Most of the "\text{MnO}_2\" allotriomorphic forms appear to be non-
estochiometric. This occurs also in \text{MnO}_2 which is known
under the name hollandite. This structure contains large
square channels between double rutile-like chains of
(\text{MnO}_2) octahedra: it is stabilized by partial occupation
of the channels by cations such as \text{Na}, \text{K}, \text{Ba} and \text{Pb}.

Refinement of the mixed-valence compound \text{K}_1.33\text{MnSO}_1.6
prepared by Strobel and Le Page (\text{U. Crystal Growth 86,}
645 (1982)) was carried out to a final R of 1.9 % using
precise single crystal X-ray data at room temperature
(\text{AgK}\alpha radiation, all reflections measured up to \theta = 30°,
space group 14/m checked by equivalent reflections after
absorption correction; 436 independent reflections were
included in the refinement).

Channel cation position (\text{K}^+) is not G0 but G0x
(\alpha = \pm 0.624\%) with a site occupancy of 1/3. Rotation
photographs show diffuse streaks between the reciprocal
lattice-planes perpendicular to c* (c hollandite axis is
along the channel direction). These streaks are probably
due to cation ordering. Their spacing (corresponding to
\text{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 \text{Å}).

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
\text{MnO}_2 is largely decided.

Previous studies on titanohollandite \text{Ax(Ti}_8-y\text{By)}\text{O}_{16}
by Seyal and Schuler (\text{Solid State Ions 1, 77 (1980)})
indicate two kinds of arrangement in these materials:
-ordering in channels without correlation between chan-
nels and without ordering between Ti and B in the frame-
work.
-ordering in both tunnel and framework such as in
\text{Ba}_1.3(\text{Mg}_{1.2}\text{Ti}_{1.6})\text{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.

Previous studies on titanium hollandite \text{Ax(Ti}_8-y\text{By)}\text{O}_{16}
by Seyal and Schuler (\text{Solid State Ions 1, 77 (1980)})
indicate two kinds of arrangement in these materials:
-ordering in channels without correlation between chan-
nels and without ordering between Ti and B in the frame-
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\text{Ba}_1.3(\text{Mg}_{1.2}\text{Ti}_{1.6})\text{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 \text{K}_1.33\text{MnSO}_1.6

05.2-21 \text{STRUCTURE REFINEMENT OF MANGANESE AND POTAS-
SIUM OXIDE \text{K}_1.33\text{MnSO}_1.6. ORDER-DISORDER OF CATIONS IN HOLL-
LANDITE STRUCTURES-TYPE.} By J. Vicat, S. Fanchon,
P. Strobel and D. Tran Qui, Laboratoire de Cristallogra-
phe, C.N.R.S., associé à l'U.S.M.G., 166 X, 38042 -
Grenoble Cedex, France.

The electrical conductivity of the polycrys-
talline samples /x=0.0, 0.1, 0.2, 0.3, 0.5/ and the single crystals /x=0.0, 0.05, 0.40
(Okoska-Kolosowska, Lutz, Gron, Krok and My-
drza 1983, Mat. Res. Bull., in press) has been measured /two-point DC method/ in the tem-
perature range of 60-450 K. For the polycrys-
talline samples it was found that the electri-
cal conductivity for a given concentration x
monotonically increases with the temperature
increase; it points to its semiconductor/ty-
ppe \text{p} character. The electrical conductivity for a given temperature decreases with in-
crease 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 octa-
hedral sites of \text{Cr}^+ ions in the equal amount
/x/2/3x/, it implies a tendency to decrease /the holes descending from the ca-
tion vacancies/ via \text{p} \text{z} \text{g} \text{e} \text{t} \text{c} \text{t} \text{ion} with the electrons from the \text{Cr}^+ ions. For the single
crystals the electrical conductivity at low
temperatures practically does not depend on
temperature, whereas the low-temperature acti-
vation energy decreases with increase of x,
what is linked with the resistivity anisotro-
py. It seems, that the chemical formula of the spinel series under study is:

\text{Zn}_{1-x}\text{Ga}_{2/3}x\text{Li}_{2/3}x\text{Al}_{2}/3x\text{Si}_{2}/3x\text{Se}_4\text{.}

05.2-22 \text{ELECTRICAL CONDUCTIVITY OF SPINELS}
\text{Zn}_{1-x}\text{Ga}_x\text{Cr}_{2/3}x\text{,} By T. Gron and
J. Warzatewicz, Czestochowa University, Institute of Physics, Katowice, Poland.

05.2-23 \text{MODELING OF THE STRUCTURE OF SILICAS - ROLE OF CLOSED RINGS.} By Y.T. Thatcharei and W.A. Tiller,
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