

05.1-14 STRUCTURAL STUDY OF THE PHASE TRANSITION IN  $(\text{NH}_4)_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$ . 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  $(\text{NH}_4)_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$  (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  $\text{NH}_4^+$  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 3.99 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 upto  $\sin\theta/\lambda = 1.0\text{Å}^{-1}$ , 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  $\text{NH}_4^+$  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  $\gamma$ -PAMC. By W. Depmeier, Chimie appliquée, Université de Genève, Geneva, Switzerland. Between 344K and 396K,  $\gamma$ -PAMC, i.e., Bis(n-propylammonium)Tetrachloromanganate(II),  $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{MnCl}_4$ , 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  $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{ZnCl}_4$ . By F.J. Zuniga and G. Chapuis, Institut de Cristallographie, BSP Dorigny, CH-1015 Lausanne (Switzerland).

Compounds of the type  $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{ZnCl}_4$  (short  $\text{C}_n\text{Zn}$ ) 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  $\text{ZnCl}_4$  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  $\text{ZnCl}_4$  layers.

$\text{C}_3\text{Zn}$  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)  $\alpha=92.65$  (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  $\text{C}_5\text{Zn}$  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  $\text{C}_14\text{Zn}$ , the monoclinic ( $P2_1/c$   $a=10.254$  (1)  $b=7.3980$  (7)  $c=47.659$  (5)  $\alpha=92.794$  (7)) to orthorhombic ( $Pnma$   $a=10.3$  (1)  $b=7.5$  (1)  $c=47.8$  (1)) transition occurs at 362 K.

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  $\beta=99^\circ$  with space group symmetry  $P2_1$ . 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  $C5Zn$ . 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  $C5Zn$  and  $C14Zn$  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.

#### 05.1-17 DUPLEX CHARACTER OF DEFECT ZINC BLENDE

STRUCTURE OF  $\alpha$  AND  $\gamma$   $Ga_2Se_3$ . By S.Z. Ali, National Physical Laboratory, New Delhi 110012 and M.Y. Khan, Jamia Millia Islamia, New Delhi 110025, INDIA.

X-ray powder patterns of  $\alpha$  and  $\gamma$   $Ga_2Se_3$ , both belonging to cubic defect zinc blende structure, give lattice parameters:

$$a_{\alpha} = 5.433(1) \text{ \AA} \text{ from sharp lines with } h+k+l=4n,$$

$$\left\{ \begin{array}{l} = 5.445(4) \text{ \AA} \text{ from reflections } hkl \text{ all odd,} \\ a_{\gamma} = 5.463(1) \text{ \AA} \text{ from all } hkl \text{ reflections.} \end{array} \right.$$

However, the powder pattern information for both phases is grossly inadequate as regards structure delineation. Our single crystal work shows that both structures are duplex in character. All strong, sharp reflections of  $\alpha$  phase with  $h+k+l=4n$  have diffuse components on the low angle side of  $\theta$  Bragg with corresponding lattice parameter  $\sim 5.445$   $\text{\AA}$ . Weak reflections with  $hkl$  even and  $h+k+l=2(2n+1)$  are diffuse with lattice parameter again  $5.445$   $\text{\AA}$ , same as for the strong, diffuse,  $hkl$  all odd, spots each of which has a remarkable set of streaks extending to all neighbouring reciprocal lattice nodes with  $h+k+l=4n$  or  $2(2n+1)$ . In the case of  $\gamma$   $Ga_2Se_3$  all reciprocal lattice nodes of high intensity have diffuse, broad spots on the high angle side of  $\theta$  Bragg with lattice parameter  $\sim 5.41$   $\text{\AA}$ , smaller than that of the sharp spots. The unique set of streaks however is missing in the  $\gamma$  phase. The duplex character of both phases is similar to that of neutron-irradiated  $BeO$  (Austerman, S.B. and Miller, K.T., phys. stat. sol. (1965), 11, 241).

05.1-18 HIGH-TEMPERATURE INVESTIGATIONS OF MAGNETITE ( $Fe_3O_4$ ). By N. Tzafaras, W. Adlhart, H. Jagodzinski, Institut für Kristallographie und Mineralogie der Universität München, München, Federal Republic of Germany.

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  $Fe_{1-y}O$  develops. The reversible transformation  $Fe_3O_4 \rightleftharpoons Fe_{1-y}O$  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 ( $a_0=8.396$   $\text{\AA}$  at 298K,  $a_0=8.545$   $\text{\AA}$  at 1273K expansion coefficient  $\alpha_0=14.9 \cdot 10^{-6}/K$  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 R-factor rising from 4.6% at 573K to 8.5% at 1073K.

05.1-19 CRITICAL NEUTRON SCATTERING IN THE 3-d ISING METAMAGNET  $DyPO_4$ <sup>a)</sup>. By A.H. Millhouse H. Dachs, and M. Steiner, Hahn-Meitner-Institut, Glienicke Strasse 100, D-1000 Berlin 39, Germany.

The critical neutron scattering near the critical line of  $DyPO_4$  has been investigated as a function of temperature, magnetic field, and hydrostatic pressure. At atmospheric pressure and at  $T_N$  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.  $T_N$  is not sensitive to pressure up to 5 kbar but the transition at  $T_N$  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.

a) This work was supported by - Der Bundesminister für Forschung und Technologie, Bonn -.