05.1-10 *CONFORMATIONAL ORDERING IN TETRAHEDRAL ZWEIER SINGLE CHAINS: FOUR SUCCESSIVE PHASE TRANSITIONS IN KPO_3.* By W.W. Schmahl, Mineralogisches Institut der Universität Kiel, West Germany.

Zweier single chains of (corner linked) identical rigid tetrahedra have 3 conformational degrees of freedom. All conformations may be derived from the chain of aristotype symmetry (line group $2_1/mmg$, Fig.1) by variation of 3 parameters, such as φ, τ_1 and τ_2 (Fig. 2). These parameters are defined in a way to reflect the symmetry of the chain. The aristotype symmetry with $\varphi = \tau_1 = \tau_2 = 0$ may only exist as a space and time average because of the non-zero thermal displacements at any temperature. The phase transitions of potassiumpolyphosphate, KPO_3, illustrate several ways of conformational ordering reducing the chain symmetry. The evolution and interaction of the ordering mechanisms was monitored by DSC, birefringence measurements and single crystal diffractometry. From the melt the phase KPO_3-HT crystallizes at 1111 K with space group Bbmm corresponding to the aristotype symmetry of the phosphate zweier single chains which run parallel to b. However, large statistical displacements from a symmetric arrangement lead to "split" atomic positions (JOST & SCHULZE, Acta Cryst., 1971, B27, 1345-1369). On cooling, this phase transforms at 922 K to KPO_3-H, Pbnm, due to antiferro-type ordering of the parameter φ in neighbouring chains. The mirror planes perpendicular to the chain are lost, but there is still a mirror plane parallel to the chain, i.e. $\langle\tau_1\rangle = \langle\tau_2\rangle = 0$. At a second phase transition at 768 K additional ordering with respect to the τ-type degrees of freedom sets in. In this third phase (KPO_3-H', $P2_12_12_1$) the chains are characterised by $\langle\varphi\rangle \neq 0$, $\langle\tau_1 = \tau_2\rangle \neq 0$, and chain-symmetry 2_1. On further cooling the $\tau_1 = \tau_2$ ordering scheme of the H'-phase breaks down at 724 K by a first order transition to an ordering with $\tau_1 \neq \tau_2$. The paraphase of this phase, KPO_3-Z, $P2_1/n$, is the H-phase. The φ-ordering pattern is still preserved but no conformational symmetry except the repeat period is kept. However, the distortion corresponding to the new $\tau_1 \neq \tau_2$-ordering mechanism creates a monoclinic shear strain which makes the existing φ-ordering pattern unstable with respect to a more complicated antiferro-type ordering pattern of the parameter φ. Thus there is another first order transition at 524 K to the phase KPO_3-T, $P2_1/a$, where a new φ-ordering pattern is created while the τ-ordering mechanism characterizing the Z-phase continues without substantial change. The paraphase of KPO_3-T is KPO_3-HT.

Fig.1

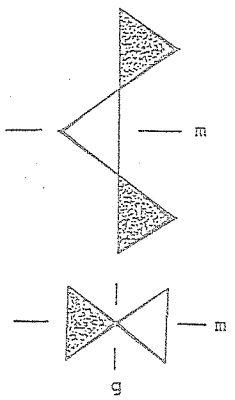
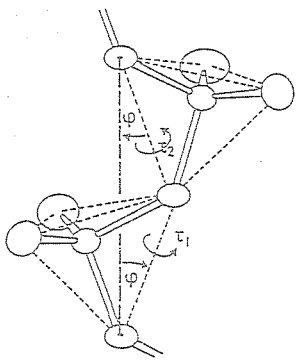


Fig.2



05.1-11 ELECTRON DIFFRACTION STUDIES OF MIXED VALENCE HOLLANDITES AND STRUCTURAL TRANSITION IN $CsTi_8O_{16}$. By J.L. Hodeau, E. Fanchon, J. Vicat, P. Strobel and J.A. Watts*, Laboratoire de Cristallographie, associé à l'U.S.T.M.G., C.N.R.S., 166 X, 38042 Grenoble Cedex (France). *Division of Mineral Chemistry, C.S.I.R.O., Melbourne, Australia.

Hollandite type phases $A_x(B,B')_8O_{16}$ with mixed valence framework cations (B and B' are the same atoms with different valencies) are useful materials for the study of inter- and intra-tunnel A-vacancy ordering, because there is no B/B' substitutional disorder at the octahedral coordinated B sites. For instance, Ti/Mg disorder could explain the domains observed in the commensurate $Ba_{1.2}(Ti,Mg)_8O_{16}$ compound [Fanchon E. et al. (1987) Acta Cryst. B, to be published]. In materials with a common B cation the conduction mechanism is complex since both ionic and electronic conduction occur.

We have studied some $A_x(Mn^{3+}, Mn^{4+})_8O_{16}$ hollandites stabilized by partial occupation of the tunnels by A cations such as K^+, Rb^+, Ag^+, Pb^{2+}, (K^+, H_3O^+). Under the synthesis conditions used, one dimensional order occurs with no correlation between adjacent tunnels in K^+ and Rb^+ compounds, and the modulation wave vector of the A-vacancy intra-tunnel order is commensurate : $q^* = c^*/3$. With Pb^{2+}, an inter-tunnel short range order exists and the modulation along the tunnel corresponds to the incommensurate value $q^* \sim 0.24c^*$. The (K^+, H_3O^+) compound exhibits diffuse planes in electron diffraction pattern ; powder neutron diffraction data show an additional nuclear or magnetic short-range ordering between 100 K and 4.2 K. The latter compound and $K_{1.33}Mn_8O_{16}$ have an antiferromagnetic ordering at 11 K and 18 K respectively [Strobel P., Vicat J. and Tran Qui D., (1984) J.S.S.C. 55, 67-73].

Single crystals of caesium titanate are three-dimensionally ordered at room temperature, with a 2a x 2a x 2c face centered cell. Electron and X-ray diffraction studies show a reversible order-disorder transition near 320°C with no significant hysteresis. Over the small temperature range at the transition, the sharp superlattice spots are progressively replaced by diffuse planes with $q^* = 0.5\ c^*$. From the value of the modulation wave vector length q^*, the composition of the crystals studied is $Cs^+Ti^{3+}Ti^{4+}{}_7O_{16}$. This compound was found to be semiconducting at room temperature with $\rho = 0.42\ \Omega$ cm [Reid A.F. and Watts J.A. (1970) J.S.S.C. 1, 310-318]. The structural transition can be related to the localisation of the 3d electrons of Ti^{3+} and/or caesium ordering. We can compare this transition to the known electrical and structural transitions in titanium oxides (Ti_4O_7...), the structures of which are closely related to that of rutile.

We are grateful to Dr. Ian Grey for useful discussion.