additional anomaly at about 560K, which is a further, new phase transition. A re-examination of DTA curves confirmed this transition and lead us to the assumption of still another transition at 464K. This transition should be verified in a forth-coming experiment. Consequently the proposed phase sequence of CACr is:

Phase#	1	2	3	4	5	6					
	o/c	483K	o/?	456K	/?/?	464K	t/c	560K	t/i	610K	c/n

Each phase is summarized above by two letters. The first one is about the crystal system: o=orthorhombic, t=tetragonal, c=cubic. The second one is about the modulation: c=commensurate, i=incommensurate, n=none. For both informations, ?=to be established. Transition temperatures between phases are given.

The crystal symmetries have been determined from the splitting of the main reflections (formerly cubic reflections of phase 6, ferroelastic phase transitions) in the X-ray powder diffraction experiment.

We tried to verify all phases in a single crystal X-ray precession experiment with a Huber heating device. Until now, we have not been able to identify phases 4 and 5. There is evidence that phase 5 which has been found in the powder diffraction experiment at HasyLab is incommensurately modulated.

At the conference we will present in detail the results of the temperature dependent X-ray powder and single crystal experiments.

PS-21.03.17 PHASE TRANSITIONS OF Na_2SO_4 AND STRUCTURE REFINEMENTS AT SEVERAL TEMPERATURES. By S.E. Rasmussen* and J.-E. Jørgensen. Department of Chemistry, University of Aarhus, Denmark.

Sodium sulphate, Na_2SO_4 , has been reported to exist in five polymorphous forms labelled I-V and structure analysis and thermal analysis have been reported on most of the polymorphs. We have reinvestigated the system by differential thermal analysis, DTA, and differential scanning calorimetry, DSC, and by X-ray powder diffraction at several temperatures in order to examine the Na_2SO_4 system with one and the same batch of material in one and the same laboratory by two independent methods.

Guinier transmission techniques were applied both with film methods and with diffractometer methods. The X-ray results confirm the existence of the crystalline phases labelled I, II, III, and V, whereas the phase IV whose existence in the temperature range 458-514K was alleged by Brodale, G.E. and Giaouque, W.F. (1972), J. Phys. Chem. 76, 737-743, on the basis of calorimetric data does not appear to have a powder diagram which confirms the independent existence of this phase. The DSC measurements do, however, indicate the existence of a slight thermal effect near 500K.

Rietveld refinements have been carried out on the structures of I and III at several temperatures and of V at room temperature. The structure of II which exists in a narrow temperature interval around $220^\circ \pm 5^\circ\text{C}$ is presently being investigated.

Heats of reactions have been measured for the transitions: V-I, I-II, II-III and III-I. The transition I-II has been found to be reversible whereas the other transitions are not.

PS-21.03.18 PHASE TRANSITION IN THE ORGANO METALLIC COMPOUND $\text{U}(\text{C}_5\text{H}_5)_3\text{Cl}$. By P. Raison^a, A. Delapalme* and G.H. Lander^b. a. Laboratoire Léon Brillouin (CEA-CNRS), CE - Saclay, 91191 Gif-sur-Yvette, France; b. Commission of the European Communities, I.T.E. P2340, D-7500, Karlsruhe, Germany.

The goal of this paper is to summarize together the results yielded by neutron diffraction and inelastic neutron scattering to characterize the phase transitions with the temperature observed in the organometallic compound UCp_3Cl . It is a part of the thesis of P. Raison to be published in Molecular Physics.

We have used neutron diffraction technique on single crystal sample to examine the symmetry of the unit cell of the organometallic compound $\text{U}(\text{C}_5\text{H}_5)_3\text{Cl}$ as a function of temperature below 300K. Two phase transitions occur. The first, at 245K, results in a change of space group but the monoclinic symmetry is retained ($\text{P2}_1/\text{n} \rightarrow \text{Pn}$); the second, at 78K, results in the material becoming triclinic. The crystallographic work is important because to compare observed and calculated values of structure factors, we need a great number of reliable small observations together with difficult calculation of complicated models. We show that at 300K it is not possible with the diffraction alone to determine whether the structure is statistically or dynamically distributed.

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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.

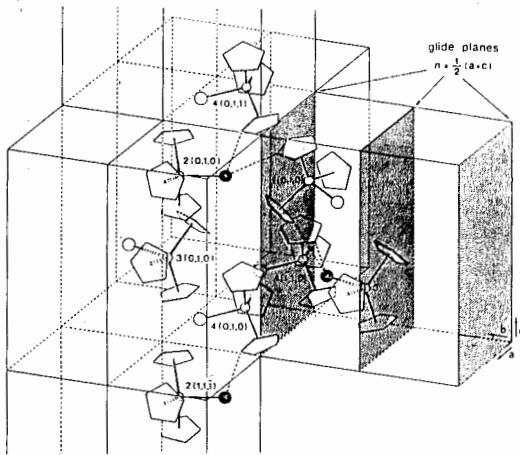


Figure. Representation of the structure of UCp_3Cl at 120K as determined by a crystallographic refinement of the neutron intensities from a single crystal. The large circles are the chlorine atoms. The dashed lines from these to the H atoms at the corners of the Cp rings indicate the short Cl-H distances 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 $[T_{6-n}T'_nO_{12}]_2$, 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

