05.1.14 STRUCTURAL STUDY OF THE PHASE TRANSITION IN (NH$_4$)$_2$ CuCl$_4$.2H$_2$O. 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 0R9.

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$_2$O (space group P4$_2$/mm, a = 7.596 (4), c = 20.213 (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$_3$ hydrogens bonded to the closer chlorines (Bhakay-Tamhane, Sequeira and Chidambaram, Acta Cryst. B35 (1980) 2925).

The structure consists of a pseudo one-dimensional network of ammonium ions, the inter-ammonium distance along z-axis is 3.93 Å while in the x-y plane it is 5.37 Å. The X-ray diffraction studies, carried out at 115 K (1990 unique reflections up to sinG/λ = 1.0 Å$^{-1}$, collected at Ottawa) indicate a fully ordered structure with the space group P 42/m (a = 7.540(2), c = 17.976 (2) 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$_3$ hydrogens bonded to the closer chlorines (Bhakay-Tamhane, Sequeira and Chidambaram, Acta Cryst. B35 (1980) 2925).

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The two non-equivalent NH$_4^+$ ions which are both in an approximately cubic environment of chlorine atoms, are related by a z = ½ 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[(-propylammonium)tetrachloromanganate(II)], (C$_3$H$_7$NH$_3$)$_2$MnCl$_4$, forms a modulated structure as indicated by satellite reflection peaks 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 modulation vectors, the mutual dependence (or independence) of the modulation vectors, and the cause of the modulation vectors will be presented.
An important characteristic of the room temperature phase concerns the packing of the aliphatic chains. The periodic array of the C atoms within a single layer can be described by a monoclinic cell with a=7.9 b=10.3 c=2.54 and β=99° with space group symmetry P21. This type of packing is not mentioned in the list given by Segerman (Acta Cryst. 19, 789,1965).

Three additional transitions appear in calorimetric studies when n=odd and larger than 4. The transition enthalpy of the first one by increasing temperature, is small and no changes could be observed on a powder diagram for C6Hn. In the next transition, important structural transformations occur such as an abrupt increase of the c lattice constant, characteristic for the reorientation of the chains. The corresponding phases of CSn and CI42n are orthorhombic with lattice constants a=10.19(2) b=7.09(1) c=27.9(1) and a=10.3(1) b=7.6(1) c=57.5(1) respectively.

In this series of compounds, the transition from an ordered monoclinic phase to a quasi-liquid high temperature phase occurs in successive steps, including an intermediate orthorhombic phase with space group symmetry Pnma. In this state, the disordered chains oscillate between two equilibrium positions related by a plane of symmetry.


The cation distribution of magnetite(spinel structure) has been investigated with a high-temperature X-ray camera. At temperatures above 1273K the NaCl-structure of Fe3O4 develops. The reversible transformation Fe3O4→Fe3O4 can be performed by a slight variation of the oxygen partial pressure without destroying the single crystal. The kinetics of this transformation can be explained by diffusion of the iron-cations to the octahedral vacancies.

The lattice constant of magnetite was measured as a function of the temperature (a0=5.390 Å at 298K, a0=5.454 Å at 1273K expansion coefficient α=4.9 10^-5/K at 1273K).

Structural refinements at 573K and 1073K yield an increase of the oxygen parameter X, indicating an increase of the O-Fe distance. We assume that this effect stems from anharmonic motions which may also explain the U-factor rising from 4.6% at 573K to 8.5% at 1073K.

05.1-19 CRITICAL NEUTRON SCATTERING IN THE 3-d ISING HETMAGNET DyPO4, By A.H. Millhouse, H. Dachs, and H. Steiner, Hahn-Meitner-Institut, Glionicker Strasse 100, D-1000 Berlin 39, Germany.

The critical neutron scattering near the critical line of DyPO4 has been investigated as a function of temperature, magnetic field, and hydrostatic pressure. At atmospheric pressure and at TN the behaviour of the critical scattering is in agreement with theoretical predictions for the 3-d Ising model. As one moves along the critical line to lower temperatures the critical scattering peak weakens and disappears below 1.85 K. This indicates a change over from second- to first-order behaviour below this temperature. Magnetic domain effects do not vanish above this temperature in agreement with light-scattering measurements (Jahn, I.R., et al. Solid State Commun. 28, 421 (1978)). That strains are important in this system was confirmed by measurements under hydrostatic pressure. TN is not sensitive to pressure up to 5 kbar but the transition at TN becomes anomalous. It appears to be second-order for increasing temperature and first-order for decreasing temperature. This cannot be understood in terms of present theory.

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