Examination of Fig. 5 clearly reveals hexagonal arrays of seven white spots, although irregularities exist because of the faulting (such as indicated by the arrows) which occurs on a very fine scale.

We conclude that the atomic arrangement in the F phase is that of a hypothetical structure proposed by Frank & Kasper (1959) and can be thought of as composed of hexagonal kagomé tiles. Diffraction pattern intensities and high-resolution images are consistent with expectations from the proposed structure.
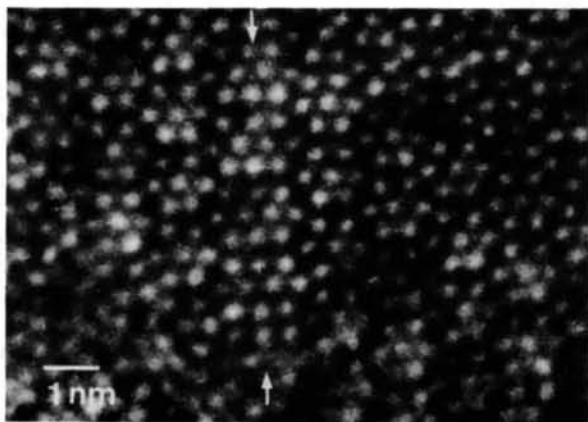
Fig. 5. [0001] high-resolution image of the F phase recorded at 300 kV showing bright spots arranged in a $3^6 + 3^2$ 434 (1:6) net. The two arrows indicate a fault line in the structure. (1 nm = 10 Å.)

Table 2. *Crystallographic data for the F phase, assuming tessellation of perfect hexagons and triangles*

Space group: $P6/mmm$
Lattice parameters: $a_0 = 12 \cdot 6$, $c_0 = 4 \cdot 6$ Å, $\gamma = 120°$
Atoms per unit cell (Z):   52

Number	Wyckoff position	Coordinates			Value of variable
2	c	$\frac{1}{3}, \frac{2}{3}, 0$	$\frac{2}{3}, \frac{1}{3}, 0$		
2	e	$0, 0, z$	$0, 0, \bar{z}$		$z = \frac{1}{4}$
6	j	$x, 0, 0$ $\bar{x}, 0, 0$	$0, x, 0$ $0, \bar{x}, 0$	$\bar{x}, \bar{x}, 0$ $x, x, 0$	$x = \frac{1}{3}$
6	k_1	$\{ x, 0, \frac{1}{2}$	$0, x, \frac{1}{2}$	$\bar{x}, \bar{x}, \frac{1}{2} \}$	$x_1 = \frac{1}{3}$
6	k_2	$\bar{x}, 0, \frac{1}{2}$	$0, \bar{x}, \frac{1}{2}$	$x, x, \frac{1}{2}$	$x_2 = \frac{2}{3}$
6	l_1	$\{ x, 2x, 0$	$\overline{2x}, \bar{x}, 0$	$x, \bar{x}, 0 \}$	$x_1 = \frac{1}{9}$
6	l_2	$\bar{x}, \overline{2x}, 0$	$2x, x, 0$	$\bar{x}, x, 0$	$x_2 = \frac{4}{9}$
6	m	$x, 2x, \frac{1}{2}$ $\bar{x}, \overline{2x}, \frac{1}{2}$	$\overline{2x}, \bar{x}, \frac{1}{2}$ $2x, x, \frac{1}{2}$	$x, \bar{x}, \frac{1}{2}$ $\bar{x}, x, \frac{1}{2}$	$x = \frac{2}{3}$
12	o	$x, 2x, z$ $\bar{x}, \overline{2x}, z$ $x, 2x, \bar{z}$ $\bar{x}, \overline{2x}, \bar{z}$	$\overline{2x}, \bar{x}, z$ $2x, x, z$ $\overline{2x}, \bar{x}, \bar{z}$ $2x, x, \bar{z}$	$x, \bar{x}, z$ $\bar{x}, x, z$ $x, \bar{x}, \bar{z}$ $\bar{x}, x, \bar{z}$	$x = \frac{2}{9}$ $z = \frac{1}{4}$

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The Structure of $K_{1 \cdot 33}Mn_8O_{16}$ and Cation Ordering in Hollandite-Type Structures

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Abstract

Crystal data: $M_r = 747 \cdot 5$, tetragonal, $I4/m$, $a = 9 \cdot 866$ (3), $c = 2 \cdot 872$ (1) Å, $V = 279 \cdot 6$ (2) Å^3, $Z = 8$ ($K_{0 \cdot 167}$ MnO$_2$), $D_x = 4 \cdot 442$ g cm^{-3}, λ(Ag $K\alpha$, graphite monochromator) = $0 \cdot 56005$ Å, $\mu = 49 \cdot 9$ cm^{-1}, $F(000) = 353 \cdot 5$, $T = 295$ K, final $R = 1 \cdot 9\%$ for 436 unique reflections. In this mixed-valence compound $K_x Mn_{8-x}^{4+} Mn_x^{3+} O_{16}$ ($x = 1 \cdot 33$) the channel cation position (K^+) is not at $00\frac{1}{2}$ but at $00z$ with $z = 0 \cdot 375$. It is shown that the symmetry of hollandite-type structures ($A_x B_8 O_{16}$) is determined by the relative sizes of the framework (B) and the channel (A) cations. Single-crystal rotation photographs around **c** show extra

diffuse levels between reciprocal-lattice planes perpendicular to c. These extra levels, attributed to channel-cation ordering, have spacings which indicate that, in a given channel, the order involves three unit cells in the c direction. The presence of vacancies in the channels allows a relaxation of the K^+ cations and a minimization of the K–K electrostatic repulsion *via* a displacement of the K^+ cations from the centers of their square-prismatic channel sites toward the neighboring vacancies. It seems likely that either diffuse or superstructure reflections should occur in most $A_xB_8O_{16}$ hollandite-type compounds studied so far. In the former case long-range ordering occurs among the A cations and vacancies along a given channel without a correlation between adjacent channels, as in $K_{1.33}Mn_9O_{16}$ where the K ordering is one-dimensional. In the latter case the ordering is accompanied by a strong correlation between channels leading to a three-dimensional ordering.

Introduction

In hollandite-type structures $A_xB_8O_{16}$ ($x \leq 2$) the A atoms are located in channels parallel to the shortest axis ($c \simeq 3$ Å) of the tetragonal (or monoclinic for small cation-radii ratio r_B/r_A) unit cell (Fig. 1). Each cell contains two channels, one at the origin and the other in the middle of the cell. The positions of the A cations in the channels have been investigated in several hollandite-type crystals. Byström & Byström (1950) placed the Ba^{2+} cations of a natural hollandite, $BaMn_8O_{16}$, at the $00\frac{1}{2}$ position of the space group $I4/m$. The A cations would be at the center of a square-prismatic environment of O atoms. But recent studies on $Ba_{1.4}(Sn, Cr)_8O_{16}$ (Cadée & Verschoor, 1978) and $Ba(Ti_6Al_2)O_{16}$ (Sinclair, McLaughlin & Ringwood, 1980) indicate that the A cations are displaced from the special position $00\frac{1}{2}$ along the c axis. The structure of Mn minerals such as $(Ba, Pb)_{1.25}Mn_8O_{16}$ (hollandite) and $(K, Sr, Na)_{1.42}Mn_8O_{16}$ (cryptomelane) have recently been refined (Post, Von Dreele & Buseck, 1982). They belong to the space group $I2/m$. The Ba^{2+} and K^+ cations are at the special position $00\frac{1}{2}$ while the Pb^{2+} and Sr^{2+} cations are displaced along the c axis. In cryptomelane the Na^+ cations were placed at the 000 position in the channel, at the center of the plane formed by four O(1) atoms. This square-planar coordination is rather unusual for the Na^+ cations.

Because of their particular structural features, hollandite-type compounds were considered as potential candidates for one-dimensional ionic conductivity (Yoshikado, Ohachi, Taniguchi, Onoda, Watanabe & Fujiki, 1982). Owing to the A-cation disordering and the partial occupancy of the channel sites, cationic conductivity along the c axis with a low activation energy has been conjectured for these compounds. However, Sinclair et al. (1980) pointed out that the channels contain narrow square-shaped bottlenecks. Moreover, as shown by Beyeler & Schüler (1980) most of the oxides with a hollandite-type structure such as $A_x(Ti, Mg)_8O_{16}$ exhibit diffuse streaks or superstructure reflections, indicating some kid of cation ordering. The A-cation distribution has also been studied by electron microscopy for $Ba_x(Ti, Mg$ or $Ga)_8O_{16}$ (Bursill & Grzinic, 1980) and for $K_{1.33}(Sb, Mg)_8O_{16}$ (Pring, Smith & Jefferson, 1983).

This article reports a precise structural refinement of synthetic $K_{1.33}Mn_8O_{16}$. We thought it would be of interest to investigate a hollandite-type manganese oxide containing only one kind (K) of A cation in the channels.

Experimental

Natural samples of manganese hollandite-type compounds usually contain a variety of A cations in the channels (Post et al., 1982). On the other hand, synthesis from aqueous solutions unavoidably leads to inclusion of H_3O^+ in the channels in addition to the desired cation (Strobel, Vicat & Tran Qui, 1984). Single crystals with the formula $K_xMn_8O_{16}$ have been grown by anodic oxidation of Mn^{II} dissolved in a molten $K_2O–V_2O_5$ eutectic at 778 K (Strobel & Le Page, 1982). They are black and acicular crystals, the elongated dimension being along the c axis. The crystal used for X-ray data collection on a Nonius CAD-4 automatic diffractometer was a rectangular parallelepiped, delimited by the (100), (010) and (001) faces, measuring $0.110 \times 0.072 \times 0.110$ mm along the a, b, and c directions, respectively.

The lattice parameters were refined from the angle values of 25 reflections measured over the range $17° < 2\theta < 30°$. Their values are compared to those of natural hollandite and cryptomelane (Post et al., 1982) in Table 1. The intensities of all reflections with $5° < 2\theta < 60°$ were collected with the following conditions: ω-scan mode up to $2\theta = 40°$ and $\omega–2\theta$ mode up to $2\theta = 60°$; scan speed calculated after a pre-scan
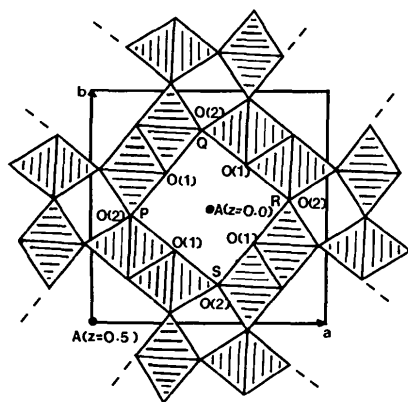

Fig. 1. Projection of the hollandite-type structure $A_xB_8O_{16}$ along c; BO_6 octahedra are shown.

Table 1. *Unit-cell parameters and final refinement data for $K_{1.33}Mn_8O_{16}$, and comparison with results for natural manganese oxide crystals*

	$K_{1.33}Mn_8O_{16}$*	(Ba, Pb)Mn_8O_{16}† (Hollandite)	(K, Sr, Na)Mn_8O_{16}† (Cryptomelane)
a (Å)	9·866 (3)	10·026 (3)	9·956
b (Å)		9·729 (3)	9·706
c (Å)	2·872 (1)	2·8782 (7)	2·8705 (9)
γ (°)		91·03 (2)	90·95 (3)
V (Å^3)	279·55 (15)	280·72 (13)	277·35 (17)
Space group	$I4/m$	$I2/m$	$I2/m$
Number of reflections	436	599	623
Number of parameters	23	48	53
R (%)	1·9	1·65	2·99
wR (%)	2·3	2·15	3·94
Occupancy site in the channel	0·355 (3)	0·327	0·355

* This work.
† Post *et al.* (1982).

to give $\sigma(I)/I = 2\%$ (maximum time: 4 min); scan width $\Delta\omega = (1\cdot5 + 0\cdot2\,\mathrm{tg}\theta)°$; counter aperture $\Delta l = (3 + 1\cdot5\,\mathrm{tg}\theta)$ mm. The total number of measured reflections was 3670. The intensities were corrected for the variation of the standard reflections and for absorption (transmission factor varies between 0·59 and 0·68). They were converted into structure factors by applying Lorentz-polarization corrections. Equivalent reflections were averaged according to the four-point symmetry; this gave a total of 750 independent reflections. The internal reliability factor of equivalent structure factor sets $[(1/N)\sum(|F_{av} - F_o|/F_{av})$ with $N = $ total number of measured reflections] was 1·7%, which confirms the tetragonal symmetry. The 750 reflections were then averaged according to the centrosymmetric point group $4/m$ giving a final total of 436 independent reflections with an internal reliability factor (between Friedel pairs) of 0·7%.

Structural refinement

All calculations were carried out by the use of the *SDP* package on a PDP 11/70 computer. Initial atomic coordination of the framework atoms of Ba(Ti_6Al_2)O_{16} (Sinclair *et al.*, 1980) was used for Mn, O(1) and O(2). Full-matrix least-squares refinement with isotropic temperature factors for all atoms yielded an R factor of 0·06 ($R = \sum|F_o - k|F_c||/\sum F_o$). Difference Fourier maps based on least-squares results showed two peaks at $\pm 00z$ ($z \approx 0·62$) corresponding to 3 or 4 e Å^{-3}. Thus the K atoms were placed at these 4(e) positions. A final refinement of the positional and anisotropic thermal parameters for all atoms and the K site occupancy factor converged to $R = 1\cdot9\%$ and $wR = 2\cdot3\%$ $\{wR = [\sum w(F_o - k|F_c|)^2/\sum wF_o^2]^{1/2}\}$. The occupancy factor of the K sites is 0·335 (3), corresponding to the formula $K_{1.33}Mn_8O_{16}$. Difference Fourier maps based on these results yielded no significant residual peaks

Table 2. *Atomic positions and equivalent isotropic thermal parameters for $K_{1.33}Mn_8O_{16}$ (e.s.d.'s in parentheses)*

$$B_{eq} = \tfrac{4}{3}\sum_i \sum_j \beta_{ij}\mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
K[4(e)]*	0	0	0·3754 (12)	1·51 (5)
Mn[8(h)]	0·34891 (3)	0·16621 (2)	0	0·336 (6)
O(1)[8(h)]	0·15445 (17)	0·20295 (17)	0	0·511 (31)
O(2)[8(h)]	0·54206 (17)	0·16496 (18)	0	0·561 (33)

* Population 0·1675 (14).

$(0\cdot2-0\cdot3$ e Å$^{-3})$. $(\Delta/\sigma)_{max} = 0\cdot14$. Positional and thermal parameters are listed in Table 2.*

Discussion

The framework of a hollandite-type structure (B_8O_{16}) is built up of edge-sharing BO_6 octahedra forming double rutile chains (Wells, 1975). These chains are linked together by corner-sharing, generating open channels which contain the A cations (Fig. 1). Magnetic-susceptibility measurements indicate that $K_{1.33}Mn_8O_{16}$ contains Mn^{3+} and Mn^{4+} cations (Strobel *et al.*, 1984). The structural refinement gives Mn-O distances in the range 1·895–1·95 Å. The average distance (1·920 Å) is in good agreement with the sum of the ionic radius of O^{2-} (1·38 Å) and the average radius for Mn^{3+} and Mn^{4+} (0·54 Å) (Shannon, 1976). There is no evidence of ordering between Mn^{3+} and Mn^{4+}.

Since the K atoms occupy the $0,0,\pm0\cdot375$ positions they are not at the center of the O(1) square-prismatic environment, but shifted by 0·359 Å along the four-fold axis. As a consequence, the K coordination polyhedra comprise four short and four long K–O distances, 2·741 and 3·095 Å respectively (Table 3). The two K-atom positions at $z = 0·375$ and $z = 0·625$ along the channel (which cannot be occupied simultaneously) are separated by 0·718 Å which is four times the thermal root-mean-square displacement (0·185 Å) along the $\mathbf{c}$ direction (Fig. 2). Therefore, the displacement from the $00\frac{1}{2}$ position is not due to an anomalously large anisotropic vibration.

If the A cations were at $00\frac{1}{2}$ positions, that is the center of the square-prismatic polyhedron, the A–A distances would be too short. The A cations are thus displaced but the displacement is not enough to minimize the electrostatic repulsion. This minimization is achieved by generating vacancies in the A sublattice to allow appropriate A–A distances. This means that it is impossible to reach the stoichiometric composition ($x = 2$ in $A_xB_8O_{16}$) except in the case of

Table 3. *Interatomic distances* (Å) *and angles* (°) *in the coordination polyhedra of* $K_{1.33}Mn_8O_{16}$

K–O(1)	2·741 (2) ×4	O(1)–Mn–O(1)	81·90 (5) ×2
K–O(1)	3·095 (2) ×4	O(1)–Mn–O(1)	96·08 (5) ×2
K–O(2)	3·355 (2) ×4	O(1)–Mn–O(2)	169·67 (5) ×1
Mn–O(1)	1·955 (2)	O(1)–Mn–O(2)	92·62 (5) ×2
Mn–O(1)	1·934 (1) ×2	O(1)–Mn–O(2)	91·23 (5) ×2
Mn–O(1)	1·908 (2)	O(1)–Mn–O(2)	86·36 (5) ×2
Mn–O(1)	1·895 (2) ×2	O(1)–Mn–O(2)	174·66 (5) ×1
		O(1)–Mn–O(2)	93·9 (5) ×2
Mean	1·920	O(1)–Mn–O(2)	98·73 (5) ×2

high-pressure synthesis. Several hollandite-type compounds with full occupation of the channel sites (see Table 4) were obtained using this technique. The A-A repulsion increases with the cation charge: the high-pressure synthesis of $A_x(Si_6Al_2)O_{16}$ with $x = 2$ is possible for $A = K$ (Ringwood, Reid & Wadsley, 1967), but $x = 1·5$ is the maximum that one can achieve for $A = Ba$ or Sr (Reid & Ringwood, 1969).

Symmetry of hollandite-type compounds

Hollandite-type compounds crystallize with either tetragonal symmetry (space group $I4/m$) or monoclinic symmetry. To make the comparison easier, the monoclinic compounds are more conveniently described in the non-standard space group $I2/m$ instead of the standard group $C2/m$ for which the angle β is near 135° ($I2/m$ is derived from $I4/m$ merely by substitution of the fourfold axis by a twofold axis). Among the manganese oxides ($A_xMn_8O_{16}$), $K_{1.33}Mn_8O_{16}$ has tetragonal symmetry; however, if the K cation is replaced by (Ba, Pb) as in hollandite or (K, Sr, Na) as in cryptomelane, the symmetry becomes $I2/m$ (see Table 1). The structural distortion which lowers the symmetry from tegragonal to monoclinic has been discussed by Post *et al.* (1982), who also studied the dependence of the symmetry on the A and B cation radii. Another way to express this dependence following geometrical factors is taken into consideration here.

Tetragonal a and c parameters are plotted as a function of the ionic radii of the framework cation
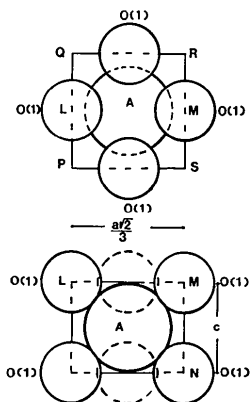
Fig. 2. The square-prismatic environment of the A cation of $A_xB_8O_{16}$.

Table 4. *Stoichiometric compounds with hollandite structure type* ($A_2B_8O_{16}$) *obtained by high-pressure synthesis*

Compounds	Parameters a (Å)	c (Å)	References
$K_2Cr_8O_{16}$	9·772	2·941	Endo, Kume, Kinomura & Koizumi (1976)
$Rb_2Cr_8O_{16}$	9·823	2·950	Okada, Kinomura, Kume & Koisumi (1978)
$K_2Cr_2V_6O_{16}$	9·871	2·959	
$K_2V_8O_{16}$	9·943	2·911	
$K_2V_8O_{16}$	9·963 (5)	2·916 (2)	Abriel, Rau & Range (1979)
$K_{1.8}V_8O_{16}$*	9·996 (8)	2·899 (7)	
$Tl_{1.74}V_8O_{16}$*	10·064 (3)	2·899 (1)	
$K_2Al_2Ge_6O_{16}$	9·72 (1)	2·86 (1)	Kume, Matsumoto & Koizumi (1966)
$K_2Al_2Si_6O_{16}$	9·36 (1)	2·74 (1)	Ringwood, Reid & Wadsley (1967)
$K_2Al_2Ti_6O_{16}$	10·04	2·94	Bayer & Hoffman (1966)
$Rb_2Al_2Ti_6O_{16}$	10·10	2·94	
$Rb_2Al_2Ge_6O_{16}$	9·78 (1)	2·86 (1)	Reid & Ringwood (1969)
$Na_2Al_2Ge_6O_{16}$	9·648 (5)	2·856 (5)	
$Ba_{1.5}Al_3Si_5O_{16}$*	9·410 (5)	2·72 (1)	
$Sr_{1.5}Al_3Si_5O_{16}$*	9·32 (1)	2·72 (1)	

$Ba_2Al_3Si_5O_{16}$ } could not be formed
$Sr_2Al_3Si_5O_{16}$

* Non-stoichiometric compounds.

B (Fig. 3). The average straight lines correspond to:

$$a(\text{Å}) = 4·4r_B + 7·36 \qquad (1)$$

$$c(\text{Å}) = 1·4r_B + 2·12. \qquad (2)$$

They show that the a axis is more sensitive to the variation of r_B than the c axis. The effect of the ionic radius of the A cation is rather small: for example, the cell parameters of $Rb_2Ge_6Al_2O_{16}$ and $Na_2Ge_6Al_2O_{16}$ differ by $\Delta a = 0·013$ Å and $\Delta c = 0·004$ Å, respectively, whereas the ionic radii of Rb and Na differ by 0·43 Å (1·61 and 1·18 Å respectively). The nonstoichiometry and the A-cation shifts lead to an increase of the a parameter and a small decrease of c (compare the lattice parameters of $K_2V_8O_{16}$ and those of $K_{1.8}V_8O_{16}$, Table 4).

A distortion occurs (and the symmetry is lowered) when the A cation is too small with respect to the size of the square-prismatic environment. The channel square section (Fig. 1) has an edge corresponding to $PQ = a\sqrt{2}/3$. The edge and height of the square prism
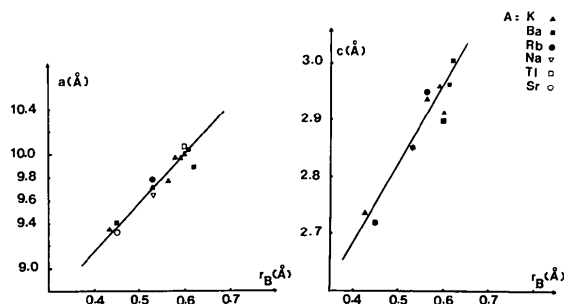
Fig. 3. Variation of a and c parameters of the tetragonal hollandite-type structure $A_xB_8O_{16}$ *versus* ionic radius of the B cation.

formed by the eight O(1) (Fig. 2) are $a/3$ and c, respectively. The tetragonal cell will not be distorted if the sum of the radii of the A cation and the O atom is greater than or equal to the A–O(1) distance (Fig. 2b) (the A-atom shift along the c axis is not taken into account):

$$2(r_A + r_{Ox}) > LN \tag{3}$$

or

$$2(r_A + r_{Ox}) > [c^2 + (2/9)a^2]^{1/2}. \tag{4}$$

Substituting (1) and (2) into (4) we obtain

$$r_A > [1.59(r_B^2 + 3.20r_B + 2.61) - r_{Ox}]^{1/2}, \tag{5}$$

which can be approximated by:

$$r_A > 1.26(r_B + 1.6) - r_{Ox}. \tag{6}$$

This purely geometrical approach defines two domains in the diagram shown in Fig. 4; the borderline between the tetragonal domain and the monoclinic one is given by equation (6). With the exception of the $A = $ Na point (Na is the smallest A cation found in hollandite-type compounds) equation (5) or (6) is in good agreement with experimental results. The relative size of the A and B cations is a fundamental factor in the crystal symmetry of the $A_xB_8O_{16}$ compounds.

Order and disorder in hollandite-type structures

A single-crystal rotation photograph, taken with Mo $K\alpha$ radiation around c for $K_{1.33}Mn_8O_{16}$, is shown in Fig. 5. It clearly shows diffuse-scattering streaks corresponding to a reciprocal distance of $c^*/3$. This indicates the existence of a superstructure involving a tripling of the cell along the c axis whereas the periodicity is unaffected along the a and b axes. These streaks cannot be accounted for by an ordering of the Mn^{3+} and Mn^{4+} framework cations. Instead, they

are probably caused by an additional ordering of the K^+ cations. In a given channel, six A sites along the c axis (three cells) are to be occupied by two K^+ cations (each site will have a site occupancy of $\frac{1}{3}$) (see Fig. 6). By taking into account the electrostatic repulsion, there are three possible K-atom distributions. All of these include an ordering of the K atoms and the vacancies in the channel, following the sequence K–K–□–K–K–□.... Such an ordering has been formed in other structures: it occurs, for example, for the Fe cations and vacancies in α-Fe_2O_3 (Patrat, de Bergevin, Pernet & Joubert, 1983). The fact that the additional scattering occurs in diffuse streaks and not in discrete diffraction spots means that not only one ordering of the K cations (and vacancies) occurs in the structure of $K_{1.33}Mn_8O_{16}$: the order in a given channel is not correlated with that in adjacent channels. A similar A–A–□ sequence has been proposed for the hollandites $Ba_{1.33}(Ti, Mg)_8O_{16}$ and $Ba_{1.33}(Ti, Ga)_8O_{16}$ (Bursill & Grzinic, 1980) and $K_{1.33}Mg_{3.11}Sb_{4.89}O_{16}$ (Pring, Smith & Jefferson, 1983). In these compounds, however, electron diffraction patterns and HRTEM images show that superstructure spots appear with a tripling of the unit cell along c. In Bursill & Grzinic's model the Ba-atom ordering is three-dimensional whereas in $K_{1.33}Mn_8O_{16}$ the K-atom ordering is one-dimensional.

Fig. 5. Rotation photograph of X-ray scattering of $K_{1.33}Mn_8O_{16}$. Diffuse-scattering streaks between indexed Bragg planes are clearly shown.
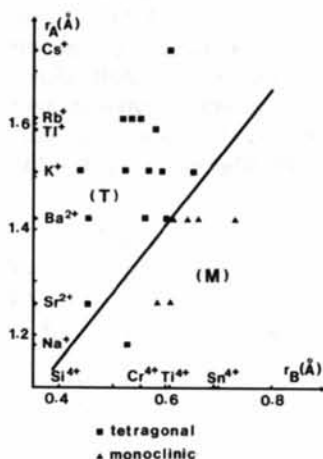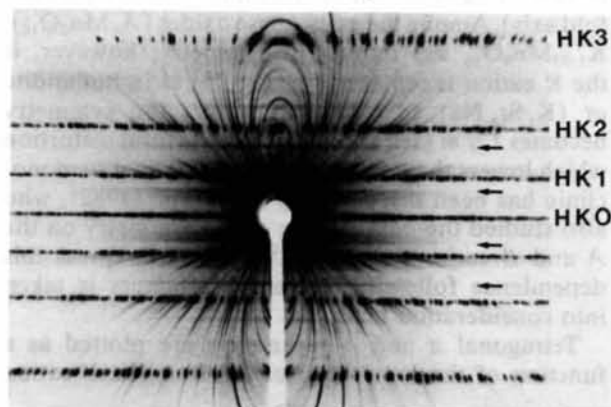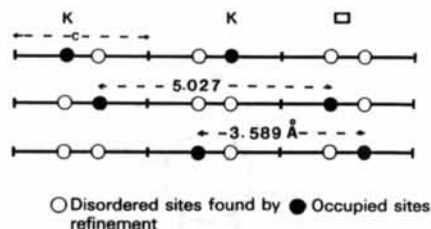

Fig. 4. Symmetry of hollandite-type compounds following ionic radii r_A and r_B; (T) and (M) mean domains with tetragonal and monoclinic symmetry respectively.

Fig. 6. Channel site occupation in $K_{1.33}Mn_8O_{16}$, the three distributions of K^+ cations and vacancies (□) follow the sequence K–K–□.

This type of K–K–□ ordering allows a relaxation of the strong electrostatic repulsion. The K atoms move towards the vacancies. They shift by $0.125c$ away from the $00\frac{1}{2}$ position toward a neighboring empty site. Sequentially there exist two K–K distances: a short one of 3.589 Å and a longer one of 5.027 Å, both greater than the c parameter. This shift agrees well with the results of Beyeler & Schüler (1980) for $Cs_{1.33}(Ti, Mg)_8O_{16}$. From the intensities of the diffuse-scattering streaks these authors concluded that the Cs atoms are shifted toward the vacancies by $0.12c$. Relative intensities of the diffuse streaks for $Cs_{1.33}(Ti, Mg)_8O_{16}$ and $K_{1.33}Mn_8O_{16}$ are quite similar. The vacancy ordering is consistent with the poor ionic conductivity found for $K_{1.33}Mn_8O_{16}$ (Strobel et al., 1984).

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The $ASnO_3$ (A = Ca, Sr) Perovskites

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Abstract

The crystal structures of the perovskites $ASnO_3$ (A = Ca, Sr) have been solved. $CaSnO_3$: $M_T = 206.77$, orthorhombic, $Pbnm$, $a = 5.532$ (2), $b = 5.681$ (2), $c = 7.906$ (2) Å, $V = 248.46$ (8) Å^3, $Z = 4$, $D_x = 5.52$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, μ(Mo $K\alpha$) = 11.3 mm^{-1}, $F(000) = 376$, $T = 295$ K. Its structure was refined from 381 (346 observed) X-ray single-crystal data to $R = 0.026$. $SrSnO_3$ single crystals, previously reported as cubic ($a = 8.0682$ Å), were studied by electron microscopy and X-ray techniques, showing the presence of multitwinning which gives rise to the fictitious 'double' cubic cell. The real cell has $a = 5.707$ (2), $b = 5.707$ (2), $c = 8.064$ (2) Å, $V = 262.64$ (8) Å^3, $Z = 4$, $D_x = 6.43$ Mg m^{-3}, $M_T = 254.31$, $T = 295$ K, and probably the same space group as $CaSnO_3$. Because of the twin, the structure was solved topologically, by a novel use of the expressions given by O'Keeffe & Hyde [*Acta Cryst.* (1977), B33, 3802–3813] by assuming an Sn–O bond length of 2.062 Å, equal to that derived for $CaSnO_3$.

Introduction

The perovskite structure is one of the most studied among the oxide structures (Goodenough & Longo, 1970; Galasso, 1969; Goodenough, 1971).

The aristotype, $SrTiO_3$, is cubic with just the unit-cell dimension as unique parameter (Megaw, 1973) but many different versions showing lower symmetry are well known (Muller & Roy, 1974). Among them are rhombohedral, as the $LaAlO_3$ phases (Geller &