

Channel Structures Based on Octahedral Frameworks: The Crystal Structure of TiTi_5Se_8 , TiV_5Se_8 , and TiCr_5Se_8 and Its Relationships to TiCr_3S_5 , Hollandites, and Psilomelane*

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TiTi_5Se_8 , TiV_5Se_8 , and TiCr_5Se_8 are monoclinic, space group $C2/m$, $Z = 2$, TiV_5S_8 type with lattice parameters

$$\begin{aligned} a &= 18.773(2), b = 3.5834(1), c = 9.1065(7)\text{Å}, \beta = 104.13(1)^\circ (\text{TiTi}_5\text{Se}_8) \\ a &= 18.354(1), b = 3.4656(1), c = 8.9036(3)\text{Å}, \beta = 104.03(1)^\circ (\text{TiV}_5\text{Se}_8) \\ a &= 18.699(1), b = 3.5942(1), c = 8.9418(9)\text{Å}, \beta = 104.70(1)^\circ (\text{TiCr}_5\text{Se}_8). \end{aligned}$$

A unified scheme is developed for the TiV_5S_8 , TiCr_3S_5 , hollandite, and psilomelane structures on the basis of ideal close packing.

Introduction

In the course of a study on ternary chalcogenides of thallium and the early transition metals we prepared a series of isotopic compounds TiT_5Se_8 ($T = \text{Ti, V, Cr}$) crystallizing with the TiV_5S_8 structure type (1). There is an apparent similarity of this typical tunnel structure to the TiCr_3S_5 structure type (2) on the one side and to hollandite and psilomelane on the other side. In view of the current interest in compounds with tunnel structures as model substances for one-dimensional ionic conductivity, it was

* Dedicated to Professor M. J. Sienko on the occasion of his 60th birthday.

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promising to investigate the structural relationships between these compounds in more detail.

Experimental

The title compounds were prepared from TiSe , Se , and the corresponding transition metal. Stoichiometric amounts of the powdered components were intimately mixed and sealed into evacuated silica tubes. The samples were gradually heated to 1350 K, kept at this temperature for several days, and finally allowed to cool to ambient temperature in the course of three weeks. Well-developed single crystals of appropriate size for X-ray investigations could be iso-

lated from the crushed samples. The compounds crystallize in the form of elongated rectangular platelets and exhibit metallic luster.

Preliminary crystallographic investigations performed with rotating crystal and Weissenberg techniques showed Laue symmetry $2/m$, the unique crystallographic axis being coincident with the long crystal axis. Systematic extinctions were observed for hkl : $h + k = 2n$ indicating $C2/m$, $C2$, or Cm as possible space groups. The dominating habitus planes are parallel to (001); preferred cleavage occurs along [010]. Rotating crystal photographs of crystals turned around the axis perpendicularly to the habitus plane showed a pronounced rhombohedral subcell. The similarity of the lattice dimensions and of the relative intensities suggested that the three compounds were members of an isotypic series.

The lattice constants given in the abstract were obtained by least squares refinement of the 2θ values of 32 reflections measured on a computer controlled four circle diffractometer (Philips PW 1100, graphite monochromated $MoK\alpha$ radiation).

Integrated intensities were collected with continuous θ - 2θ scans up to a $\sin \theta/\lambda$ limit of 0.64. The usual background, Lorentz, and polarization corrections were applied. Absorption effects were accounted for by a spherical absorption correction. Equivalent reflections were averaged yielding unique sets of 684 ($TiTi_5Se_8$), 647 (TiV_5Se_8), and 409 ($TiCr_5Se_8$) observed intensities with $I \geq 3 \sigma(I)$.

Structure Refinement

Composition, symmetry, and lattice dimensions indicated isotypy with TiV_5S_8 (1). Least squares refinements were hence started in space group $C2$ with the atomic positions of TiV_5S_8 . The y parameter of Ti was arbitrarily fixed at 0.0. A critical inspection of the results showed that during

the refinements the free y parameters had been shifted close to the special values 0.0 and 0.5, which was taken as an indication that the correct space group was $C2/m$. This was also suggested by the statistics of the normalized structure factors and by the fact that the isostructural compounds ACr_5S_8 ($A = K, Rb, Cs, Ba_{0.5}$) have been refined in the centrosymmetric space group (3, 4). Refinement in $C2/m$ yielded only insignificantly higher R values ($TiTi_5Se_8$: $R = 0.040$ vs 0.040, TiV_5Se_8 : $R = 0.066$ vs 0.064, $TiCr_5Se_8$: $R = 0.059$ vs 0.058). All calculations were performed with programs of the X-Ray system (5). Scattering factors for neutral atoms were taken from Cromer and Mann (6), corrections for anomalous dispersion from the International Tables for X-Ray Crystallography (7). The final positional and thermal parameters are given in Table I. The significant interatomic distances are compiled in Table II. Lists of the $|F_0|$ values can be obtained from the authors on request.

Discussion

The compounds $TiTi_5Se_8$, TiV_5Se_8 and $TiCr_5Se_8$ are isotypic and crystallize with the TiV_5S_8 structure type (1). The crystal structure is characterized by a three-dimensional framework of TX_6 -octahedra (T = transition metal, X = chalcogen) sharing edges and faces to form channels parallel to [010] which accommodate the thallium atoms. The transition metal atoms are on three different crystallographic sites. In consideration of the type of connection their coordination octahedra are not equivalent. The octahedra centered by $T(1)$ (in the special position $4d$) are connected to those centered by $T(3)$ by common edges. The octahedra centered by $T(2)$ and by $T(3)$ have one face in common.

The present series $TiTi_5Se_8$ allows one to study the influence of the transition metal on the crystal structure. The unit cell vol-

TABLE I
POSITIONAL AND THERMAL PARAMETERS OF TiTi_5Se_8 , TiV_5Se_8 , AND TiCr_5Se_8 (SPACE GROUP $C2/m$)

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}^a	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti	2a	0	0	0	5.67(5)	3.11(5)	3.55(4)	—	1.28(3)	—
Ti 1	2d	0	0.5	0.5	0.82(8)	0.94(9)	0.40(7)	—	0.02(6)	—
Ti 2	4i	0.7919(1)	0	0.1510(1)	0.82(6)	0.81(7)	0.40(6)	—	0.01(4)	—
Ti 3	4i	0.1540(1)	0	0.4939(1)	1.01(6)	0.93(7)	0.57(6)	—	0.08(4)	—
Se 1	4i	0.6606(0)	0	0.0007(1)	0.94(4)	0.91(5)	0.55(4)	—	0.07(3)	—
Se 2	4i	0.2584(0)	0	0.3382(1)	0.97(4)	0.72(4)	0.46(4)	—	0.23(2)	—
Se 3	4i	0.5860(0)	0	0.3162(1)	1.00(4)	1.01(5)	0.57(4)	—	0.12(3)	—
Se 4	4i	0.9268(0)	0	0.3233(1)	0.76(4)	0.90(5)	0.45(4)	—	0.02(3)	—
$R = 0.040$ ($R_w = 0.049$)										
Ti	2a	0	0	0	2.74(5)	2.75(6)	2.69(6)	—	0.67(4)	—
V 1	2d	0	0.5	0.5	0.49(11)	2.44(14)	0.82(11)	—	0.09(8)	—
V 2	4i	0.7900(1)	0	0.1479(2)	0.26(8)	1.80(10)	1.16(9)	—	0.28(6)	—
V 3	4i	0.1490(1)	0	0.4955(2)	0.41(8)	1.53(9)	1.01(8)	—	0.18(6)	—
Se 1	4i	0.6595(1)	0	0.0021(1)	0.36(5)	1.27(7)	1.16(6)	—	0.18(4)	—
Se 2	4i	0.2583(1)	0	0.3418(1)	0.39(6)	1.00(6)	1.02(6)	—	0.271(4)	—
Se 3	4i	0.5849(1)	0	0.3151(1)	0.58(6)	1.20(6)	1.01(6)	—	0.25(4)	—
Se 4	4i	0.9278(1)	0	0.3178(1)	0.36(6)	1.14(6)	1.17(6)	—	0.24(4)	—
$R = 0.066$ ($R_w = 0.064$)										
Ti	2a	0	0	0	13.0(4)	2.5(2)	3.7(2)	—	1.2(2)	—
Cr 1	2d	0	0.5	0.5	0.8(3)	0.3(3)	0.9(3)	—	0.2(3)	—
Cr 2	4i	0.7954(3)	0	0.1664(6)	0.9(2)	0.5(2)	0.9(2)	—	0.1(2)	—
Cr 3	4i	0.1571(3)	0	0.4819(6)	1.0(2)	0.6(3)	0.7(2)	—	0.3(2)	—
Se 1	4i	0.6681(2)	0	0.9930(4)	1.1(2)	0.3(1)	0.8(1)	—	0.3(1)	—
Se 2	4i	0.2604(2)	0	0.3425(4)	1.1(2)	0.1(1)	1.0(2)	—	0.4(1)	—
Se 3	4i	0.5850(2)	0	0.3211(4)	1.2(2)	0.3(2)	1.0(1)	—	0.2(1)	—
Se 4	4i	0.9262(2)	0	0.3387(4)	0.7(1)	0.5(2)	0.9(1)	—	0.1(1)	—
$R = 0.059$ ($R_w = 0.067$)										

^a The U_{ij} are multiplied by 100.

TABLE II
INTERATOMIC DISTANCES (IN Å)

TiTi_5Se_8		TiV_5Se_8		TiCr_5Se_8	
Ti—Se1	3.506(1) (4×)	Ti—Se1	3.398(1) (4×)	Ti—Se1	3.635(3) (4×)
—Se3	3.441(9) (4×)	—Se3	3.344(4) (4×)	—Se3	3.418(3) (4×)
—Se4	3.540(8) (2×)	—Se4	3.403(4) (2×)	—Se4	3.633(4) (2×)
Ti1—Se3	2.594(6) (2×)	V1—Se3	2.526(4) (2×)	Cr1—Se3	2.525(4) (2×)
—Se4	2.571(6) (4×)	—Se4	2.519(3) (4×)	—Se4	2.491(2) (4×)
Ti2—Se1	2.511(9), 2.552(3) (2×)	V2—Se1	2.433(5), 2.499(2) (2×)	Cr2—Se1	2.490(6), 2.494(5) (2×)
—Se2	2.653(3) (2×)	—Se2	2.610(2) (2×)	—Se2	2.581(5) (2×)
—Se4	2.633(10)	—Se4	2.613(5)	—Se4	2.537(6)
Ti3—Se2	2.686(7), 2.651(6) (2×)	V3—Se2	2.689(4), 2.608(3) (2×)	Cr3—Se2	2.550(7), 2.616(4) (2×)
—Se3	2.539(5) (2×)	—Se3	2.460(3) (2×)	—Se3	2.476(4) (2×)
—Se4	2.510(7)	—Se4	2.426(4)	—Se4	2.504(7)
Ti1—Ti3	3.412(1) (4×)	V1—V3	3.246(2) (4×)	Cr1—Cr3	3.483(5) (4×)
Ti2—Ti2	3.337(9) (2×)	V2—V2	3.198(4) (2×)	Cr2—Cr2	3.523(5) (2×)
—Ti3	3.144(7)	—V3	3.100(4)	—Cr3	3.042(7)

umes (593.6, 549.3, and 581.3 Å³ for TlTi_5Se_8 , TlV_5Se_8 , and TlCr_5Se_8 , respectively) do not vary smoothly as might be expected from the atomic radii of Ti, V, and Cr. The unit cell volume of TlV_5Se_8 is by ~6% smaller than that of TlCr_5Se_8 . The same trend is also observed with binary selenides, e.g., the phases with compositions near $T\text{Se}$ (8–10) (NiAs type) and composition $T_3\text{Se}_4$ (11) ($T = \text{Ti, V, Cr}$). By comparison of the interatomic distances in the TlT_5Se_8 phases (Table II) one is led to tentatively attribute the smaller unit cell volume of TlV_5Se_8 to increased T – T interactions: The mean T –Se distance decreases continuously from TlTi_5Se_8 to TlCr_5Se_8 . The smallest value for the average T – T distance is, however, observed in the vanadium compound. While in TlCr_5Se_8 the distance Cr(2)–Cr(3) corresponding to the face sharing octahedra is clearly shorter than the Cr–Cr distances corresponding to edge sharing, the difference is less pronounced in TlV_5Se_8 . Here the atoms V(2) and V(3) are displaced from the centers of the octahedra giving rise to the formation of shorter distances ($d_{\text{V}(1)\text{--V}(3)} = 3.246 \text{ \AA}$, $d_{\text{V}(2)\text{--V}(2)} = 3.198 \text{ \AA}$). TlTi_5Se_8 takes an intermediate position.

The average Se–Se distance is 3.63 Å in TlTi_5Se_8 , 3.54 Å in TlV_5Se_8 , and 3.58 Å in TlCr_5Se_8 . The size of the channels varies considerably, as can be seen from the Tl–Se distances. The average Tl–Se distance in TlV_5Se_8 (3.377 Å) is close to the sum of the ionic radii for Tl^+ and Se^{2-} (1.40 + 1.98 Å). In TlTi_5Se_8 and TlCr_5Se_8 the average Tl–Se distance is distinctly larger. This is reflected by an elevated temperature factor U_{11} of Tl in both compounds.

A General Construction Scheme for the TlV_5S_8 , the TlCr_3S_5 , the Hollandite, and the Psilomelane Type of Structure

The TlV_5S_8 structure type is closely related to the TlCr_3S_5 type (Figs. 1a,b). Both

structures are characterized by three dimensional frameworks of TX_6 octahedra with channels accommodating one (TlV_5S_8) or two (TlCr_3S_5) rows of thallium atoms. These structural relationships correspond to those of the hollandite family (12) and psilomelane (13) (Figs. 1c,d).

The four structure types can be derived from a mixed close packed structure formed by the anions X , together with the large cations M . The small cations T (mainly transition metal ions) occupy the octahedral interstices formed by the anions only. The stacking of the close packed layers is hbc . The c layers are mixed, the h layers consist of anions only.

Two kinds of ordered layers can be distinguished: one with stoichiometry MX_2 in the TlV_5S_8 type and in the hollandites, the other one with stoichiometry MX in the TlCr_3S_5 type and in psilomelane (Fig. 2).

Based on ideal close packing the four structure types can be consistently described with monoclinic unit cells showing the following common features.

- (a) The channels are parallel to the direction of the unique axis b , the length of this axis corresponding to the elementary translation (a_H) within the close packed layers disregarding chemical order (Fig. 2).
- (b) The close packed layers are parallel to one of the basal planes (001) or (100). For the sake of convenience this plane will be defined as (001) in this discussion. For this purpose TlCr_3S_5 and psilomelane are set up in the nonstandard space group $A2/m$.
- (c) The elementary stacking vector between two layers is parallel to the (010) plane with components \mathbf{p} and \mathbf{s} parallel and perpendicular to the [100] direction. The length of \mathbf{p} is given by $p = a_H\sqrt{3}/3$, the length of \mathbf{s} by $s = a_H\sqrt{2}/3$.

The crystal structures and their unit cells can be described in terms of $a_H (= b)$ and

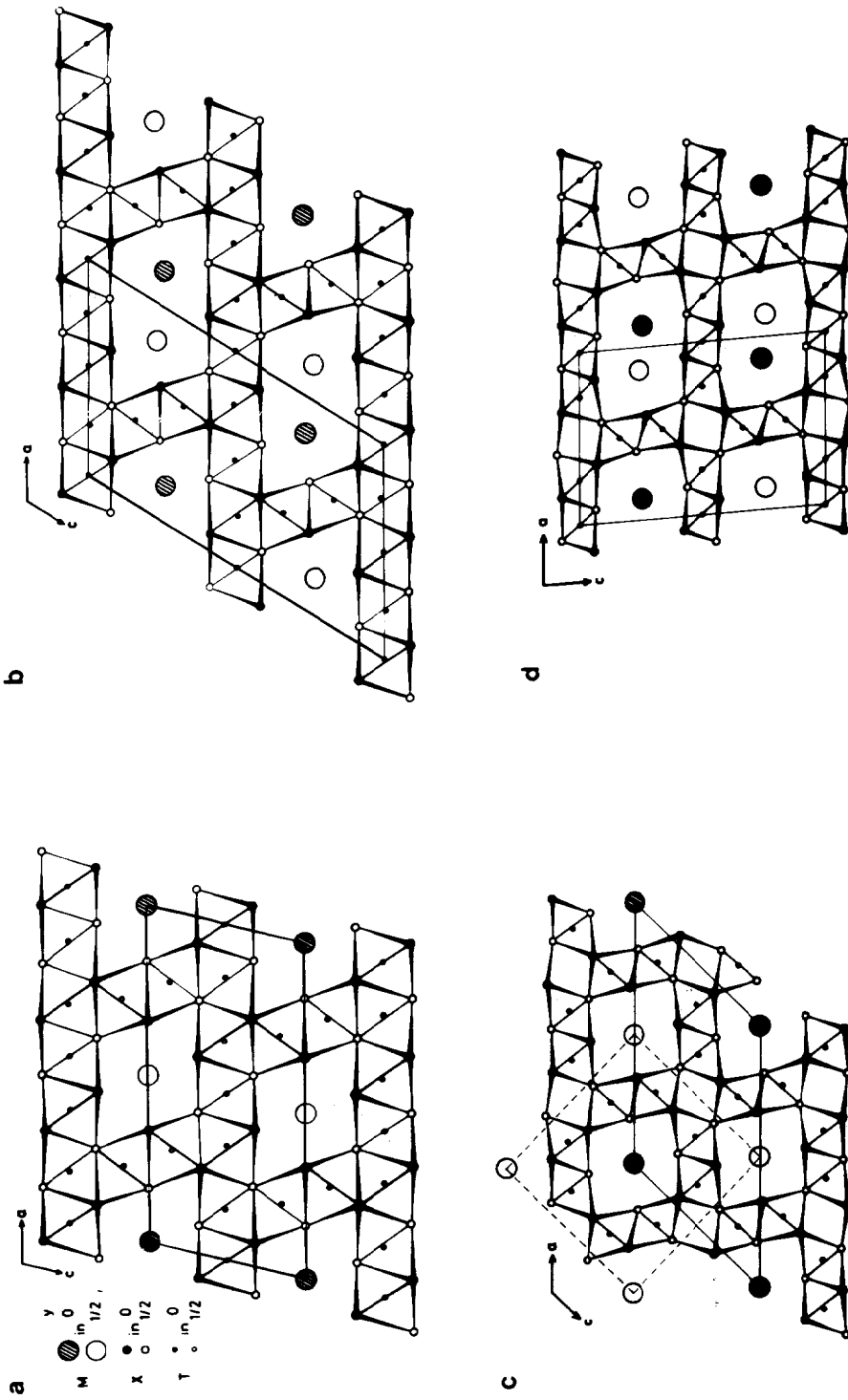


FIG. 1. Projections along the channel direction of the crystal structures of (a) $TiTi_3Se_8$, (b) $TiCr_3S_8$, (c) $Ba_{0.7}Sn_{2.6}Cr_{1.4}O_8$ (monoclinic hollandite phase; the pseudo-tetragonal cell is indicated by dotted lines), (d) $(Ba_1H_2O)_2Mn_3O_{10}$. M: Ti, Ba; X: Se, O; T: transition metal ($Sn_{2.6}$, $Cr_{1.4}$).

three integers:

- l : length of a in units of p ($a = l \times p$),
- m : distance between two equivalent ordered layers in units of s (number of layers),
- n : lateral displacement between two equivalent ordered layers in units of p .

By the latter two definitions the stacking vector \mathbf{t} between two equivalent ordered layers is $\mathbf{t} = m\mathbf{s} + n\mathbf{p}$. The following relationships can easily be derived:

$$\operatorname{tg}(\beta - 90^\circ) = \frac{np}{ms} = \frac{1}{\sqrt{2}} \frac{n}{m}$$

$$\text{or } \operatorname{tg}\beta = -\frac{1}{\sqrt{2}} \frac{n}{m}$$

$$\frac{a}{b} = \frac{l}{\sqrt{3}}$$

$$\frac{c}{a} = \sqrt{2} \frac{m}{l \sin \beta}$$

An orthogonal unit cell can be obtained consisting of $l \times m$ layers with $a_{\text{ortho}} = a$, $b_{\text{ortho}} = b$, $c_{\text{ortho}} = l \times m \times s$.

The values of l , m , and n are not arbitrary: l is determined by the ordering in the mixed layer (e.g., 9 and 6 for MX_2 and MX layers, respectively). m must be a multiple of 3 because of the hhc stacking sequence. n can adopt values given by

$$n = m/3 + 3n'$$

For $m = 3$, n' can be an integer $0 \leq n' < l/3$. In the case of $m = 6$ neighboring ordered layers are not equivalent, having a stacking vector with a nonintegral component perpendicular to \mathbf{s} , given by $(1 \pm 3/2)\mathbf{p} + \mathbf{b}/2$. Therefore the stacking vector to the next equivalent layer is $\mathbf{t} = 6\mathbf{s} + (2 \pm 3)\mathbf{p}$ (i.e., $n' = \pm 1$).

As seen from Table III the subseries with $l = 9$ (MX_2 layers) contains one more hypothetical structure besides the TiV_5S_8 type and the hollandite type. The subseries with

TABLE III

POSSIBLE CHANNEL STRUCTURES BASED ON CLOSE PACKING DEFINED IN TERMS OF l , m , AND n

l	m	n	Structure type
9	3	1	TiV_5S_8
		4	Hollandite
6	3	7	} Hypothetical structures
		1	
		4	
6	6	-1^a	Psilomelane
		5	$TiCr_3S_5$

^a A negative value of n corresponds to a unit cell with an acute angle β . Choosing $|n|$, an equivalent setting with a unit cell having $\beta' = 180 - \beta$ is obtained.

$l = 6$ (MX layers) and $m = 6$ has only two members, realized by the $TiCr_3S_5$ type and by psilomelane. It should be noted that in these two structures the stacking of the equivalent mixed layers (i.e., every second mixed layer) is the same (because of $n \equiv -1 \pmod{6} \equiv 5 \pmod{6}$). There are two hypothetical structures with MX layers and $m = 3$.

Within one subseries (i.e., for a given l and m) the different lateral displacement of the mixed layers, as characterized by n , leads to a different arrangement of the channels. In the oxide phases the channels form an almost orthogonal array (Figs. 1c,d). As a consequence the oxygen octahedra at the corners of the channels share two opposite faces with neighboring octahedra. These octahedra are not occupied by T atoms. In the chalcogenide phases the arrangement of the channels requires only

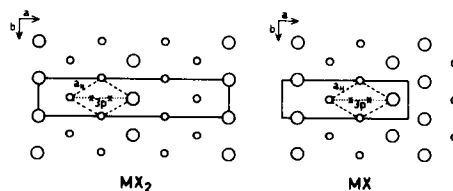


FIG. 2. The two anion-cation mixed layers of composition MX_2 and MX . The pseudo-hexagonal cell (a_H) and the component $3p$ of the stacking vector between equivalent layers are also shown.

one face to be shared, and all chalcogen octahedra are occupied. Therefore the stoichiometries of the $[T_mX_n]$ frameworks in TiV_5S_8 and $TiCr_3S_5$ are different from those in hollandite $[T_4O_8]$ and psilomelane $[T_5O_{10}]$, respectively.

The unit cell dimensions of the known compounds crystallizing in the TiV_5S_8 and $TiCr_3S_5$ types of structure are listed in Table IV. The very good agreement between β , a/b , and c/a calculated for the ideal model and the values of the real structures of the chalcogenide phases is remarkable in view of the apparent deformations observed on the local scale. Greater deviations from the ideal model are present in the hollandites and psilomelane, for which two representatives, monoclinic $Ba_{0.7}Sn_{2.6}Cr_{1.4}O_8$ (14) and monoclinic $(Ba,H_2O)_2Mn_5O_{10}$ (13) are included in Table IV. In the hollandite phases the deviations from the

sphere packing model tend to enhance the pseudo-tetragonal symmetry of the structure. Actually some hollandites are tetragonal (12, 15). The relations between the monoclinic cell as derived from the sphere packing model, and the (pseudo) tetragonal cell can be seen from Fig. 1c and Ref. (14).

The question of ionic mobility in cation deficient hollandites is controversial (16). The title compounds do not indicate non-stoichiometry with respect to thallium. The crystals, however, have been picked up from samples prepared at stoichiometric compositions. In the case of the isotypic sulfide TiV_5S_8 , Schöllhorn *et al.* (17) report on the electrochemical topotactic extraction of thallium and its electrochemical exchange against lithium. These authors postulate mobility of the cations within the channels of the $[V_5S_8]$ framework at room

TABLE IV
UNIT CELL PARAMETERS OF COMPOUNDS WITH THE TiV_5S_8 AND THE $TiCr_3S_5$ TYPE OF STRUCTURE INCLUDING ONE HOLLANDITE PHASE AND PSILOMELANE

	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$\beta(^{\circ})$	a/b	c/a
TiV_5S_8	17.465	3.301	8.519	103.94	5.29	0.488
$TiTi_5Se_8$	18.773	3.583	9.1065	104.13	5.24	0.485
TiV_5Se_8	18.354	3.4656	8.9036	104.03	5.30	0.485
$TiCr_3Se_8$	18.699	3.5942	8.9418	104.70	5.20	0.478
KCr_3S_8	17.798	3.447	8.598	105.00	5.16	0.483
$RbCr_3S_8$	17.835	3.452	8.654	104.74	5.17	0.485
$CsCr_3S_8$	17.915	3.464	8.732	104.62	5.17	0.487
$Ba_{0.5}Cr_3S_8$	17.771	3.425	8.566	104.68	5.19	0.482
Ideal				103.26	5.10	0.484
$TiCr_3S_5^a$	11.98	3.454	19.29	122.1	3.47	1.61
$TiCr_3Se_5$	12.40	3.59	20.08	121.3	3.45	1.62
Ideal				120.51	3.46	1.64
$Ba_{0.7}Sn_{2.6}Cr_{1.4}O_8$ (hollandite phase)	14.728	3.108	10.012	134.37	4.47	0.680
Ideal				133.31 ^b	5.20	0.648
$(Ba,H_2O)_2Mn_5O_{10}^a$ (psilomelane)	9.56	2.88	13.85	92.50	3.32	1.45
Ideal				96.72	3.46	1.42

^a Unit cell set up in $A2/m$.

^b $\beta = 93^{\circ}$ for the usual pseudotetragonal cell set up in space group $I2/m$.

temperature. In view of the higher polarizability of the anions and of the metallic character of the framework, nonstoichiometric transition metal sulfides and selenides with channel structures are probably more realistic model substances for one-dimensional ionic conductivity than oxide phases. This should be especially true for the vanadium and titanium compounds.

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