05.1-14 STRUCTURAL STUDY OF THE PHASE TRANSITION IN $(NH_4)_2\ CuCl_4.2H_2O$. By Sandhya Bhakay-Tamhane, Neutron Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay-400085, India and E.J. Gabe, Chemistry Division, National Research Council of Canada, Ottawa, Canada K1A OR9.

Single-crystal diffraction study of the title compound was carried out above and below the critical temperature (200.5 K) to elucidate the structural changes due to order-disorder phase transition in the salt.

The room-temperature neutron diffraction study of the mixed salt $(NH_4)_2\ CuCl_4.2H_2O$ (space group $P4_2/mnm$, a = 7.596 (4), c = 7.976 (4) Å, Z = 2) carried out at Trombay, refined to an R-factor on F of 0.022. The results revealed a partial disorder of the ammonium tetrahedra in the ratio 0.64:0.36 in favour of the configuration with the NH_4^+ hydrogens bonded to the closer chlorines (Bhakay-Tamhane, Sequeira and Chidambaram, Acta Cryst. B36 (1980) 2925). The structure consists of a pseudo one-dimensional network of ammonium ions, the inter-ammonium distance along z-axis is 3.99Å while in the x-y plane it is 5.37Å. The X-ray diffraction studies, carried out at 115 K (1990 unique reflections upto $\sin\theta/\lambda = 1.0Å^{-1}$, collected at Ottawa) indicate a fully ordered structure with the space group $P\bar{4}2_1m$ (a = 7.540(2), c = 7.915 (2) Å, Z = 2), which is a subgroup of the room temperature space group. This space group is in agreement with a recent Raman scattering study of the crystal (Bansal, Sahni and Roy, J. Phys. Chem. Solids 40 (1979) 109). The least-squares refinement of the structure gave a final R value on F as 0.035.

The two non-equivalent NH_4^+ ions which are both in an approximately cubic environment of chlorine atoms, are related by a $z = \frac{1}{2}$ translation, which implies parallel ordering of the ammonium ions in the low-temperature phase. As against this, there is an antiparallel ordering in the room-temperature phase due to the mirror plane perpendicular to the c-axis. The evolution of ordering in this salt will be discussed.

05.1-15 THE MODULATED STRUCTURE OF γ-PAMC. By W. Depmeier, Chimie appliquée, Université de Genève, Geneva, Switzerland.

Between 344K and 396K, γ-PAMC, i.e., Bis(n-propylammonium)Tetrachloromanganate(II), $(C_3H_7NH_3)_2MnCl_4$, forms a modulated structure as indicated by satellite reflexions of two different kinds. The results of the refinement of the average structure as well as the possible superspace group (Janner, Janssen & de Wolff (1979) in Modulated Structures - 1979, AIP Conference Proceedings No.53) and a model for the modulated structure, both based on the most prominent A-satellites have been published (Depmeier, Acta Cryst. (1981), in press). Important questions concerning the true superspace group, the temperature dependence of the modulation vectors, the mutual dependence (or independence) of the two modulation vectors and the cause of the modulation are still under active investigation and latest results will be presented.

05.1-16 PHASE TRANSITIONS IN $(C_nH_{2n+1}NH_3)_2ZnCl_4$. By F.J. Zuniga and G. Chapuis, Institut de Cristallographie, BSP Dorigny, CH-1015 Lausanne (Switzerland).

Compounds of the type $(C_nH_{2n+1}NH_3)_2ZnCl_4$ (short CnZn) show a series of phase transitions in the solid state as derived from calorimetry (Socias et al. phys. stat. sol. (a),57,404,1980). To understand the transition mechanisms, the structures of different phases at various temperatures have been investigated.

The low-temperature phases of all investigated compounds have the same type of structure. Layers of isolated $ZnCl_4$ tetrahedra alternate with layers of alkylammonium ions. Each N atom is linked to three Cl atoms by hydrogen bonds. If n>4, the alkylammonium layer is formed by interpenetrating chains attached to consecutive $ZnCl_4$ layers.

C3Zn shows a single transition at 310 K with a second-order character. The ordered low-temperature phase is monoclinic, ($P2_1/n$, a=10.219(2)Å b= 7.3632(9) c=20.077(2) α=92.65(1) at 295 K). The high-temperature phase is orthorhombic (Pnma a= 10.243(1) b=7.3828(6) c=20.213(2)) with disordered alkylammonium ions. The transition is of the order-disorder type.

The same type of transition can be found for all odd n and for the even with n>12. In C5Zn the order-disorder transition takes place at 256 K. The room temperature phase is Pnma (a= 10.323 (4) b=7.406(3) c=25.171(8)) with disordered alkylammonium chains.

In C14Zn, the monoclinic ($P2_1/c$ a=10.254(1) b= 7.3980(7) c=47.659(5) α=92.794(7)) to orthorhombic (Pnma a=10.3(1) b=7.5(1) c=47.8(1)) transition occurs at 362 K.