

Bond Strength Considerations Applied to Cation Coordination in Normal and High-Pressure Oxides

R. D. SHANNON

Central Research Laboratory, E. I. duPont de Nemours, Wilmington, Delaware

J. CHENAVAS, AND J. C. JOUBERT

Laboratoire des Rayons X C.N.R.S., 38-Grenoble, France

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For cations with radius ratios close to the critical value of .414, 2 rules are developed to predict a preference for tetrahedral or octahedral coordination: (1) If for $M_aX_bO_c$ the ratio $\gamma = a/b$ is greater than a certain critical value (generally $\gamma_c \cong 1.0$), X prefers tetrahedral coordination; (2) the greater the M-O bond strength, the greater the tendency for octahedral coordination of X. These rules follow from a consideration of Pauling's electrostatic valence rule and reflect the probability of having strong M-O bonds to compete with X-O bonds. The coordination of Te^{6+} , V^{5+} , As^{5+} , Ge^{4+} , Ti^{4+} , Fe^{3+} , Ga^{3+} , Al^{3+} , B^{3+} , Be^{2+} , and Zn^{2+} in many oxides are consistent with these rules. Exceptions occur when the cations are found in highly stable structures such as perovskite, spinel, quartz, garnet, scheelite, and K_2SO_4 . When applied to high-pressure transitions these rules allow one to predict that small γ values and strong M-O bonds will lower the pressure at which an increase in the coordination of X should occur.

I. Introduction

Among the most important factors determining cation coordination is the radius ratio r^+/r^- (1).¹ Radius ratios using different sets of radii were discussed by Shannon and Prewitt (3) and Whittaker and Muntus (4). Regardless of the radii values used, the tetrahedral coordination of smaller cations, e.g., $IVCl^{7+}$, IVS^{6+} , $IVCr^{6+}$, IVP^{5+} , $IIIN^{5+}$, and $IIIC^{4+}$ is strongly correlated with the radius ratio. However, when this ratio approaches the critical value, 0.414, many cations freely accept either tetrahedral or octahedral coordination, e.g., Ge^{4+} (.39), V^{5+} (.39), As^{5+} (.36), Mo^{6+} (.43), and W^{6+} (.43). In these cases, there are many examples of compounds containing tetrahedrally coordinated cations,

¹ The coordination of Cu^+ , Hg^{2+} , Sb^{3+} , Pd^{2+} , Pt^{2+} , Au^{3+} , and Te^{4+} is strongly influenced by electronic configuration and polarizability (2); these considerations are not important for cations discussed in this paper.

and compounds containing octahedrally coordinated cations, and a few compounds which contain both. We will consider some of the variables which favor either 4- or 6-coordination. Understanding such behavior is valuable to the chemist in preparing new compounds, in predicting the feasibility of high-pressure phase transformations involving coordination changes, and in predicting the coordination number of cations in unknown structures.

Considerable structural data from $M_aX_bO_c$ ² systems at normal and high pressures shows that there are systematic compositional trends which characterize compounds containing 6-coordinated X ions and opposing trends which characterize compounds containing 4-coordinated X ions. From these trends and a

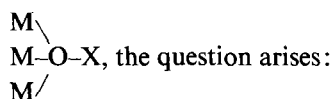
² Although we primarily discuss ternary oxides, many examples used are quaternary and higher oxides; for these, all cations other than X are referred to as M cations.

consideration of Pauling's electrostatic valence rule (5), we formulate some general rules which apparently govern the CN of X ions in oxides at normal pressure and then attempt to show how these rules govern the ease of high-pressure transformations. We first examine in detail the applicability of these rules to vanadates, arsenates, germanates, and silicates, and then briefly show how the coordination numbers of Te^{6+} , Ti^{4+} , Fe^{3+} , Ga^{3+} , Al^{3+} , B^{3+} , Be^{2+} , and Zn^{2+} are also consistent with these rules. We will then see how these coordination rules can help us better understand certain high-pressure transformations.

II. General Rules

The starting point for our discussion is Pauling's electrostatic valence rule (5) and its extension by Baur (6-8). Pauling's rule states that the sum, p_x , of the electrostatic bond strengths³ received by the anions is on the average equal to the valence of the anion. Baur's extension of this rule states that individual distances in a coordination polyhedron vary directly with the sum of the anion bond strengths⁴. Thus, an oxygen ion surrounded by 2 tetrahedrally coordinated P^{5+} ions has $p_x = 2.5$ and the 2 P-O distances would elongate accordingly. Applying these considerations to oxide systems with highly charged X ions, we can estimate the probable coordination of the X ion.

If we consider $\text{M}_a\text{X}_b\text{O}_c$ where X is tetrahedral V^{5+} , As^{5+} , Ge^{4+} , or Si^{4+} , and take a hypothetical group of atoms



Which factors make this tetrahedral coordination unstable? Clearly, the more M cations surrounding the O^{2-} ions and the higher their charge, the higher the value of p_x . According to Baur's rule, the distance $d(\text{X}-\text{O})$ thus increases. The situation becomes

³ ($p_x = \sum s_i = \sum Z_i / \text{CN}$ where s_i is the electrostatic bond strength, Z_i is the formal charge of the cation, and CN is its coordination number.)

⁴ $d(\text{X}-\text{O}) = a + bp_x$ where a and b are constants.

more and more unstable as p_x increases. If 1 or 2 oxygen ions in the tetrahedron receive a large p_x , the tetrahedron can distort locally, but if a certain critical value is reached, we expect a compensation to occur by a change of the X-coordination to V or VI.

Starting from the composition $\text{M}_a\text{X}_b\text{O}_c$ we have derived several empirical rules for predicting the coordination of X. These rules reflect the probability of having strong M-O bonds to compete with the X-O bond—the greater this probability, the greater the tendency for X to have a $\text{CN} > \text{IV}$.

Rule 1

When the ratio of M cations to X cations (γ) is greater than a certain critical value, γ_c ,⁵ the coordination of X is generally tetrahedral. When this ratio is less than ~ 1.0 , the tendency for X to have a CN of V or VI is greatly increased.⁶ This rule gives an approximate measure of the probability of finding 2 X cations bonded to the same O^{2-} ion. The lower the value of γ , the greater is this probability and the more unstable the tetrahedral coordination. Of course this is only important when the valence of X is greater than that of M, which is normally the case for $\text{X} = \text{Si}^{4+}$, Ge^{4+} , V^{5+} , and As^{5+} . This rule is less important for tri- and divalent X ions.

Rule 2

The greater the M-O bond strength, the greater the tendency for 6-coordination of X. High M-O bond strengths imply for M: (1) high formal charges, (2) small ionic radii and (3) high electronegativities (9).⁷ These parameters are intimately related. The electronegativity need be considered only when the size and charge of M ions are similar, e.g.,

⁵ For the cases in this paper $\gamma_c = .7-1.0$. However, γ_c will vary from one cation to another.

⁶ Since it is well known that many structures accept foreign cations from ppm to several percent, it is apparent that for very large values of γ , this rule breaks down. Extreme case of these exceptions occur in certain particularly stable structures such as rock salt, perovskite, and spinel where it is possible to have octahedral cations even though γ is in a range characteristic of tetrahedral coordination.

⁷ Electronegativity values used in this paper are from S. Batsonov, *Russ. Chem. Rev.* 37, 332 (1968).

for the pairs $\text{Mg}^{2+}\text{-Co}^{2+}$, $\text{Sc}^{3+}\text{-In}^{3+}$, or $\text{Ca}^{2+}\text{-Cd}^{2+}$. This rule is related to Pauling's ionic bond strength modified by the electronegativity factor.⁸

Rule 2 must be applied in conjunction with Rule 1. Thus, if $\gamma > 1.0$ where we expect 4-coordinated X ions, but M has a high bond strength, it is possible that the second factor is enough to increase the CN of X to 6, e.g., VPO_5 , GeP_2O_7 , SiP_2O_7 , MoP_2O_8 , or WP_2O_8 .⁹ The bond strength of M may be increased by (1) replacing M by a smaller cation or by a cation having a higher charge, or electronegativity or (2) lowering the coordination number of M.

Hydrogen-containing compounds present special problems. The H atoms in water molecules should not have much influence because the oxygen valence is already saturated and the oxygens cannot be strongly bonded to other ions.

In contrast, the H atoms in OH^- ions bonded to the X atom should strongly influence the preference for higher coordination. The ideal ionic bond strength of H^+ in an OH^- is 1.0, compared with the ideal bond strength 1.25 for 4-coordinated P^{5+} , V^{5+} , and As^{5+} . The influence of the OH^- ion on coordination is illustrated in the structures of GaOOH , $\text{Ga}(\text{OH})_3$, AlOOH , $\text{Al}(\text{OH})_3$, and $\text{FeGe}(\text{OH})_6$. Despite the stability of tetrahedral Ga^{3+} , both Ga hydroxides contain octahedral Ga^{3+} . Although both tetrahedral and octahedral Al^{3+} occur frequently, both Al hydroxides contain octahedral Al^{3+} . Finally, octahedral Ge^{4+} is rare and until recently was known only in the perovskites $\text{La}_2\text{MgGeO}_6$, and BaCaZrGeO_6 , the rutile form of GeO_2 , and several spinels. The existence of octahedral Ge^{4+} in the compound $\text{FeGe}(\text{OH})_6$ illustrates the effect of the hydroxyl ion.

⁸ For a predictive system to be of value, it must use only those variables evident from the composition, i.e., the relative number of M ions, their charge, size, and electronegativity. Because we don't know a priori the CN of M, we use bond strength and choose the most normal value, noting that a change from the normal CN of M can affect the CN of X.

⁹ The examples used throughout the text and in Tables I-IV were taken from Wyckoff (10) unless specific references are indicated.

III. Results

A. Vanadates

In ternary oxides $\text{M}_a\text{V}_b\text{O}_c$ V^{5+} is 4-, 5-, or 6-coordinated. Table I shows that when $\gamma > 1$, V^{5+} is tetrahedrally coordinated in all known vanadates, whereas when the ratio M:V decreases the coordination tends to increase.

When $\gamma = 1$, most compounds contain tetrahedral V^{5+} . However, $\text{Mg}_2\text{V}_2\text{O}_7$ (11) and $\text{Hg}_2\text{V}_2\text{O}_7$ (12) contain 5-coordinated V^{5+} and VPO_5 (13) contains octahedral V^{5+} .

The entire $\text{M}_2\text{V}_2\text{O}_7$ series from $\text{Sr}_2\text{V}_2\text{O}_7$ to $\text{Ni}_2\text{V}_2\text{O}_7$, comprising at least 5 different structure types, contain only tetrahedral V^{5+} except for $\text{Hg}_2\text{V}_2\text{O}_7$ and $\text{Mg}_2\text{V}_2\text{O}_7$. Hg^{2+} has a high electronegativity ($x = 2.0$) and in $\text{Hg}_2\text{V}_2\text{O}_7$ is characterized by relatively short bonds varying from 2.09–2.29 Å. Five coordinated V^{5+} in $\text{Mg}_2\text{V}_2\text{O}_7$ is not consistent with Rule 2.

When $\gamma < 1$, all compounds but one contain distorted octahedral V^{5+} , as shown by Evans and Block (14). The exception is ZrV_2O_7 (15), and the large number of compounds in this family (16) suggest that it falls in the category of exceptionally stable structures. In fact, the similarity to the NaCl structure was noted by Levi and Peyronel (17) and Tillmanns *et al.* (18).

There are apparently no known vanadates containing OH^- groups from which to draw conclusions. Vanadates containing H_2O groups are numerous; however, most of them have $\gamma < 1$, where V is 6-coordinated as expected. It is apparent from $\text{Ca}^{\text{V}}\text{V}_2\text{O}_6$ (19) $\text{Ca}^{\text{V}}\text{V}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ (20) and $\text{Na}_3^{\text{IV}}\text{VO}_4 \cdot 12\text{H}_2\text{O}$ (21) that the presence of water molecules does not have a strong effect on the coordination of V^{5+} . However, in KVO_3 (22) V^{5+} is tetrahedral, whereas in $\text{KVO}_3 \cdot \text{H}_2\text{O}$ (23) V^{5+} is 5-coordinated. Evans has suggested that in $\text{KVO}_3 \cdot \text{H}_2\text{O}$ one of the oxygens in the VO_5 group forms a hydrogen bond with the water molecule. It is possible that this hydrogen bond provides the extra strength necessary to increase the coordination of V in $\text{KVO}_3 \cdot \text{H}_2\text{O}$.

We have tried to quantify the tendency for 6-coordination in vanadates. Using the concept

TABLE I

VANADATES CONTAINING TETRAHEDRAL V^{5+}									
Compound	Structure Type	\bar{Y}	$\langle \delta \rangle$	Ref.	Compound	Structure Type	\bar{Y}	$\langle \delta \rangle$	Ref.
Li_3VO_4	wurtzite	3.0	3.51	1	$FeVO_4$		1.0	7.32	11
$Na_3VO_4 \cdot 12H_2O$		3.0		2	$CrVO_4$		1.0	7.44	
$Cu_5V_2O_{10}$		2.5	4.61	3	$Sr_2V_2O_7$		1.0	5.84	12
Ca_2VO_4Cl	spodiosite	2.0	4.66	4	$Pb_2V_2O_7$	chervertite	1.0	5.84	13
$Ba_3V_2O_8$	$Ba_3P_2O_8$	1.5	4.88	5	$M_2V_2O_7$	thortveitite	1.0	6.05	14
					M = Cd, Mn				
$Sr_3V_2O_8$			5.01		$Zn_2V_2O_7$		1.0	6.33	8
$Ca_3V_2O_8$		1.5		6	$Co_2V_2O_7$		1.0	6.34	8
$M_3V_2O_8$	$Mg_3V_2O_8$	1.5	5.7	7,8,9	MVO_3		1.0	5.3	
M = Zn, Co, Mg, Ni					M = NH ₄ , Rb, K				
$Cu_3V_2O_8$		1.5	5.64	10	MVO_3	pyroxene	1.0	5.6	15
MVO_4	zircon	1.0	6.5		M = Li, Na				
M = Sc, Lu, Yb, Tm, Er, Ho, Y, Dy, Tb, Gd, Eu, Sm, Nd, Pr, Ce					ZrV_2O_7	ZrP_2O_7	0.33		16
VANADATES CONTAINING 5-COORDINATED V^{5+}									
$Hg_2V_2O_7$		1.0		17	CaV_2O_6		0.5	7.33	18
$Mg_2V_2O_7$		1.0	6.39	8	$K_3V_5O_{14}$		0.6	6.52	
$KVO_3 \cdot H_2O$		1.0	7.79		$CaV_2O_6 \cdot 2H_2O$	metarossite	0.5	8.29	
VANADATES CONTAINING OCTAHEDRAL V^{5+}									
VPO_5		1.0	11.58	19	$K_2Zn_2V_{10}O_{28} \cdot 16H_2O$		0.40	8.58	23
MV_2O_6	brannerite	0.5	7.02	20	CsV_3O_8		0.33	7.65	24
M = Cd, Co, Mg, Zn, Cu									
$VO(OCH_3)_3$			12.77	21	V_2O_5		0.0	10.0	
$Ca_3V_{10}O_{28} \cdot 17H_2O$	pascoite	0.30	8.77	22					

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TABLE I—*contd.*

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that the strength of the M–O vs the X–O bond is the determining factor, we have computed a quantity $\langle\phi\rangle$, the mean ionic potential (24)

$$\langle\phi\rangle = \frac{a}{a+b} \frac{Z_M}{r_M} + \frac{b}{a+b} \frac{Z_X}{r_X}$$

where Z_M = formal charge on M

r_M = effective ionic radius of M.

for $M_aX_bO_c$.¹⁰ Table I shows that for the tetrahedral vanadates $\langle\phi\rangle = 12$ –28, for 5-coordinated vanadates $\langle\phi\rangle = 23$ –27, and for 6-coordinated vanadates $\langle\phi\rangle = 25$ –55. Although there is no sharp dividing line between coordinations, the groupings give an indication of the expected coordination of V^{5+} .

¹⁰ Although it is not possible to use the conventional Z/r for H^+ because the apparent radius of H^+ is negative, the ionic potential of H^+ was estimated by Cartledge (24) to be 9 compared with Li, Na, and K, whose ionic potentials are 1.7, 1.1, and 0.8, respectively.

B. Arsenates

In good agreement with the radius ratio of 0.36 most arsenates contain tetrahedral As^{5+} (Table II). In addition, the tetrahedral arsenates all have $\gamma > 0.5$. The arsenates with the $PbSb_2O_6$ type structure (10) and $As_2O_5 \cdot 5/3H_2O$ (25) contain octahedral As^{5+} and follow Rule 1. $HAsP_2O_8$ and $NaAsP_2O_8$ (26) contain octahedral As^{5+} , in accordance with Rule 2. Like ZrV_2O_7 , $ZrAs_2O_7$ (27) contains tetrahedral As^{5+} in contradiction to Rule 1, but is presumably stabilized by the ZrP_2O_7 structure. There are two compounds having mixed coordination, $Co_8As_3O_{16}$ (28) and $Mg_{8.5}As_3O_{16}$ (29), which should contain only tetrahedral arsenic but unexpectedly also contain octahedral As^{5+} .

C. Germanates

Table III shows that most germanates with $\gamma > 0.67$ have tetrahedral germanium. The

TABLE II

ARSENATES CONTAINING TETRAHEDRAL As⁵⁺

Compound	Structure Type	γ	Ref.	Compound	Structure Type	γ	Ref.
Mn ₇ SbAsO ₁₂		8.0	25	NaMASO ₄		2.0	
				M = Ba, Sr, Ca			
Mn ₉ (OH) ₉ (H ₂ O) ₂ AsO ₃ (AsO ₄) ₂		5.0	26	Pb ₄ KAs ₃ O ₁₂		1.67	
Fe ₃ AsO ₄ ·8H ₂ O		3.0	27	Pb ₅ As ₃ O ₁₂ Br		1.67	
Na ₃ AsO ₄ ·12H ₂ O		3.0		Ca ₅ As ₃ O ₁₂ F		1.67	
Na ₂ HAsO ₄ ·7H ₂ O		3.0	28	M ₃ As ₂ O ₈		1.5	39,40
				M = Pb, Ba, Sr, Ca, Cd, Cu, Co			
Cu ₃ AsO ₄ (OH) ₃		3.0	29	BaNi ₂ As ₂ O ₈		1.5	41
Ca ₂ BAsO ₄ (OH) ₄		3.0	30	CuZn ₂ As ₂ O ₈		1.5	42
(NH ₄) ₂ HAsO ₄		3.0	31	Ca ₂ MnAs ₂ O ₈ ·2H ₂ O		1.5	
MH ₂ AsO ₄		3.0		ZrH ₂ As ₂ O ₈ ·H ₂ O		1.5	43
M = NH ₄ , Ca, K							
KCaAsO ₄ ·8H ₂ O		2.0		PbFe ₂ As ₂ O ₈ (OH) ₂		1.5	
CsMASO ₄ ·6H ₂ O		2.0		MAsO ₄	Zircon	1.0	
M = Mn, Fe, Co, Ni				M = Lu, Ho, Od, Eu, Er, Dy, Sm, Tb, Tm, Yb, Sc, Tl			
Cu ₂ AsO ₄ (OH)·3H ₂ O		2.0		MAsO ₄	Monazite	1.0	
				M = La, Nd, Ce, Pr			
Zn ₄ As ₂ O ₈ (OH) ₂ ·2H ₂ O		2.0	32	MAsO ₄		1.0	
				M = B, Al			
CaHAsO ₄ ·2H ₂ O		2.0	33	Mg ₂ As ₂ O ₇	Thortveitite	1.0	44
MHAsO ₄ ·H ₂ O		2.0	34	MAsO ₃		1.0	
M = Sr, Ca				M = Li, Na			
CaHAsO ₄			35	MAsO ₄ ·2H ₂ O		1.0	
				M = Tl, Fe, Al			
CaCuAsO ₄ OH		2.0		ZrAs ₂ O ₇	ZrP ₂ O ₇	0.5	
M ₂ AsO ₄ OH		2.0	36				
M = Mn, Cu, Zn							
LiMoO ₂ AsO ₄		2.0	37				
Ca ₂ AsO ₄ Cl	Spodiosite	2.0	4				
Na ₄ As ₂ O ₇		2.0	38				
KMASO ₄		2.0					
M = Ba, Sr, Ca							

ARSENATES CONTAINING VI As⁵⁺

HAsF ₂ O ₆	3.0	45	MAs ₂ O ₆	PbSb ₂ O ₆	0.5
			M = Sr, Hg, Cd, Co		
NbAsF ₂ O ₆	3.0	45	As ₂ O ₅ · $\frac{5}{3}$ H ₂ O		0.0

ARSENATES WITH MIXED COORDINATION

Mg _{8.5} As ₃ O ₁₆	2.83	46	Co ₈ As ₃ O ₁₆	2.66	47
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TABLE III

GERMANATES CONTAINING TETRAHEDRAL Ge⁴⁺ (44)

Compound	Structure Type	γ	Compound	Structure Type	γ
Li ₄ GeO ₄		4.0	Ba ₂ MgGe ₂ O ₇		1.50
Mg ₃ GeO ₄ F ₂	norbergite	3.0	M = Mg, Zn, Mn, Fe, Co		
Na ₂ ZnGeO ₄		3.0	Sr ₂ MgGe ₂ O ₇		
Ca ₃ GeO ₅	alite	3.0	M = Mg, Zn, Mn, Fe, Co		
SrH ₂ GeO ₄		3.0	(M ₂ MgGe ₂ O ₇) ₂	akermanite	1.50
Na ₂ GeO ₃ ·6H ₂ O		2.0	(M ₂ ZnGe ₂ O ₇) ₂	nardystonite	
KNa ₃ (AlGeO ₄) ₄	nepheline	2.0	M = Ca, Sr, Ba		
M ₂ GeO ₄	phenakite	2.0	Mg ₆ (OH) ₈ Ge ₄ O ₁₀	serpentine	1.5
M = Be, Zn, (Li+Al), (Li-Cs)			Bi ₄ Ge ₃ O ₁₂	elytine	1.33
M ₂ GeO ₄	olivine	2.0	Na ₈ Gd ₄ Ge ₁₀ O ₃₀ (OH) ₄		1.2
M = Mg, Ca, Sr, Ba, Cd, Mn			MGeO ₄	scheelite	1.0
M ₂ GeO ₄	spinel	2.0	M = U, Ce, Th, Hf, Zr		
M = Ni, Co, Mg, Fe			ThGeO ₄	zircon	1.0
CaMgGeO ₄	monticellite	2.0	M ₂ Ge ₂ O ₇	thortveitite	1.0
Ca ₂ GeO ₅	andalusite	2.0	M = Sr, In		
Al ₂ GeO ₅	kyanite	2.0	Er ₂ Ge ₂ O ₇		1.0
M ₂ GeO ₅		2.0	BeGeO ₃	pseudowollastonite	1.0
M = Lu, Yb, Er, Ho, Dy, Tb, Y			SrGeO ₃		
Na ₂ GeO ₃		2.0	Li ₂ Ge ₂ O ₅		1.0
Li ₂ GeO ₃		2.0	MGeO ₃	pyroxene	1.0
M ₂ Pb ₂ Ge ₂ O ₇	barysilitelike	2.0	M = Mg, Fe, Co, Mn, Cu		
M = K, Rb, Cs			MAlO ₂ O ₆	feldspar	1.0
Ca ₃ M ₂ Ge ₃ O ₁₂	garnet	1.67	M = K, Na		
M = Al, Ga, In, Sc, V, Cr, Fe			Mg ₃ (OH) ₂ Ge ₄ O ₁₀	talc	0.75
Cd ₃ M ₂ Ge ₃ O ₁₂	garnet	1.67	Ni ₃ (OH) ₂ Ge ₄ O ₁₀	talc	0.75
M = Al, Ga, In, Sc, V, Cr, Fe			NaAlGe ₃ O ₈	albite	0.67
Mn ₃ M ₂ Ge ₃ O ₁₂	garnet	1.67	BaTiGe ₃ O ₉	benitoite	0.67
M = Al, Ga, V, Cr, Fe			GeO ₂	quartz	0.0
Ca ₂ Ce ₃ Ge ₃ O ₁₂ Cl	apatite	1.67			

GERMANATES WITH VI_{Ge} 4 (43)

BaCaZrGeO ₆	perovskite	3.0	FeGe(OH) ₆	stottite	1.0
La ₂ MgGeO ₆	perovskite	3.0	Li ₂ ZnO ₃ O ₈	spinel	1.0
GeP ₂ O ₇		2.0	Li ₂ CoGe ₃ O ₈	spinel	1.0
LiRhGeO ₄	spinel	2.0	Zn ₂ Ge ₃ O ₈	spinel	0.67
LiCrGeO ₄	spinel	2.0	GeO ₂	rutile	0.0
GeOHPO ₄		1.0			

GERMANATES WITH MIXED COORDINATION (43)

Mg ₂₈ Ge ₁₀ O ₄₈		2.80	M ₄ ^{VI} Ge ₂ ^{IV} Ge ₇ O ₂₀		0.44
V ₁ Ge ₃ ^{IV} Ge ₂ O(PO ₄) ₆		1.20	M = Li, Na, K, Ag		
M ₃ HGe ₇ O ₁₆ ·4H ₂ O	pharmacosiderite	0.57	CaGe ₂ O ₅	titanite	0.33
M = Li, Na, K, Rb, Cs, Ag, Tl			MGe ₄ O ₉	benitoite	0.25
M ₂ ^{VI} Ge ₃ ^{IV} Ge ₃ O ₉	wadeite	0.50	M = Ca, Sr, Ba, Pb		
M = Na, K, Rb, Ag, Tl					

exceptions, $\text{FeGe}(\text{OH})_6$ (30), $\text{Ge}(\text{OH})\text{PO}_4$ (31), GeP_2O_7 (16), and $\text{Ge}_5\text{O}(\text{PO}_4)_6$ (32), illustrate the importance of the bond strengths of H^+ and P^{5+} (Rule 2). The remaining exceptions with $\gamma > 1$ have either the very stable spinel or perovskite structures.

There are numerous examples of germanates with mixed tetrahedral and octahedral Ge^{4+} . All of these compounds but one can perhaps be considered transitional with γ between 0.67 and 0.25. $\text{Mg}_{28}\text{Ge}_{10}\text{O}_{48}$ (33) is anomalous unless one accepts the rationalization that it is made up of Mg_6GeO_8 rock-salt layers and Mg_2GeO_4 olivine layers. One final exception is the case of GeO_2 in the high-temperature quartz form. It is well known that high temperatures frequently favor a decrease in coordination, e.g., Ga_2O_3 , LiAlO_2 (34), NaFeO_2 (34), and Bi_2MoO_6 (35).

D. Silicates

Almost all silicates contain tetrahedral Si. At elevated pressures, some silicates can be prepared having octahedral Si, i.e., SiO_2 with the rutile structure (36), KAlSi_3O_8 , $\text{Sr}_x\text{Al}_{2x}\text{Si}_{4-2x}\text{O}_8$, and $\text{Ba}_x\text{Al}_{2x}\text{Si}_{4-2x}\text{O}_8$ with the hollandite structure (37) and $\text{Sc}_2\text{Si}_2\text{O}_7$ and $\text{In}_2\text{Si}_2\text{O}_7$ with the pyrochlore structure (38). However, high pressure is not always necessary to produce 6-coordinated Si^{4+} . Several modifications of SiP_2O_7 (39), the mineral thaumasite $\text{Ca}_3\text{Si}(\text{OH})_6\text{SO}_4\text{CO}_3 \cdot 12\text{H}_2\text{O}$ (40) and $\text{C}_5\text{H}_5\text{NH}_2(\text{C}_6\text{H}_4\text{O}_2)_3\text{Si}$ (41) all contain 6-coordinated Si. Liebau (42) has related 6-coordinated Si^{4+} to the high electronegativity of X and A in the compositions $m\text{SiX}_p \cdot n\text{AR}_q$. However, the concept of bond strength discussed in this paper can equally well account for 6-coordinated Si^{4+} . Thus, thaumasite has OH^- groups surrounding Si and SiP_2O_7 has P^{5+} ions bonded to the O ions adjacent to Si.

E. Other XO_n Groups

A number of other cations exhibit variable coordination, e.g., W^{6+} , Mo^{6+} , Te^{6+} , Ti^{4+} , Fe^{3+} , Ga^{3+} , Al^{3+} , B^{3+} , Be^{2+} , and Zn^{2+} . Bond strength considerations help in understanding the variations of CN of these cations, much as in the tetravalent and pentavalent examples

already discussed. However, as the valence of X decreases, the relative importance of the nature of the M–O bonds should diminish. Thus, we expect to find less accord with the rules when looking at the structures of compounds with tri- and divalent cations such as Al^{3+} and Zn^{2+} . Nevertheless, Rules 1 and 2 seem to provide a good indication of the expected coordination of these tri- and divalent ions.

For the remaining cations, it is convenient to note that, according to Rules 1 and 2, (1) large amounts of alkali or alkaline-earth atoms relative to the number of X atoms should lead to lower X coordination and (2) large numbers of OH^- ions or highly charged ions like P^{5+} or As^{5+} should lead to higher CN .

Although we do not provide a detailed discussion of the coordination of Mo^{6+} and W^{6+} , it will be noted here that all combinations of Mo^{6+} or W^{6+} with P^{5+} or OH^- result in octahedral coordination, i.e., NaMoPO_6 , AgMoPO_6 (43), LiMoAsO_6 (44), MoP_2O_8 (45), $\text{Mo}(\text{OH})_3\text{PO}_4$, $(\text{MoO}_2)_2\text{P}_2\text{O}_7$, $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$, WOP_2O_7 , and $\text{W}_2\text{O}_3(\text{PO}_4)_2$. Furthermore, the heteropolymolybdates and heteropolytungstates, $(\text{M}, \text{M}')_8\text{W}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ (10) with low γ values, also have octahedral Mo^{6+} and W^{6+} .

Te^{6+} and Ti^{4+} are rarely tetrahedral. It is significant that the only reported cases of tetrahedral Te^{6+} — K_2TeO_4 , Rb_2TeO_4 , Cs_2TeO_4 (46), $\text{Li}_{.5}\text{Dy}_{.5}\text{TeO}_4$ ¹¹ and $\text{Na}_{.5}\text{Dy}_{.5}\text{TeO}_4$ ¹¹ (47)—contain large cations which do not form strong bonds. The tellurates with smaller cations, Li_2TeO_4 (48) and Na_2TeO_4 (46) contain octahedral Te^{6+} .

Structures reported to contain tetrahedral Ti^{4+} are Ba_2TiO_4 (49, 50), Ba_3TiO_5 (51), Li_4TiO_4 (52), $\text{LnTi}_{.5}\text{Mo}_{.5}\text{O}_4$ and $\text{LnTi}_{.5}\text{W}_{.5}\text{O}_4$ (53). As with Te^{6+} , these compounds contain a large proportion of cations which have weak bonds. The presence of both tetrahedral Te^{6+} and Ti^{4+} in the K_2SO_4 and scheelite structures could perhaps be ascribed to the stability of these structures.

¹¹ These scheelite phases were originally reported by Schieber (47). However, attempts to repeat the syntheses by Sleight (personal communication) have not succeeded, and there is some doubt about their existence.

TABLE IV
EFFECT OF M-O BOND STRENGTHS ON THE CO-
ORDINATION OF X IONS IN MXO₂ COMPOSITIONS

Compound X = Fe ³⁺	CN of X	Compound X = Ga ³⁺	CN of X
HFeO ₂	VI	HGaO ₂	VI
LiFeO ₂	VI	LiGaO ₂	IV
NaFeO ₂	IV, VI	NaGaO ₂	IV
KFeO ₂	IV	KGaO ₂	IV
X = Al ³⁺		X = B ³⁺	
HAIO ₂	VI	HBO ₂	III, III + IV, IV
LiAlO ₂	IV, VI	LiBO ₂	III
NaAlO ₂	IV	NaBO ₂	III
KAlO ₂	IV	KBO ₂	III

Similarly, 5-coordinated Ti⁴⁺ in La₂TiO₅ (54), Y₂TiO₅ (55), and K₂Ti₂O₅ (56) is consistent with Rules 1 and 2. Five-coordinated Ti⁴⁺ in Ba₂(TiO)Si₂O₇ (57) would not have been easy to divine from the coordination rules.

The effect of the M-O bond strength on the coordination of Fe³⁺, Ga³⁺, Al³⁺, and B³⁺ is illustrated by the ABO₂ structures in Table IV. In these phases, it is clear that as M gets smaller and its electronegativity increases, the coordination of X tends to increase. This is particularly noticeable for FeOOH, GaOOH, AlOOH, and γ HBO₂.

Compounds containing tetrahedral Fe³⁺ generally contain alkali or alkaline earth ions, e.g., Li₃FeO₄ (58), β -NaFeO₂ (59), BaFe₂O₄ (60), and BaCaFe₄O₈ (61). Ca₂Fe₂O₅ and Na₃Fe₅O₉ (62) contain both tetrahedral and octahedral Fe³⁺. The one exception is FePO₄, which has the relatively stable quartz structure. The rare earth iron garnets with mixed tetrahedral and octahedral Fe³⁺ do not seem to follow the rules well but tetrahedral Fe³⁺ could be stabilized by the garnet structure.

There are only a few gallates available for analysis. GaNbO₄ (63), GaSbO₄, GaPO₄·2H₂O (64), H₃OGa₃(OH)₆(SO₄)₂, Ga(OH)₃, and GaOOH (65) have octahedral Ga³⁺ as might be anticipated from Rule 2. Li₅GaO₄

(65), LiGaO₂, NaGaO₂ (63), KGaO₂, RbGaO₂, and CsGaO₂ (67) have tetrahedral Ga³⁺ as anticipated. GaPO₄ contradicts Rule 2 but belongs to the quartz family like FePO₄.

Compounds containing Al³⁺ which illustrate the effectiveness of Rule 2 in predicting octahedral coordination are Ca₃Al₂(OH)₁₂, Sr₃Al₂(OH)₁₂, Al(PO₃)₃, AlPO₄·2H₂O, AlPO₄(Mn, Fe)(OH)₂·H₂O, MgAl₂(OH)₂(PO₄)₂, AlSbO₄, AlAsO₄·2H₂O, Al(OH)SO₄·5H₂O, KAl₃(OH)₆(SO₄)₃, Al₄Ta₃O₁₃(F, OH), and BeAl₂O₄. Two exceptions as for Ga³⁺ and Fe³⁺, are AlPO₄ and AlAsO₄. Another exception is K₂Al₂O(OH)₆, which contains Al₂O₇ groups of Al-O tetrahedra.

The application of the rules to borates is more difficult because of the formation of complex borate polyanions (68) which contain both trigonal and tetrahedral B³⁺. As in the cases of the arsenates and germanates with mixed coordination, the coordination rules do not appear to be valid for polyanion borates. Nevertheless, for borates containing only trigonal or only tetrahedral B, the B coordination can be correlated with bond strength considerations. Most borates contain either trigonal B³⁺ or a mixture of trigonal and tetrahedral B³⁺. High pressure has frequently been used to prepare compounds containing only tetrahedral B. However, compounds containing only 4-coordinated B³⁺ can be prepared without pressure. Thus, the compounds BPO₄, BaSO₄, γ -HBO₂, Na₂B(OH)₄Cl, CuB(OH)₄Cl, NaB(OH)₄·2H₂O, CaBSO₄·OH, Al₆B₅(OH)₃O₁₅, MgB₂O(OH)₆, and Ca₂B(OH)₄AsO₄, which contain only tetrahedral B, are consistent with Rule 2.

The effect of hydroxyl ions can be seen in the following examples. Co₂B₂O₅, Mg₂B₂O₅, and Mg₂[B₂O₄(OH)](OH) (69) contain only trigonal B³⁺; MgB₄O₇ contains mixed trigonal and tetrahedral B, and MgB₂O(OH)₆ only tetrahedra. Tetrahedral B³⁺ in CuB₂O₄ (70) is explained by the value of $\gamma = 0.50$, the high electronegativity of Cu²⁺ ($x = 2.0$), and the square planar coordination of Cu²⁺ which results in short bonds of 1.98 Å.

This can be contrasted with the existence of trigonal B³⁺ in CaB₂O₄ (71), SrB₂O₄ (72), and BaB₂O₄ (73). Tetrahedral B³⁺ in SrB₄O₇ is evidently a result of the γ value of 0.25, but only

tetrahedral coordination in SrB_4O_7 is not consistent with mixed coordinations in BaB_4O_7 , CdB_4O_7 , ZnB_4O_7 (74), MgB_4O_7 (75), KB_5O_8 (75), and RbB_5O_8 (76).

Thus, Rule 2 appears to be effective in predicting tetrahedral B^{3+} coordination, whereas Rule 1 is not applicable as anticipated. However, even Rule 2 does not explain the curious behavior of the borates MBO_3 . Compounds with small ($r_M = .53-.87 \text{ \AA}$) and large ($r_M = .95-1.05 \text{ \AA}$) M^{3+} cations have trigonal B with the calcite and aragonite structures, respectively (77, 78) whereas those with intermediate size M cations ($r_M = .87-.95 \text{ \AA}$) have tetrahedral B with a vaterite or pseudovaterite structure (79-81).

We next consider the divalent ions Be^{2+} and Zn^{2+} . The only case of three coordinated Be^{2+} is Y_2BeO_4 (82) in accordance with Rules 1 and 2. SrBe_3O_4 (83) and $\text{Ca}_{12}\text{Be}_{17}\text{O}_{29}$ (84) have mixed 3- and 4-coordination. All other known Be oxides are believed to contain tetrahedral Be^{2+} .

The large number of Zn-containing oxides makes it impossible to include a complete list. To simplify analysis we assume that Zn^{2+} has a strong tendency for tetrahedral coordination and then look for compounds which, according to Rules 1 and 2, should have octahedral coordination. These include ZnSO_4 , ZnWO_4 , ZnMoO_4 (85), $\text{Na}_2\text{Zn}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{K}_2\text{Zn}_2(\text{SO}_4)_3$, $\text{Zn}_2(\text{OH})_2\text{SO}_4$, $\text{Zn}_2\text{Te}_3\text{O}_8$, ZnP_2O_6 (86), $\text{Zn}_2\text{P}_2\text{O}_7$ (87), $\gamma\text{Zn}_3\text{P}_2\text{O}_8$ (88), ZnSb_2O_6 , $\text{Zn}_3\text{V}_2\text{O}_8$ (89), $\text{Zn}_4\text{As}_2\text{O}_8 \cdot (\text{OH})_2 \cdot 2\text{H}_2\text{O}$ (90), and $\text{ZnOH} \cdot \text{Cl}$. In contradiction $\text{Zn}(\text{OH})_2$, contains all tetrahedral Zn, while $\text{CdZn}_2\text{P}_2\text{O}_8$ and $\text{Zn}_3\text{P}_2\text{O}_8$ (91), contain both tetrahedral and octahedral Zn.

Finally, we include several miscellaneous examples of unusual coordination which can be correlated with Rules 1 and 2. Five-coordinated Sn^{4+} and Zr^{4+} in K_2SnO_3 and K_2ZrO_3 (92) are consistent with $\gamma = 2.0$ and weak K-O bonds. Similarly, tetrahedral Tl^{3+} in Li_5TlO_4 (93) and $\text{Sr}_4\text{Tl}_2\text{O}_7$ (94), and tetrahedral In^{3+} in $\text{Sr}_7\text{In}_2\text{O}_5$ (95) are consistent with $\gamma \geq 1$ and weak M-O bonds.

Tetrahedral Cr^{4+} in Ba_2CrO_4 , Sr_2CrO_4 , Ba_3CrO_5 , and Na_4CrO_4 (96, 97) and tetrahedral V^{4+} , Co^{4+} , Fe^{4+} , and Mn^{4+} in the

$\text{Ba}_3\text{M}^{4+}\text{O}_5$ phases (51) are consistent with $\gamma \geq 2.0$.

IV. Application of Coordination Rules to High-Pressure Transformations

Since the coordination rules are apparently successful in rationalizing the coordination of many cations in a large variety of structures at normal pressures, they should also be useful in predicting how easily a particular coordination change proceeds with the application of high pressures. Thus, the lower the ratio γ and the stronger the M-O bonds, the lower should be the pressure required to obtain an increase of the coordination of X from 4 to 6. In this section we attempt to show that Rules 1 and 2 do indeed appear to govern the pressure at which certain transitions occur. Unfortunately, very few systems are known in sufficient detail and many transition pressures give in the literature are not equilibrium values. Therefore, more data will be required to make satisfactory conclusions. Nevertheless, we have collected as many pertinent results as possible to qualitatively evaluate the validity of our hypotheses.

Before predicting relative pressures necessary for a particular phase transformation in two compounds containing the same X cation, we must make certain restrictions. We will describe 2 kinds of transitions: one involving 2 compounds with the same stoichiometry, e.g., MXO_3 and $\text{M}'\text{XO}_3$, and the other with different stoichiometries, e.g., M_2XO_4 and MXO_3 . The restrictions are: (1) there must be an available structure for the high-pressure phase for both compounds; (2) the size of M and X must allow the existence of a high-pressure structure in both compositions M_2XO_4 and MXO_3 ; and (3) there must not be intermediate phases to complicate the transition. In the following discussion, these restrictions are illustrated.

Consider transforming the 2 olivines Ca_2GeO_4 and Mn_2GeO_4 into dense phases with octahedral Ge^{4+} . According to Rule 2, the critical pressure should be lower for Mn_2GeO_4 than for Ca_2GeO_4 . The olivine Ca_2GeO_4 transforms to the K_2NiF_4 structure at 110 kbar (900°C) (98), whereas Mn_2GeO_4

TABLE V
 APPLICABILITY OF COORDINATION RULES TO HIGH-PRESSURE TRANSITIONS

Compound	Transitions in Agreement with Rule 1		Transitions in Agreement with Rule 2	
	Y	Transition Pressure	Compound	Transition Pressure
$VI_{Mn}^{IV} GeO_3$ (pyroxene)	1.0	25 Kbar, 700°C (a)	$IV_{Li}^{IV} AlO_2$ (tetr. wurtzite)	25 Kbar, 530°C (e) 35 Kbar, 850°C (f)
$VI_{Mn}^{IV} GeO_4$	2.0	60 Kbar, (b) 700°C	$IV_{Na}^{IV} AlO_2$ (wurtzite)	110 Kbar (g) 40 Kbar, 400°C (h)
$NaAl^{IV} Ge_3O_8$ (feldspar)	0.4	25 Kbar, 1000°C (c)	$SrCeO_3$ (pseudowollastonite)	50 Kbar, 950°C (i)
$NaAl^{IV} GeO_4$ (nepheline)	2.0	120 Kbar, 1000°C (d)	$BaCeO_3$ (pseudowollastonite)	95 Kbar, 950°C (j)
(a) A. E. Ringwood, M. Seabrook, J. Geophys. Res. 68 , 4601 (1963)			$Na^{IV} Al^{IV} Ge_3O_8$ (feldspar)	25 Kbar, 1000°C (c)
(b) N. Morimoto, S. Akimoto, K. Koto, and M. Tokonami, Science 165 , 586 (1969)			$K^{IV} Al^{IV} Ge_3O_8$ (feldspar)	35 Kbar, 1000°C (c)
(c) A. E. Ringwood, A. F. Reid, A. D. Wadsley, Earth Planet. Sci. Letters 2 , 38 (1967)			$CaGeO_3$ (wollastonite)	40 Kbar, 700°C (a)
(d) A. F. Reid, A. D. Wadsley, A. E. Ringwood, Acta Cryst. 22 , 736 (1967)			$CdGeO_3$ (pyroxene)	10 Kbar, 700°C (a)
(e) C. H. Chang, J. L. Margrave, J. Amer. Chem. Soc. 90 , 2020 (1968)				
(f) M. Marezio, J. P. Remeika, J. Chem. Phys. 44 , 3143 (1966)				
(g) A. F. Reid, A. E. Ringwood, Inorg. Chem. 1 , 443 (1968)				
(h) C. J. M. Rooymans, Ph.D. Thesis, Univ. of Amsterdam (1967)				
(i) Y. Shimizu, Y. Syono, S. Akimoto, High Temp.-High Press. 2 , 113 (1970)				

assumes the Sr_2PbO_4 structure at 60 kbar (700°C) (see Table V) with both Ge^{4+} and Mn^{2+} 6-coordinated (99).

The existence of a stable intermediate phase can strongly increase the critical pressure necessary to induce the small size cation into an octahedral site; for instance, for CaGeO_3 and SrGeO_3 with the pseudowollastonite structure, CaGeO_3 should undergo a phase transition to the perovskite structure at a lower pressure than SrGeO_3 . Actually, at 50 kbar (900°C) SrGeO_3 goes to a cubic perovskite (100), whereas at 40 kbar CaGeO_3 transforms to an unexpected garnet phase $\text{Ca}_3(\text{CaGe})\text{Ge}_3\text{O}_{12}$ (101) in which only $\frac{1}{4}$ of the Ge^{4+} ions are octahedral (see Table V). Therefore although the pressure required to produce octahedral Ge^{4+} in CaGeO_3 is indeed lower than in SrGeO_3 , the pressure required to produce the CaGeO_3 perovskite phase is about 120 kbar (900°C) (102); we attribute this increase to the stability of the intermediate garnet phase.

If 2 compounds with similar structures undergo transitions to similar structure types, and crystal chemical considerations suggest no intermediate phases, we can predict with some confidence which one will have the lowest critical pressure. For example, SrGeO_3 goes to a cubic perovskite at 50 kbar compared to 95 kbar for BaGeO_3 in accordance with Rule 2 (Table V). Similarly CdGeO_3 with pyroxene structure (103) transforms at 10 kbar to a garnet $\text{Cd}_3(\text{CdGe})\text{Ge}_3\text{O}_{12}$, whereas CaGeO_3 having a pseudowollastonite structure requires 40 kbar for the same transformation. In this case, the larger difference in pressure is due both to size and electronegativity differences of Cd (0.95 Å; $\chi = 1.7$) and Ca (1.00 Å; $\chi = 1.0$).

The effects of Rule 2 are also observed in the transitions from $\text{Na}^{\text{IV}}\text{Al}^{\text{IV}}\text{Ge}_3\text{O}_8$ (feldspar) to $\text{Na}^{\text{VI}}\text{Al}^{\text{VI}}\text{Ge}_3\text{O}_8$ (hollandite type) at 25 kbar in contrast to 35 kbar for the transition between $\text{K}^{\text{IV}}\text{Al}^{\text{IV}}\text{Ge}_3\text{O}_8$ (feldspar) and $\text{K}^{\text{VI}}\text{Al}^{\text{VI}}\text{Ge}_3\text{O}_8$ (hollandite type) (104). Another example is the transition between $^{\text{IV}}\text{Li}^{\text{IV}}\text{AlO}_2$ (tetragonal wurtzite) and $^{\text{VI}}\text{Li}^{\text{VI}}\text{AlO}_2$ (αNaFeO_2 type) at 25 kbar vs 40 kbar for a similar transition in NaAlO_2 (34).

For transitions of 2 compounds having

different composition, e.g., MGeO_3 and M_2GeO_4 , the coordination of M in both phases should be the same and high-pressure structures must be available for both compounds. For example, consider $^{\text{VI}}\text{Mn}_2^{\text{IV}}\text{GeO}_4$ and $^{\text{VI}}\text{Mn}^{\text{IV}}\text{GeO}_3$. In accordance with Rule 1, only 25 kbar are necessary to prepare the ilmenite form of $^{\text{VI}}\text{Mn}^{\text{VI}}\text{GeO}_3$, whereas 60 kbar are required to produce $^{\text{VI}}\text{Mn}_2^{\text{VI}}\text{GeO}_4$ with the Sr_2PtO_4 structure (99). A further example of the applicability of Rule 1 is the transition of $\text{NaAlGe}_3\text{O}_8$ (feldspar structure \rightarrow hollandite structure) at 25 kbar vs NaAlGeO_4 (nepheline \rightarrow CaFe_2O_4) at 120 kbar (104).

From the preceding considerations, we can make some predictions concerning high-pressure phase transitions involving an increase of cation coordination number. It should be easier to increase the CN of a cation when: (1) It is surrounded by OH^- ions than by O^- ions; (2) The anions in the coordination polyhedron are bonded to small highly-charged cations like P^{5+} or S^{6+} than when the anions are bonded to larger cations with a low charge like Na^+ , K^+ .

Specifically, we can predict that whereas the $^{\text{IV}}\text{ZnO}$ (wurtzite) to $^{\text{VI}}\text{ZnO}$ (rocksalt) transformation requires more than 100 kbar, the transition of $^{\text{IV}}\text{Zn}(\text{OH})_2$ to a form $^{\text{VI}}\text{Zn}(\text{OH})_2$, perhaps with the $\text{Cd}(\text{OH})_2$ structure, should occur at a considerably lower pressure. Similarly, we might anticipate the high-pressure synthesis of $\text{Be}(\text{OH})_2$ with the $\text{Cd}(\text{OH})_2$ structure.

If we consider the possibility of octahedrally-coordinated ions like Be^{2+} , B^{3+} , P^{5+} , S^{6+} , or Cr^{6+} we can predict the most likely type of compounds. These will contain a large proportion of highly-charged tetrahedral cations. Thus, 2 likely candidates for obtaining $^{\text{VI}}\text{Be}^{2+}$ at high pressure are BeP_2O_6 , possibly isomorphous with NiP_2O_6 (86), and BeSO_4 , isomorphous with CrVO_4 (10). Similarly, octahedral B^{3+} may be possible in $\text{B}(\text{PO}_3)_3$, isomorphous with $\text{Al}(\text{PO}_3)_3$ (10). High-pressure synthesis of VPO_5 or $\text{Te}_2\text{P}_2\text{O}_{11}$ might stabilize 5- or 6-coordinated P^{5+} . The former should be isomorphous with V_2O_5 . Note that synthesis of high-pressure NbPO_5 and TaPO_5 have not resulted in an increase in P^{5+} coordination (105). Evidently a higher

TABLE VI

EFFECTIVE IONIC RADII OF SMALL CATIONS IN OCTAHEDRAL COORDINATION

Ion	Effective ionic radius for CN = VI
Be ²⁺	.45 ^a
B ³⁺	.27 ^a
Si ⁴⁺	.40 ^b
P ⁵⁺	.38 ^a
S ⁶⁺	.29 ^a
Cr ⁶⁺	.44 ^a

^a Ref. (9).^b R. D. Shannon and C. T. Prewitt, *Acta Cryst.* **B25**, 925 (1969).

pressure than 60 kbar is necessary. Finally, ^{VI}Cr⁶⁺ and ^{VI}S⁶⁺ should be most probable in compounds like M⁶⁺P₂O₈ or M₂P₂O₁₁ isomorphous with MoP₂O₈ (10) and Mo₂P₂O₁₁ (10).

We must also remember that the difficulty of obtaining these phases will increase as cation size decreases and charge increases. Table VI shows estimated octahedral radii for these ions. We have included ^{VI}Si⁴⁺ as a standard to gauge the relative difficulty of preparing compounds with small 6-coordinated cations. From this table it should be easiest to prepare compounds with ^{VI}Be²⁺ and hardest to prepare those with ^{VI}S⁶⁺.

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