05.2–21 STRUCTURE REFINEMENT OF MANGANESE AND POTASSIUM OXIDE $K_{1.33}Mn_8O_{16}$. ORDER-DISORDER OF CATIONS IN HOLLANDITE STRUCTURES-TYPE. By J. Vicat, E. Fanchon, P. Strobel and D. Tran Qui, Laboratoire de Cristallographie, C.N.R.S., associé à l'U.S.M.G., 166 X, 38042 - Grenoble Cedex, France.

Most of the "MnO_2" allotropic forms appear to be non-stoichiometric. This occurs also in α-MnO_2 which is known under the name hollandite. This structure contains large square channels between double rutile-like chains of (MnO_6) octahedra : it is stabilized by partial occupation of the channels by cations such as Na, K, Ba and Pb.

Refinement of the mixed valence compound $K_xM^{4+}_{8-x}Mn^{3+}_xO_{16}$, prepared by Strobel and Le Page (J. Crystal Growth 56, 645 (1982)) was carried out to a final R of 1.9 % using precise single crystal X-ray data at room temperature (AgKα radiation, all reflections measured up to θ = 30°, space group I4/m checked by equivalent reflections after absorption correction ; 436 independent reflections were included in the refinement).

Channel cation position (K^+) is not 00½ but 00z (z = ± 0.624) with a site occupancy of 1/3. Rotation photographs show diffuse streaks between the reciprocal latticeplanes perpendicular to c* (c hollandite axis is along the channel direction). These streaks are probably due to cation ordering. Their spacing (corresponding to c*/3) indicates that the order involves three unit-cells in the c direction. There are six possible sites as found by the refinement; only two of them are occupied which gives three possibilities as indicated by figure 1 (with K-K distances of 3.589 and 5.027 A).

The ordering in a given channel is not correlated to that of the adjacent ones. Because of their channel structure, hollandite compounds have been studied as one-dimensional fast ionic conductors : the poor ionic conductivity of $K_{1.33}Mn_8O_{16}$ (Strobel, Vicat, Tran Qui, 1984, to be published) is consistent with the ordering of the K atoms in the channel.

Previous studies on titanium hollandite $A_x(Ti_{8-y}B_y)O_{16}$ by Beyeler and Schüler (Solid State Ionics 1, 77 (1980)) indicate two kinds of arrangement in these materials :
-ordering in channels without correlation between channels and without ordering between Ti and B in the framework.
-ordering in both tunnel and framework such as in $Ba_{1.2}(Mg_{1.2}Ti_{6.8})O_{16}$. A structural study of the last compound is in progress ; it should give more insight into the order-disorder problem in hollandite-type compounds.

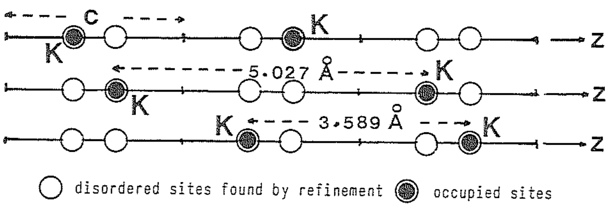

Fig. 1. Channel sites occupation in $K_{1.33}Mn_8O_{16}$

05.2–22 ELECTRICAL CONDUCTIVITY OF SPINELS $Zn_{1-x}Ga_{2/3x}Cr_2Se_4$. By T. Groń and J. Warczewski, Silesian University, Institute of Physics, Katowice, Poland

The electrical conductivity of the polycrystalline samples /x=0.0, 0.1, 0.2, 0.3, 0.5/ and the single crystals /x=0.0, 0.05, 0.40 (Okońska-Kozłowska, Lutz, Groń, Krok and Mydlarz 1983, Mat. Res. Bull., in press)/ has been measured /2-point DC method/ in the temperature range of 66-490 K. For the polycrystalline samples it was found that the electrical conductivity for a given concentration x monotonically increases with the temperature increase; it points to its semiconductive /type p/ character. The electrical conductivity for a given temperature decreases with increase of the concentration x, whereas the low-temperature activation energy increases. This can be explained by assuming that the amount of 2/3x of gallium introduced in place of zinc leads to the appearance in the octahedral sites of Cr^{2+} ions in the equal amount /of 2/3x/. It implies the hole concentration to decrease /the holes descending from the cation vacancies/ via recombination with the electrons from the Cr^{2+} ions. For the single crystals the electrical conductivity at low temperatures practically does not depend on temperature, whereas the low-temperature activation energy decreases with increase of x, what is linked with the resistivity anisotropy. It seems, that the chemical formula of the spinel series under study is:

$Zn_{1-x}Ga_{2/3x}[Cr^{3+}_{2-2/3x}Cr^{2+}_{2/3x}]Se_4$.

05.2–23 MODELING OF THE STRUCTURE OF SILICAS - ROLE OF CLOSED RINGS. By Y.T. Thathachari and W.A. Tiller, Dept. of Materials Science and Engineering, Stanford University, Stanford, Calif. 94305, U.S.A.

Initial Monte Carlo studies showed that an exclusion principle based upon a minimum allowed O-O separation in adjacent oxygen tetrahedra drastically restricted the relative orientations such tetrahedra can assume. This ad-hoc criterion reproduced the experimentally observed Si-O-Si angle distribution determined from the structural data of a large number of silicas and silicates. Subsequent calculations using e.g. Lennard-Jones 6-12 potential for O-O interactions, between all atoms in adjacent tetrahedra, led to quite similar results. Further studies suggest that, when extended structures are formed, this steric requirment alone causes additional and severe restrictions on the relative orientations of adjacent tetrahedra. These orientations become highly correlated over short ranges. At the level of the 2nd neighbors, the size of the closed rings (e.g. with 4 or 6 bridging oxygens) that would form is largely decided. It seems possible to work out the spatial mechanisms involved in the rearrangement of 6-rings to 4-rings and vice versa. We have the experimental data on quartz under high pressure (6-rings) and coesite (4-rings) as a guide in analyzing the families of ring structures found in the modeling procedure.

The relationships of the foregoing calculations to (i) the general requirement for extended silica structures in the amorphous-crystalline configurations and (2) the structure of vitreous silica immediately adjacent to thermally oxidizing Si and its transformation mechanism to bulk vitreous silica far from the interface are under consideration.