PS11.05.31 REVERSIBLE PHASE TRANSITION IN CRYSTALS WITH A SUPRAMOLECULAR AGGREGATE. Isabel Pascual(1), Larry R. Falvello(1), Arthur J. Schultz(2), Dianna M. Young(2), (1)University of Zaragoza, Department of Inorganic Chemistry, Faculty of Science, Plaza San Francisco s/n, E-50009 Zaragoza, Spain, (2)Intense Pulsed Neutron Source, Bldg. 360, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439-4814, USA

Crystals of *trans*-[Ni(cyan-N)$_2$(NH$_3$)$_4$], which possess a stable supramolecular ribbon formed by self-assembly of cyanurate ligands, undergo a reversible, temperature-induced phase transition. At 23º C., crystals of this molecular material are orthorhombic, space group Fmmm, with a = 12.0551 (6), b = 7.2825 (6), c = 16.0779 (7) Å, and Z = 2. The molecule lies on a site of symmetry mmm, with the cyanurate rings coplanar. At -173º C., the crystals are orthorhombic, space group Cmcm, with a = 11.998 (4), b = 7.203 (6), c = 15.736 (5) Å; and the molecule lies on a site of symmetry m2m. At the lower temperature, the molecule is distorted by bending of the cyanurate rings out of their common plane, such that the angle between the two ligand rings is 33º. Upon warming to room temperature, the structure reverts to its original form. A given crystal can be cycled through the transitions more than once. At intermediate temperatures, an intermediate structure emerges. At -50º C., the crystal has space group Cmcm, with a = 12.033 (2), b = 7.253 (1), and c = 15.937 (3) Å, and the same structural type as that at -173º C.; but the distortion of the molecule is less pronounced, with an angle of 21.6º between the planes of the two cyanurate ligands. Structural characterizations at temperatures from -250 to +80º C. are presented. The very low temperature determination was by neutron diffraction. The phase transitions have been followed in real time, using profiles of reflections that change in the transition. It has been possible to isolate a metastable Cmcm phase at room temperature. The qualitative as well as quantitative differences between the two phases are described, and the nature of the transition is discussed.

PS11.05.32 X-RAY DIFFRACTION STUDIES OF Pd - Cu POWDERS. J.Pielaszek, Z.Kaszkur, B.Mierzwa - Institute of Physical Chemistry, Polish Academy of Sciences, Warszawa, Poland.

Structural changes induced by various temperature and controlled atmosphere treatments in mixtures of Pd - Cu powders were studied by *in situ* XRD in the aim to understand behaviour of supported Pd - Cu catalysts subjected to different pre-treatments. The position sensitive detector (PSD) CPS 120 from INEL has been used to obtain temperature scans in 10 min. intervals. The samples were carefully mixed in different weight proportion of Pd and Cu blacks of average particle sizes of 200 and 300 Å respectively. Then they were loosely spread on porous glass sample holder and placed in a controlled atmosphere XRD camera mounted on the axis of the PSD. XRD patterns were recorded for two different treatments: 1) oxidation at temperatures up to 5500 C followed by reduction in hydrogen up to 5500 C for various periods of time and 2)reduction in hydrogen up to 5500 C with and without transformation of palladium into its hydride at low temperatures.

Under the first treatment it was observed that different mixed oxides were formed which subsequently were reduced and, depending on the relative composition, either intermetallic solid solutions were formed (for low copper content)or complex intermetallic Pd-Cu phases (for high copper contents).

The final results obtained for the second treatment were qualitatively similar. The transformation of palladium into hydride at the first stage of hydrogen reduction had no noticeable influence on the phases formed.

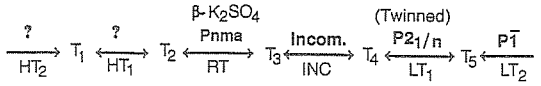
The same conditions were applied for treatment of some Pd - Cu / SiO2 model catalysts with total metal loading of 2 and 10 wt.%.

The results are being rationalized in terms of the interdiffusion between initially monometallic grains and formation of different concentration profiles and intermetallic compounds within the clusters.

PS11.05.33 PHASE TRANSITION IN THE Cs_2XBr_4 (X = Hg, Cs). C. B. Pinheiro and N. L. Spezial, Departamento de Física, ICEx - UFMG, Belo Horizonte - Brazil

Among the compounds classified in the A_2BX_4 family, several members have been considered as candidates to present incommensurate phase. Two of them, Cs_2CdBr_4 and Cs_2HgBr_4, are special ones: their lock-in phase occurs at q=0, without the appearance of a superstructure. Their room temperature (RT) structure is isomorphous to β-K_2SO_4. Decreasing temperature, an incommensurate (INC) phase appears as evidenced by the presence of satellite reflections.

Differential scanning calorimetry (DSC) and single crystal X-ray diffraction experiments have shown that both compounds present high temperature phase transitions at $T_1 \approx 820K$ and at $T_2 \approx 720K$. Their complete phase transition diagram can be represented as follows:



with Cs_2HgBr_4 presenting an extra low-temperature phase LT_3.

The disordered hexagonal phase evidenced in several members of the A_2BX_4 family (so called α-K_2SO_4 phase) has not yet been observed in Cs_2XBr_4. X-ray diffraction measurements are in progress in order to investigate the high temperature phases of such compounds.

PS11.05.34 PHASE TRANSITIONS IN Al-Zn ALLOYS. S.Popovic (1,2), B. Grzeta (1), H. Löffler (3), G. Wendrock (3); (1) Ruder Boskovic Institute, POB 1016; (2) Faculty of Science, POB 162; 10001 Zagreb, Croatia; (3) Martin-Luther Universität, D-06099 Halle, PSF 8, Germany

Phase transitions and the formation of solid solutions in alloys having 24, 40, 48, 54 and 62 at%Zn were followed *in situ* by X-ray powder diffraction. These alloys in the equilibrium state at RT are two-phase systems: α-phase (fcc, with 99at%Al) and β-phase (hcp, with more than 99.5at%Zn). As the temperature of the previously annealed alloy increased, a decrease of the peak intensities of diffraction lines took place, due to increased thermal vibration amplitudes. Also, a shift of diffraction lines due to thermal expansion was observed. The β-phase exhibited an anisotropy in thermal expansion, this being eight times larger along the *c*-axis than along the *a*-axis. A partial dissolution of the β-phase in the α-phase started at≈490 K. Above 550 K the phase transition β-α' (fcc) took place. The unit cell of the α'-phase was smaller for 0.9% than that of the α-phase at 560 K. For the alloys with the Zn content of 24, 40 and 48 at%, the β-phase was not present above 555 K. As the temperature further increased, the α- and α'-phases merged together and the solid solution, α(SS)(fcc), was formed (Popovic et al., 1993). For the alloys with the Zn content of 54 and 62 at%, the α-phase disappeared at ≈650 K, the α'-phase remaining in coexistence with the β-phase. The β-phase finally disappeared at ≈700 K, and α(SS) was formed. In the cooling cycle, a temperature hysteresis in reversal phase transitions was observed. During a repeated heating of the same specimen, a temperature delay in phase transitions for several tens K's took place. The present results indicate that minor corrections are necessary in the phase diagram of the system Al-Zn, as accepted in literature.

S. Popovic, B. Grzeta, H. Löffler, G. Wendrock, Phys. Stat. Sol. (a) 140(1993)341-352.