

New Routes in the Synthesis of Metal Oxides, I*

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Single crystals of numerous new metal oxides "rich in cations" are prepared by using methods such as dis- or conproportionation, thermal decomposition of higher valence oxides, or oxidation of metals and intermetallic compounds ("reactions with the wall"). Exchange reactions allow growth of single crystals even outside of thermodynamic equilibrium. The role of vacancies in structural chemistry as well as in "tailor-made" syntheses is emphasized and illustrated. Molecular aspects of solid state chemistry are demonstrated by cutting chains or rings and by dimerization of small entities. Many examples are provided. © 1986 Academic Press, Inc.

Inorganic solid state chemistry is still a new branch of our science. This is why we have serious difficulties in expressing accurately what we know. We do not deal with molecules as more or less small individual entities but with huge collective entities of particles. Although we now recognize that the ingenious Berzelian language of chemical formulas is applied best to molecules we also have to use it as a crutch in describing solid state compounds.

If we understand the properties of a molecule we understand the properties of the corresponding material built up from a huge number of such individuals. But for solid state compounds the unit cell—this beautiful gift of applied group theory, as offered by crystallography and the basis of structural elucidations—is inappropriate. For example, how could *one* unit cell yield true

information on collective properties such as order/disorder phenomena?

Other difficulties arise in our experimental science. We gain experience from the observation of reactions which take place in our R^3 space. Man as a pseudo-three-dimensional being can describe infinity by using his intelligence, but mentally he can grasp only small things. This is why we code three-dimensional experience with two-dimensional chemical formulas, using a letter, a page of a textbook, a tape, a drawing.

Even for molecules it is difficult to code special aspects correctly in easily readable drawings. Take the conformation of rings like S_{12} or S_{18} (*I*) as an example. How should one proceed with collections? Figure 1 shows that even with a small unit cell the common habit of drawing exhibits misinformation if the message coded in R^2 is read unbiassed. It seems remarkable that Schlegel's solution of such difficulties, proposed 100 years ago is just now beginning to enter chemistry (see Fig. 2). Such Schle-

* Editor's Comment: Due to space limitations it was not possible to publish this article in its entirety in this issue. The concluding section will be published in a future issue of the journal. The entire reference list appears in both Part I and Part II.

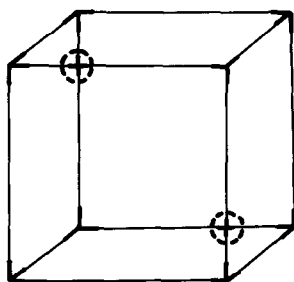


FIG. 1. Common projection of a cube on R2 creates two false corners indicated by the circled crossing points.

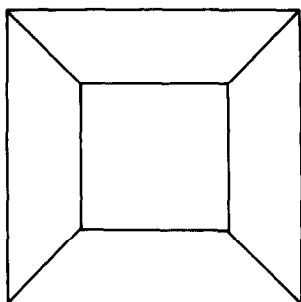


FIG. 2. Schlegel's projection of a cube on R2.

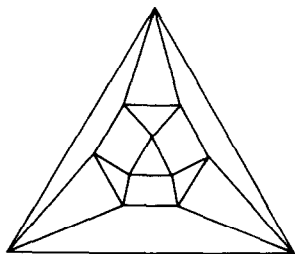
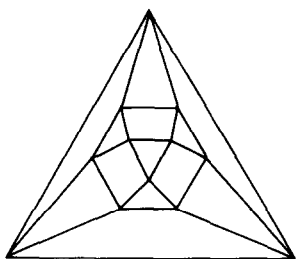


FIG. 3. Schlegel projection of the CP about the closest packing of spheres for c.c.p. (above) and h.c.p. (below).

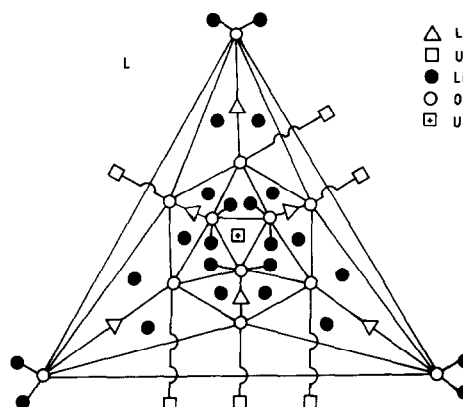


FIG. 4. Schlegel diagram of the CP surrounding the vacancy in α -Li₆UO₆. The position marked \square indicates a common face of the CP which is being viewed, with a CP of U⁶⁺ (above and below).

gel projections of polyhedra of coordination (CP) show clearly characteristic differences of similar arrangements, as exhibited in Fig. 3. The important progress we made in extending Schlegel's idea is based on information on how next nearest neighbors are connected within a given CP (Fig. 4). We

TABLE I
MOTIFS OF MUTUAL
ADJUNCTION OF K₂NiO₂

	2 O ²⁻	CN
2 K ⁺	5/5	5
1 Ni ²⁺	2/1	2
CN(O)	6	

TABLE II
MOTIFS OF MUTUAL
ADJUNCTION OF A₅MO₄
(A = Li, Na; M = Al, Ga)

	4 O ²⁻	CN
1 M ³⁺	4/1	4
5 A ⁺	4/5	4
CN(O)	1 + 5 = 6	

call such drawings "extended Schlegel projections," or Schlegel diagrams for short. With their help even complicated structures can be reconstructed step by step quite easily (2) without using stereo plots or models of unit cells.

I. New Concepts

To prepare new compounds such as polynary oxides of metals with alkali metals it is helpful to find new ways of thinking or at least to develop known concepts. Along these lines, we have modified Niggli's important concept: for example, in the case of MgO or SiO₂ he wrote MgO_{6/6} or SiO_{4/2} to indicate coordination numbers (CN). One should bear in mind that the term coordination in its strict sense is restricted to classical "complexes" such as Cs₂[CoF₆] (3). Certainly in the case of polynary metal oxides rich in cations we often encounter compounds such as K₂⁹_∞[NiO_{2/1}] (4), where the XeF₂-like (5) linear grouping O—Ni—O with the extremely short distance $d(\text{Ni—O}) = 168 \text{ pm}$ provides a striking contrast to the observed paramagnetism encountered in Ni²⁺ ($\mu = 3,0 \mu_B$; $\theta = -30 \text{ K}$). However, for collections of particles such as MgO there exists a mutual relationship of CN which should more correctly be called adjunction instead of coordination. We prefer therefore to speak of Motifs of Mutual Adjunction (MMA); (see Table I).

Such a table of MMA shows very easily how different CNs of the constituents combine, as shown in Table II. Now, however, we have actually much more than Niggli's "static" description of a geometric situation, a given arrangement of particles. We can predict what happens on substituting for some of the counter cations, as well as understand why one encounters certain combinations, such as K₂Li₃[GaO₄] (6) but not K₃Li₂[GaO₄] (see Table III).

The step from ternary to polynary oxides by use of such MMA's opens a new and fascinating world of metal oxides. So far nobody has been able to prepare K₅[GaO₄], whereas K₅[TiO₄] is easily obtainable (7). One might believe that it is the "large number of large cations" which causes the instability of K₅[GaO₄] with its "smaller" Ga³⁺ instead of the "larger" Ti³⁺. But this idea is completely wrong: CsK₄[GaO₄] (8) is easily prepared in beautiful transparent colorless single crystals.

We state that even simple metal oxides are subject to internal contradictions when the adoption of usual CN and stoichiometry are in conflict. We call this the Enstatite Syndrom (see Table IV). One of the most complicated examples that we have found is encountered in K₄[WO₅] (9). Here the con-
 1 12 1 2 3 1 15
 stitution is based on K. . .KWWWO. . .O
 with $Z^* = 2$, instead of the crystallographic $Z = 6$.

TABLE III
MOTIFS OF MUTUAL ADJUNCTION OF K₂Li₃[GaO₄]

	O(1)	O(2)	O(3)	O(4)	CN
Ga	1/1	1/1	1/1	1/1	4
Li(1)	1/1	1/1	1/1	1/1	4
Li(2)	1/1	1/1	1/1	1/1	4
Li(3)	1/1	1/1	—	2/2	4
K(1)	1/1 + 1/1	1/1 + 1/1	1/1 + (1/1 + 1/1)	1/1 + (1/1 + 1/1)	6 + 4
K(2)	1/1 + (1/1)	1/1 + (1/1)	1/1 + 1/1 + 1/1	1/1	6 + 2
CN	7 + 1	7 + 1	7 + 2	7 + 2	

TABLE IV
THE SYNDROME OF MgSiO₃: FOUR SIMPLE POSSIBILITIES AND REALITY

	¹ IO	² IO	³ IO _B	CN
1 Si	1/1	1/1	2/2	4
1 Mg	3/3	2/2	1/1	6
CN (O ²⁻):	4	3	3	NO!

	¹ IO	² IO	³ IO _B	CN
1 Si	1/1	1/1	2/2	4
1 Mg	2/2	2/2	2/2	6
CNO ²⁻ :	3	3	④	NO!
1 Mg	3/3	3/3	—	6
CNO ²⁻ :	4	4	②	NO!

← BUT: NO!

	¹ IO	² IO	³ IO _B	CN
1 Si	1/1	1/1	2/2	4
1 Mg	3/3	3/3	1/1	7
CN (O ²⁻):	4	4	3	YES

ON THE SYNDROME OF ENSTATITE: REALITY

	¹ IO	² IO	³ IO _B	⁴ IO	⁵ IO	⁶ IO _B	CN
¹ Si	1/1 161	1/1 159	1/1 + 1/1 165 166	—	—	—	4
² Si	—	—	—	1/1 162	1/1 159	1/1 + 1/1 168 168	4
¹ Mg	1/1 + 1/1 203 215	1/1 201	—	1/1 + 1/1 206 207	1/1 204	—	6
² Mg	1/1 209	1/1 203	1/1 (229)	1/1 206	1/1 199	1/1 (234)	6
CNO ²⁻ :	4	3	2(+1)	4	3	2(+1)	

IN FACT: MgMgSi₂O₇⁶O₁
THE ENSTATITE-SYNDROME

TABLE V
MAPLE ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$), kcal/Mol

	Bin.	Tern.	Δ	$\Sigma\Delta$
3 Ca^{2+}	482.2	508.7	+26.5	+79.5
2 Al^{3+}	1264.6	1298.2	+33.6	+67.2
3 Si^{4+}	2208.9	2214.8	+5.9	+18.7
3 O^{2-}	482.2	612.5	+130.3	+390.9
3 O^{2-}	608.1	612.5	+4.4	+13.2
6 O^{2-}	703.4	612.5	-90.9	-545.4
Σ	18094	18116	$\Delta = 24.1$ $= 1.3\%$	

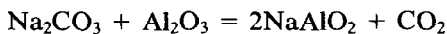
I wonder why nobody so far has tried to review the differences between the commonly used Z and the much more characteristic corresponding value of Z^* .

A useful concept to test structure determinations independently by comparison with related structures is the concept of MAPLE (10), the Madelung part of lattice energy. The sum of the MAPLE values for the binary oxides generally falls within less than 1% of the MAPLE values for the polynary oxide (see Table V).

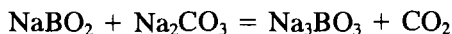
II. On the Synthesis of Metal Oxides

In the following we deal either with binary or polynary oxides of metals of composition $A_xM_yO_z$, where A stands for an alkali metal, M for a partner metal; also, $x + y > z$.

Two common routes of synthesis are generally utilized. Reactions similar to



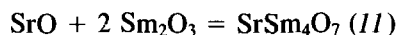
we call "industrial" ones for short. Very often it is dangerous to use these. In case of, e.g., oxoborates of the alkali metals rich in cations serious difficulties arise because reactions such as



are incomplete even after long times of

heating. This is why several phase diagrams such as $\text{A}_2\text{O}/\text{SiO}_2$ or $\text{A}_2\text{O}/\text{B}_2\text{O}_3$ are wrong.

The synthesis starting with binary constituents is more suitable:



mp ($^\circ\text{C}$): 2460 2360 2250

There are, however, two complications:

(a) A complete reaction requires a very intimate mixing of the starting components.

(b) The required relatively high temperature often leads to undesired "reactions with the wall."

In addition for single crystal growth for which no flux is known or applicable the process is sometimes complicated by thermal decomposition, or by the existence of different modifications. Thus, e.g., crystals in the high temperature form may transform upon cooling to twins or to powders in the Low Temperature-form.

TABLE VIa
PREPARATION OF
"VIRGINAL" BaO^*

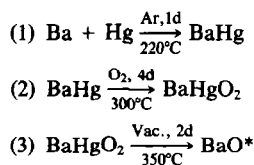


TABLE VIb
PRINCIPAL POSSIBILITIES OF EXCHANGE REACTIONS
WITH, E.G., TERNARY OXIDES AND FLUORIDES
 $A_xM_yX_z$

TYPE A. Exchange of cations A:	
	$2\text{LiInO}_2\text{solid} + \text{Na}_2\text{Osolid} = 2\text{NaInO}_2\text{solid} + \text{Li}_2\text{Osolid} \quad (13)$
TYPE M. Exchange of completing metals M:	
	$\text{Cs}_2\text{KInF}_6\text{solid} + \text{MnF}_3\text{solid} + n\text{F}_2\text{gas} = \text{Cs}_2\text{MnF}_6\text{solid} + \text{InF}_3 \quad (14)$
TYPE X. Exchange of anions X:	
	$\text{KFeS}_2\text{solid} + \text{K}_2\text{ZnO}_2\text{solid} = \text{KFeO}_2\text{solid} + \text{"K}_2\text{ZnS}_2\text{solid"}^a$
TYPE D. $\text{BaPbO}_3\text{solid} + \text{F}_2\text{gas} = \text{BaPbF}_6\text{solid} + \dots$	(15)

^a Barely investigated; no example yet known for sure.

TABLE VII
ON EXCHANGE REACTIONS: DIFFERENT TYPES

- (1) The "common" one
 $2A'MO_2 + A_2O \rightarrow 2A'MO_2 + A_2O$
 $Na > Li > K > Rb > Cs$
- (2) The "inverse" one
 $2Li_4PbO_4 + K_2O = K_2Li_6[Pb_2O_8] + Li_2O$ (16)
- (3) The "reductive" one
 $2NaCu^{III}O_2 + 2Li_2O \rightarrow 2Li_2Cu^{II}O_2 + Na_2O_2$ (17)
- (4) The "oxidative" one
 $Cs_2K[InF_6] + Mn^{III}F_3 \xrightarrow{+F_2} Cs_2[Mn^{IV}F_6]$ (14)

III. On Virginal BaO

The preparation of BaO is simple or difficult. It is simple if one does not object to preparation of samples at high temperatures, starting, e.g., with BaCO₃, BaC₂O₄, or even BaSO₄. Ba(OH)₂ · 8H₂O seems a better starting material. But here also relatively high temperatures must be used to ensure that no traces of OH remain. For certain syntheses one requires highly active samples of BaO that never have been "burnt" at high temperatures and that have never been attached to H₂O or OH⁻. Table VIa shows how we prepare what might be called "virginal" BaO (12).

IV. Exchange Reactions—The Concept of Soy

Reactions of the type

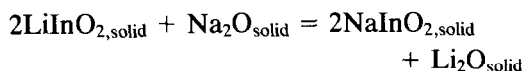


TABLE VIII
THE "CONCEPT OF SOY": "FERMENTATED" OXIDES

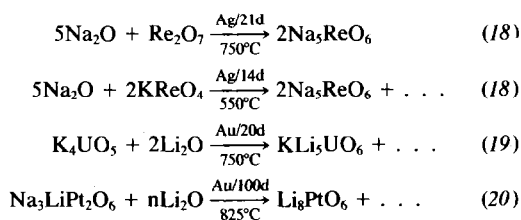
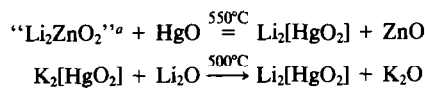


TABLE IX
SURPRISING RESULTS (21) ON EXCHANGE REACTIONS



^a Single crystal data: $a = 39.36 \text{ \AA}$, $c = 23.80 \text{ \AA}$. Structure: unknown. Space group $P3_1$ or $P3_2$.

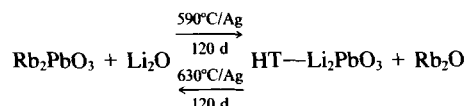
represent what we call Solid State Exchange Reactions or Exchange Reactions.

Of course, for an oxide $A_xM_yO_z$ one can in principle exchange all three of the listed partners. In addition there are other, different possibilities like those listed under Type D in Table VIb (13–15).

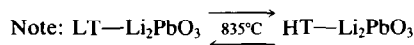
In the following we deal with exchange reactions only of the Type A. Here, as with the others, there are many different possibilities; Table VII exhibits the four most important types.

The advantage of such reactions may be illustrated by Table VIII. In some cases we observed surprising results (see Table IX). For example, the formation of Li₂[HgO₂] (13–20) was a striking warning against sim-

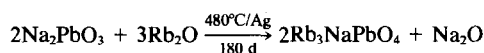
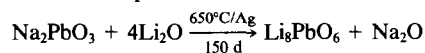
TABLE X
EXCHANGE REACTIONS [22]



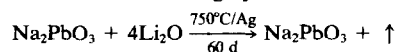
Here $\Delta H \approx 0$ and $\Delta S \approx 0$, hence $\Delta G \approx 0$



Additional examples:



But with a semiclosed Ag cylinder:



Note. In each case we obtained *single crystals*.

pleminded notions we had held. The stability of $K_2[HgO_2]$ (21) is a remarkable feature which is inexplicable at this time.

V. Exchange Reactions—Outside Thermodynamic Equilibrium

Under normal oxygen pressures it is impossible to grow single crystals of, e.g., Li_2PbO_3 or Na_2PbO_3 . In both cases heating of the powder leads to thermal decomposition. With Li_2PbO_3 there occur in addition two modifications, with a reversible of transformation point at $835^\circ C$. Here Exchange Reactions help enormously (see Tables X and XI) (22).

The results show clearly that we are outside the regime of thermodynamic equilibrium. This is an important tool for future preparations. For the first time an important borderline between the chemistry of molecules, where such reactions are typical, and inorganic solid state chemistry, where with respect to enhanced temperatures the constraints of thermodynamic equilibria hold sway, is eliminated in a controllable manner. Furthermore, no flux and no solvent has to be used.

TABLE XI

EXCHANGE REACTIONS: ADDITIVE EXAMPLES (22)

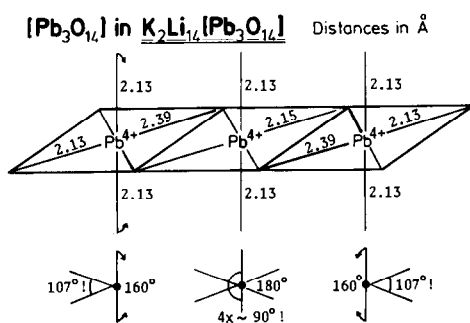
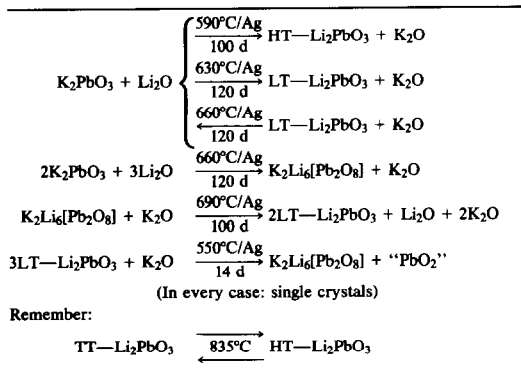
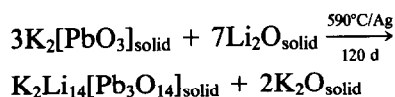


FIG. 5. Structure of the trimetric "Battleship" Pb_3O_{14} anion present in $K_2Li_{14}[Pb_3O_{14}]$.

VI. How to Cut Chains—On Battleships

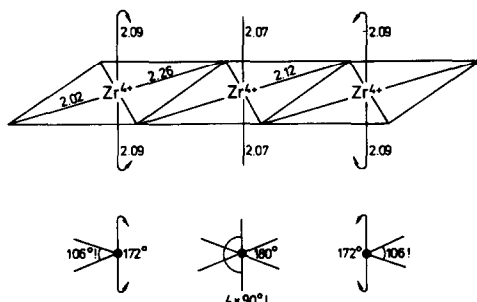
Oxoplumbates(IV) such as $BaPbO_3$ (23) are perovskites, in which Pb^{4+} adopts CN 6. In oxides such as K_2PbO_3 , one encounters *two* instead of *one* large cation per unit PbO_3 . Correspondingly, the CN 6 for Pb^{4+} can only be realized in a layer-like structure, which is very unlikely. Thus we anticipate a configuration based on $K_2[PbO_{4/2}O_{1/1}]$ with CN 5. This again leads either to a layer-like structural motif, where the part $PbO_{4/2}$ forms a chessboard-like layer, or to two chains derived from the $PdCl_{4/2}$ type of structure by capping each square group $PbO_{4/2}$ alternately with the "missing" O^{2-} . As described elsewhere this leads automatically to a tree-trunk-like densest packing of such chains, with the 2 K^+ ions filling the space between the chains (24).

Such chains can be "cut"; with the reaction

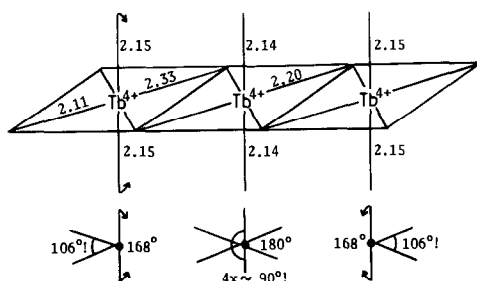


we obtained the first triple of edge-connected octahedra (25) (see Fig. 5). This part resembles a "Battleship," armed with $4/2 K^+$ per unit serving as a keel and a stern, and likewise with $28/2 Li^+$ acting like "guns" and/or torpedo launching tubes.

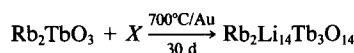
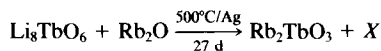
The detailed structure of $[Pb_3O_{14}]$ is remarkable. Only the octahedron in the mid-

[Zr₃O₁₄] in K₂Li₁₄[Zr₃O₁₄] Distances in ÅFIG. 6. Structure of the anion in K₂Li₁₄[Zr₃O₁₄].

dle of the trimer is nearly undistorted. It is peculiar that the six distances $d(\text{Pb}-\text{O})$ are all alike although four of them are bridging. The two flanking "PbO₄" units are farther away than expected. In addition the "head and foot" of these "octahedra" are bowed against the middle part of the group, as if they tended to be distinct tetrahedral groups on their own. This is not a peculiarity of just oxoplumbates; for, we obtained K₂Li₁₄[Zr₃O₁₄] (26) in single crystal form, with the same battleship configuration (see Fig. 6). Thus at least in this case there is a correspondence between main group and related transition elements of the corresponding subgroup. Analogous compounds with 4f elements can also be synthesized. Rb₂Li₁₄[Tb₃O₁₄] (27) corresponds to Rb₂Li₁₄[Pb₃O₁₄] (28) and is therefore a member of the K₂Li₁₄[Pb₃O₁₄] family of Battleships

[Tb₃O₁₄] in Rb₂Li₁₄[Tb₃O₁₄] Distances in ÅFIG. 7. Structure of the anion in Rb₂Li₁₄[Tb₃O₁₄].TABLE XII
A NEW "BATTLESHIP":
Rb₂Li₁₄[Tb₃O₁₄]

Preparation:

Orthorhombic $a = 1286.1$ pm $b = 792.0$ pm $c = 737.8$ pm652 $I_0(hkl)$ $R = 4.69\%$ $R_w = 3.24\%$ $Z = 2$ Space group: $Immm$

(see Fig. 7). In both of these new cases we find the same curious geometrical arrangement within the group [M₃O₁₄]. Our inability to explain such facts is decidedly depressing.

VII. More on Oxoterbates(IV)

As is shown by Table XII we obtained Rb₂Li₁₄[Tb₃O₁₄] in a series of experiments dealing with substitution reactions on Li₈[TbO₆]. After preliminary investigation (29) we now know in full detail (30) that this oxide belongs to what we call the Li₈[SnO₆] type of structure (31). This family, vaguely known since at least 1960, (32), is widespread within the periodic table of elements. The constitution is based on an arrangement $\overset{1}{\text{Li}}\overset{4}{\text{Li}}\overset{2}{\text{Li}}\overset{6}{\text{Tb}}\overset{16}{\text{O}}\text{O}_6$ correspond-

TABLE XIII
Li₆Tb₂O₇

Preparation:

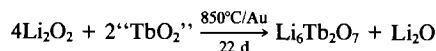
Monoclinic $a = 546.6$ pm $b = 613.5$ pm $c = 1056.3$ pm $\beta = 109.6^\circ$ 1108 of 1345 $I_0(hkl)$ $R = 9.5\%$ $R_w = 5.3\%$ $Z = 2$ Space group: $P2_1/c$

TABLE XIV
 $\text{Li}_6\text{Tb}_2\text{O}_7$ ($\sim\text{Mg}_8\text{O}_7\text{[L]}_1$): MOTIFS OF MUTUAL ADJUNCTION

	$2\overset{1}{\text{O}}$	$4\overset{2}{\text{O}}$	$4\overset{3}{\text{O}}$	$4\overset{4}{\text{O}}$	2[L]	
4 Tb	1/2 (218)	1/1 + 1/1 (220) (224)	1/1 (210)	1/1 + 1/1 (211) (212)	/	6
$4\overset{1}{\text{Li}}$	1/2 (235)	1/1 (218)	1/1 + 1/1 (198) (199)	1/1 (228)	1/2 (249)	2 + 3(+L)
$4\overset{2}{\text{Li}}$	1/2 (221)	1/1 (220)	1/1 + 1/1 (205) (214)	1/1 (227)	1/2 (236)	5(+L)
$4\overset{3}{\text{Li}}$	/	1/1 + 1/1 (191) (227)	1/1 (186)	1/1 + (1/1) (223) (268)	1/2 (269)	2 + 2(+1 + L)
CN	6	6	6	6	6	

Note. [L] = Vacancy.

ing to hexagonal closest-packing of O^{2-} . Li^+ fills $\frac{1}{2}$ of the tetrahedral, and Li^+ with Tb^{4+} , $\frac{1}{2}$ of the octahedral holes in an ordered manner. Consequently, one should look for two different variations. The first could be $\text{Li}_6(\text{Na}_2\text{Tb})\text{O}_6$; the second, $\text{Na}_6(\text{Li}_2\text{Tb})\text{O}_6$. No single crystals are available yet. In addition, it would be interesting to learn what happens, if one attempts to prepare other oxides which are only formally similar to Li_8TbO_6 , e.g., $\text{Li}_6\text{Rb}_2\text{TbO}_6$. During this course we obtained the battleship $\text{Rb}_2\text{Li}_{14}[\text{Tb}_3\text{O}_{14}]$ mentioned before. In contrast to the formation of $\text{K}_2\text{Li}_{14}[\text{Pb}_3\text{O}_{14}]$, no "chain" was cut; rather, an "oligomerization" takes place. In an effort to see more clearly how the trimer of octahedra was formed, we investigated the field of oxotribates(IV) in more detail. It turned out that other unknown oxides exist. One of these is $\text{Li}_6\text{Tb}_2\text{O}_7$ (33). Surprisingly we encounter here a "simple" derivative of the NaCl type, where, e.g., the motif is formally transposed to $\text{Li}_6\text{Tb}_2\text{O}_7[\text{L}]$ (see Table XIII).

The vacancy within the anionic part of the structure permits different types of structural motifs to be realized. The most probable one is that wherein Tb^{4+} has no oxide vacancy as a neighbor. This is what can be deduced from the enormous differ-

ence in valence between Li^+ and Tb^{4+} . The observed structure confirms this (see Table XIV). Within these restrictive conditions Li^+ tends to avoid CN 5 at best.

VIII. On the Oxidation of Metals: The Reaction "with the Wall"

In solid state chemistry one of the most serious complications while working in a "closed" or "semiclosed" system is the reaction with the wall.

In an attempt to obtain the still unknown $\text{K}[\text{NiO}_2]$ by an exchange reaction (see Table XV), we noticed the formation of beautiful crystals of $\text{Na}_3[\text{AgO}_2]$ (34). Another exchange reaction leading to the mixed va-

TABLE XV
 ON THE FORMATION OF $\text{K}_3\text{Ni}_2\text{O}_7$

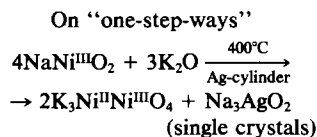
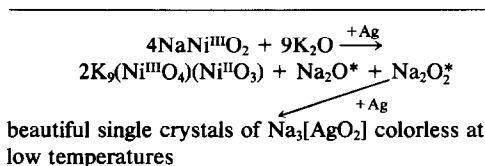
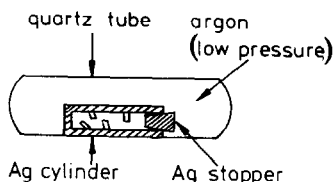
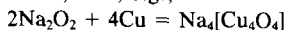


TABLE XVI

PREPARATION OF $A_4[M_4O_4]$ WITH $A = \text{Li}-\text{Cs}$, $M = \text{Cu, Ag, (Au)}$ BY REACTION WITH THE WALL

650°C, 20 d, e.g.,

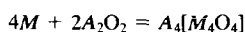


lence oxide $\text{K}_3\text{Ni}^{\text{II}}\text{Ni}^{\text{III}}\text{O}_4$ (35), with which $\text{K}_3\text{Pt}_2\text{O}_4$ is isotypic, also yielded $\text{Na}_3[\text{AgO}_2]$ (see Table XV).

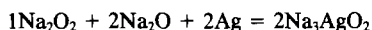
We then started to use such reactions properly: the best application is displayed in Table XVI. In this manner we obtained not only $\text{K}_4[\text{Ag}_4\text{O}_4]$, but single crystals of the other members of this family as well (36) (Table XVII) (another example to be cited here is $\text{Li}_2[\text{PdO}_2]$ (37)). Characteristic of this family is the more or less "puckered" square "ring" $[\text{M}_4\text{O}_4]$ (Table XVIII), as well as the very short distances $d(M-M)$, which indicate metal-metal bonding within the $[\text{M}_4\text{O}_4]$ unit (see Table XIX).

TABLE XVII

OXIDATION OF METALS (REACTION WITH THE WALL)



	$M = \text{Cu}$	$M = \text{Ag}$
$A = \text{Li}$	720°C	700°C
$A = \text{Na}$	690°C	640°C
$A = \text{K}$	660°C	620°C
$A = \text{Rb}$	650°C	600°C
$A = \text{Cs}$	—	560°C



480°C 10 d

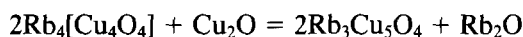
TABLE XVIII

DEVIATION OF OXYGEN ("SET-OFF") OUT OF "SQUARE" IN CASE OF THE COMPOUNDS $A_4[M_4O_4]$ ($M = \text{Cu, Ag}$)

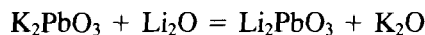
Compound	z -Parameter O^{2-}	"Set-off" [pm] [$(.25 - z)$ c -axis]
NaAgO	0.2607	5
KAgO	0.2538	2
RbAgO	0.2420	1
CsAgO	0.2380	7
LiCuO	0.2503	0
NaCuO	0.2533	1.5
KCuO	0.2258	13
RbCuO	0.2632	8

IX. How to Cut Rings

With the exchange reaction



we have once again an example where, in analogy to the reaction.



ΔH and ΔS should be equal to zero. Cu_2O acts here as the scissors. The cutting of the rings leads to a spiraling infinite chain in $\text{Rb}_3\text{Cu}_5\text{O}_4$ (38). To obtain $\text{Rb}_3\text{Cu}_5\text{O}_4$ as a pure powder one cannot use such exchange reactions: when starting with $\text{Rb}_4[\text{Cu}_4\text{O}_4] + \text{Cu}_2\text{O}$ as well as with $\text{Rb}_3\text{Cu}_5\text{O}_4 + \text{Rb}_2\text{O}$ we

TABLE XIX

OXIDES $A_4[M_4O_4]$: DISTANCES

	A	$d(M-O)$	$d(M-M)^a$ pm
$M = \text{Cu}$	Li	185	268
	Na	183	264
	K	184	261
	Rb	182	259
$M = \text{Ag}$	Li	(192)	(273)
	Na	205	295
	K	206	293
	Rb	202	293
	Cs	206	291

^a Cu_2O , 302; Ag_2O , 335; Cu , 256; Ag , 289.

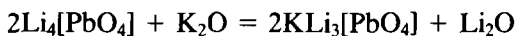
TABLE XX
OXOZINCATES

Ba[ZnO ₂]	1960 (44)
Sr[ZnO ₂]	1961 (45)
Na ₂ Zn ₂ O ₃	1965 (46)
"Li ₂ ZnO ₂ "	1971 (47)
Na ₄ [ZnO ₄]	1974 (48)
"Li ₄ ZnO ₃ "	1975 (49)
Rb ₈ [Zn ₄ O ₆], Cs ₈ [Zn ₄ O ₆]	1978 (50)
K ₂ [Zn ₆ O ₇]	1978 (51)
Na ₂ ZnO ₂	1979, 1985 (52), (unpubl.)
KNaZnO ₂	1984 (53)
NaLiZnO ₂	1984 (54)
KLiZnO ₂	1985 (55)
K ₄ [ZnO ₃]	1985 (56)
K ₂ Zn ₃ O ₄	1985 (57)
KLiZn ₃ O ₄	1985 (58)
RbLiZnO ₂	1985 (59)
RbLiZn ₂ O ₃	1985 (60)

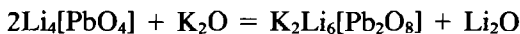
observed the reaction to the products to be incomplete. This *experimentum crucis* proves that ΔG is nearly zero.

X. How to Dimerize or Polymerize Small Entities

With the exception of Na₄[PbO₄] the whole series of oxoplumbates A₄[PbO₄] is known (39–41). In addition, Rb₃Na[PbO₄] (42) exists. All these compounds contain the tetrahedral group [PbO₄]. In attempts to determine whether with the reaction



one could synthesize a corresponding mixed plumbate such as RbLi₃[PbO₄] we encountered surprisingly a dimerization, due to the reaction

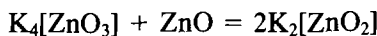
TABLE XXI
OXOCADMATES

Na ₂ CdO ₂ = "O ₃ Mn ₂ "	1969 (61)
K ₂ Cd ₂ O ₃ , Rb ₂ Cd ₂ O ₃	1971 (62), 1985 (unpubl.)
K ₂ CdO ₂ , Rb ₂ CdO ₂	1972 (63), 1985 (unpubl.)
K ₆ [CdO ₄], Rb ₆ [CdO ₄]	1985 (64)
Na ₁₄ O[CdO ₄] ₂	1978 (65)
Rb ₂ Li ₂ Cd ₃ O ₅	1985 (66)

TABLE XXII
OXOMANGANATES(II)

Na ₁₄ O[MnO ₄] ₂	1978 (68)
KLiMnO ₂ $\hat{=}$ KLiZnO ₂	1983 (69)
KNaMnO ₂ \neq KNaZnO ₂	1984 (70)
K ₂ Mn ₂ O ₃ $\hat{=}$ K ₂ Cd ₂ O ₃	1984 (71)
RbLiMn ₃ O ₄ $\hat{=}$ RbLiZn ₃ O ₄	1984 (72)
KLiMn ₃ O ₄ $\hat{=}$ KLiZn ₃ O ₄	1984 (72)
Na ₃ Li ₅ Mn ₃ O ₉ = Na ₃ (Li ₅ □)(Mn ₃ □)O ₉	1984 (73)
Li ₆ [MnO ₄] $\hat{=}$ Li ₆ [CoO ₄]	1984 (74, 75)

Two trigonal bipyramids of O²⁻ surrounding each Pb⁴⁺ share one of the edges (15). Sometimes one can combine such reactions to form a type of infinite chain. With the reaction



one polymerizes the CO₃²⁻-like planar groups [ZnO₃]⁴⁻ of K₄[ZnO₃] (43) to form the infinite chains of edge-connected (motif: SiS_{4/2}) tetrahedra in K₂[ZnO₂]; through the reaction



one desegregates the chain to form the [ZnO₃] entities.

XI. On Oxomanganates (II)

In some cases oxozincates [see Table XX and Refs. (44–60)], correspond structurally to oxocadmates (see Table XXI and Refs. (61–66)), but in other cases there are no similarities. Thus, for example, K₆[CdO₄]

TABLE XXIII
OXOFERRATES(III)

Three classes:

(A) LiFeO₂, NaFeO₂:

ordered variations of binary oxides (ZnO, MgO)

But: super-structures? No single crystals

(B) KFeO₂, RbFeO₂, CsFeO₂:

[FeO₂] = Tridymite-like?

But: no single crystals

(C) Silicate-like oxides:

(a) Na₁₄[Fe₆O₁₆] with double-chains (79)

(b) Na₈[Fe₄O₁₀] with single layers (80)

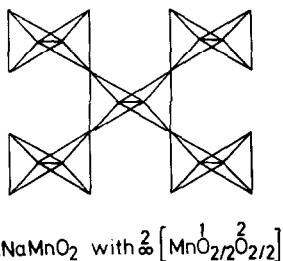
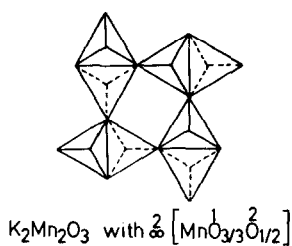


FIG. 8. Structural arrangements showing interconnection of CP about Mn^{2+} in $K_2Mn_2O_3$ and $KNaMnO_2$.

simulates $Na_6[ZnO_4]$, but no oxide A_4 (CdO_3) similar to $K_4[ZnO_3]$ is yet known.

In the synthesis of oxomanganates(III) such as $K_6[Mn_2O_6]$ (67) we found incidentally a structural correspondence between $Na_{14}[Mn^{II}O_4]_2O$ and $Na_{14}Cd_2O_9$.

Thus we started to study oxomanganates(II) more in detail. The results are summarized in Table XXII. Surprisingly, we always encounter the CN 4 with Mn^{2+} . The structural features of $K_2Mn_2O_3$ and $KNaMnO_2$ are shown on Fig. 8.

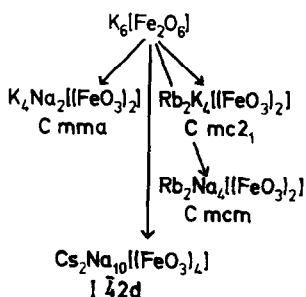


FIG. 9. Space group symmetries of some derivatives of $K_6[Fe_2O_6]$.

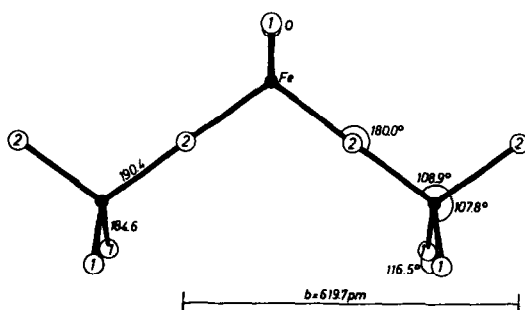


FIG. 10. Structure of a typical $\frac{1}{2}[(FeO_3)_2]$ chain in $K_4Na_2[Fe_2O_6]$.

XII. On New Silicate Analogs with the Oxoferrates(III)

So far $K_6[Fe_2O_6]$ (16) is the only known oxoferrate(III) of the alkali metals where a drastic difference exists relative to the corresponding silicates. Here we find for the first time a tetrahedra dimer with a common edge. $K_6[Ga_2O_6]$ (77) is isotypic, $K_6[Mn_2O_6]$ (67) and $Cs_6[Ga_2O_6]$ (77) are similar. We tried to correlate the existence of such a group with changes in the corresponding alkali metals. K^+ was replaced partially by smaller (Na^+), partially by larger (Rb^+) ions, or by both types (Na^+ , Cs^+) simultaneously.

Table XXIII summarizes earlier findings. Figure 9 provides crystallographic information, Figs. 10 and 11 show some typical results, Fig. 12 indicates relationships between the direction of chains with respect

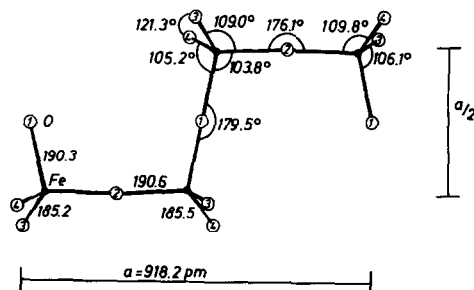


FIG. 11. Structure of a typical $\frac{1}{2}[Fe_4O_{12}]$ chain in $Cs_2Na_{10}[(FeO_3)_4]$.

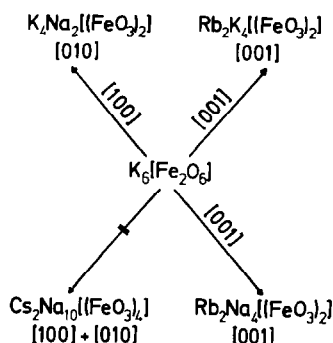


FIG. 12. Derivatives of $K_6[Fe_2O_6]$ showing directions of the chains with respect to the unit cell of $K_6[Fe_2O_6]$.

to the original unit cell of $K_6[Fe_2O_6]$. There are still more compounds in these systems.

An important question concerns the existence of corresponding oxomanganates(III) as well as oxogallates. We already have firm evidence through the coexistence of $Li_5[GaO_4]$ (80) with $Li_5[FeO_4]$ (81) and of $Na_8[Ga_2O_7]$ (82) with $Na_8[Fe_2O_7]$ (83). But it is typical for the present state of the art that nobody is presently able to predict the existence and structural properties of, e.g., $Cs_2K_4Ga_2O_6$. We are currently working on such syntheses.

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