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Intramolecular Non-Bonded Radii: Application to Synthetic and Naturally-Occurring Beryllates, Aluminates, Silicates, Germanates, Phosphates, and Arsenates

C. GLIDEWELL

Chemistry Department, University of St. Andrews, Fife KY16 9ST, Scotland, U.K.

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Molecular configurations at oxygen in natural and synthetic oxides (binary and ternary) and in beryllates, aluminates, silicates, germanates, phosphates and arsenates containing double and triple tetrahedra, single and double rings, or extended chains, are analysed in terms of a hard atom model: the configurations predicted by this model are in good overall agreement with those found experimentally.

Introduction

Intramolecular non-bonded atomic radii [1, 2] have been used to rationalise [1–4] the configurations of a wide range of molecular species having inter bond angles greater than those expected on the basis of the VSEPR model. The basis of this rationalisation is the supposition that in a molecular fragment XMY, the lower limiting value of the angle $\angle$XMY is, for given XM and YM distances, determined by the non-bonded distances X...Y. O'Keeffe and Hyde, in a study [5] of the structures of binary and ternary oxides and nitrides based on cristobalite and stuffed forms thereof were able to rationalise in detail the bond angles MOM′ using this model.

It has long been recognised that in many condensed silicates and phosphates, of both natural and synthetic origin, the interbond angles at bridging oxygen atoms are substantially larger than the approximately tetrahedral value found in ethers. The interpretation of these wide angles in phosphates and silicates has generally followed that of Cruickshank [6], who regarded the deviation of these angles from tetrahedral as a manifestation of π-bonding between occupied 2p orbitals on oxygen and formally unoccupied 3d orbitals on silicon or phosphorus. Corroborative evidence for the occurrence of such π-bonding is, however, poor [7, 8]: furthermore, it appears that angles MOM′ in these compounds are, at least in some species, deformed fairly readily by intermolecular forces; thus in bis-(triphenylsilyl) chromate $(Ph_3SiO)_2CrO_2$, there are two crystallographically distinct SiOCr angles, having values of 133.1° and 162.7° respectively [9].

The purpose of this paper is to reconsider the observed bond angles in condensed silicates, germanates, phosphates and arsenates in terms of the non-bonded distances M....M′ in the bridging fragments MOM′, and so to attempt an alternative rationalisation of the observed angles $\angle$MOM′.

Binary and Ternary Oxides

Silicon dioxide, SiO_2, exists in at least eight crystalline forms, and in all except the very high pressure form stishovite [10], which has been synthesised [11] from quartz at pressures greater than 10^5 atmospheres, and found [12] naturally occurring at Meteor Crater, Arizona, the silicon is four coordinate. The principal structural parameters of those forms containing four-coordinate silicon are summarised in Table I: all consist of three dimensional arrays of SiO_4 tetrahedra which differ in their mode of linkage. In coesite [13] for example, the groups are linked into rings of four tetrahedra, themselves linked into chains. Despite the wide range of SiOSi angles found in the polymorphs of SiO_2, from 143.4° in low quartz [14], to 180° in tridymite [15], and for some of the angles in coesite [13], the range of Si....Si distances is remarkably small. Apart from the 3.20 Å distance across the linear SiOSi bridges in coesite, the range is from 3.055 Å in high-quartz [16] to 3.12 Å in tridymite [15], all very close to the ideal 3.10 Å expected [1] in the hard atom approximation. The stable form of germanium dioxide under ambient conditions has the rutile structure [17], but there exists [18] also a form analogous to low quartz, having a Ge...Ge distance of 3.154 Å, subtending an angle at oxygen of 130.1°; this Ge...Ge distance is very close to the 3.16 Å expected.

A number of ternary oxides of general formula $M^{III}M^{V}O_4$ have structures closely related to some of the polymorphs of silicon dioxide, $Si^{IV}Si^{IV}O_4$, in which the cations are completely ordered. Thus BPO_4 and $BAsO_4$ have structures [19] analogous to that of high cristobalite, in which the M^{III}....M^{V} distances are 2.74 Å and 2.80 Å respectively: similarly $AlPO_4$ and

TABLE I. Binary Oxides of Beryllium, Silicon and Germanium.

Name	Formula	Space Group	r(M–O)/Å	<(MOM)/°	r(M...M)$_{obs}$/Å	r(M...M)$_{calc}$/Å	Ref.
–	BeO	C6mc	1.656	108.5	2.687	2.78	a
High Cristobalite	SiO_2	Fd3m	1.616	147.2	3.100	3.10	b
Low Cristobalite	SiO_2	$P4_12_12$ $P4_32_12$	1.605	146.8	3.075	3.10	c
Tridymite	SiO_2	$P6_3/mmc$	1.56	180	3.12	3.10	d
High Quartz	SiO_2	$P6_222$ $P6_422$	1.607	143.9	3.055	3.10	e
Low Quartz	SiO_2	$P3_121$ $P3_221$	1.610	143.4	3.057	3.10	f
Keatite	SiO_2	$P4_12_12$ $P4_32_12$	1.58 1.61 1.59	156 146 156	3.09 3.11 3.11	3.10	g
Coesite	SiO_2	C2/c	1.61 1.61	148 180	3.10 3.20	3.10	h
–	GeO_2	$P3_121$ $P3_221$	1.739	130.1	3.154	3.16	i

[a] G. A. Jeffrey, G. S. Parry and R. L. Mozzi, *J. Chem. Phys., 25,* 1024 (1956). [b] A. F. Wright and A. J. Leadbetter, *Phil. Mag., 31,* 1391 (1975). [c] W. A. Dollase, *Z. Krist., 121,* 369 (1965). [d] Ref 15. [e] Ref 16. [f] Ref 14. [g] J. Shropshire, P. P. Keat and P. A. Vaughn, *Z. Krist., 12,* 409 (1959). [h] Ref 13. [i] Ref 18.

TABLE II. Ternary Oxides $M^{III}M^{V}O_4$.

Compound	Space Group	r(M^{III}–O)/Å	r(M^{V}–O)/Å	<($M^{III}OM^{V}$)$_{obs}$/°	r(M^{III}...M^{V})$_{obs}$/Å	r(M^{III}...M^{V})$_{calc}$/Å	Ref.
BPO_4	$I\bar{4}$ [d]	1.44	1.54	133	2.74	2.78	a
$BAsO_4$	$I\bar{4}$ [d]	1.49	1.66	126	2.80	2.94	a
$AlPO_4$	$C222_1$ [e]	1.70	1.56	146	3.11	3.11	a
$AlAsO_4$	$P3_121$ [f] $P3_221$	1.70	1.62	144	3.16	3.27	c
$GaPO_4$	$C222_1$ [e]	1.78	1.56	139	3.12	3.17	b

[a] Ref. 19, [b] Ref. 20. [c] Ref. 21. [d] Structures in $I\bar{4}$ are analogous to high cristobalite (Fd3m). [e] Structures in $C222_1$ are analogous to low cristobalite ($P4_12_12$, $P4_32_12$). [f] Structures in $P3_121$, $P3_221$ are analogous to low-quartz ($P3_121$, $P3_221$).

$GaPO_4$, both of which are polymorphous, have forms similar to low cristobalite whose structures are known [20]; the inter-cation distances are 3.11 Å and 3.12 Å respectively, comparable with those expected. $AlAsO_4$ has a structure like that of low quartz [21]. These structures are summarised in Table II. In addition to these polymorphs there exists also a high cristobalite form of $GaPO_4$: although the positions of the oxygen atoms were not determined [22], the Ga...P distance was found to be 3.10 Å (*cf.* 3.11 Å expected). Low quartz-like forms also are known of $AlPO_4$ (Berlinite) [23], $GaPO_4$ [24] and $GaAsO_4$ [24], for which only the unit-cell dimensions have been reported. However, use of the same atomic coordinates as in $AlAsO_4$ allows inter-cation distances to be roughly estimated for these polymorphs as follows: Al...P, 3.09 Å; Ga...P, 3.10 Å; Ga...As, 3.16 Å. By contrast, $AlSbO_4$ [25] and $GaSbO_4$ [26] both crystallise with the rutile structure, with six-coordinate cations, and it is interesting to note that these antimony(V) oxides both fall in the (6,3) domain of the Mooser–Pearson plot [27], whereas save for $GaAsO_4$ which is a borderline example, all the other SiO_2-like $M^{III}M^{V}O_4$ species fall in the (4,2) domain. $BiAsO_4$ having both higher $\bar{n}$ and higher Δx, is more ionic even than $GaAsO_4$, and adopts [28] the scheelite structure in which distinct $M^{V}O_4$ anions can be discerned, and in which M^{III} is eight-coordinate: similarly the highly ionic $ScPO_4$ [29] and $ScAsO_4$ [30] adopt the zircon structure, having eight-coordinate M^{III}.

NOTE ADDED IN PROOF (1.9.77): Synthetic low tridymite (*Cc*) has r(Si–O), 1.597 Å; <(SiOSi), 150.0°; r(Si–Si), 3.085 Å. (W. H. Baur, personal communication).

A further mixed oxide containing tetrahedrally coordinated non-metal atoms, which may be mentioned here, is horlbathite [31] $CaBe_2P_2O_8$, in which there exists a three-dimensional framework of BeO_4 and PO_4 tetrahedra. The mean P–O and Be–O distances are 1.546 Å and 1.615 Å respectively: the mean BeOP angle is 128.1° and the mean Be...P distance is 2.840 Å, identical with the distance expected. The expected angle <BeOP calculated from the hard-atom contact distance and the mean Be–O and P–O distances is 127.9°.

Phosphorus forms a series of molecular oxides P_4O_{6+n} (n = 0–4) of which the structures are known for all save that having n = 1: in addition phosphorus(V) oxide exists in two continuous, non-molecular forms. The essential data are set out in Table III. It will be noted that in the molecular oxides, non-bonded distances $P^{III}...P^{III}$ are very close to the 2.90 Å expected, but that $P^{III}...P^{V}$ and $P^{V}...P^{V}$ distances are somewhat shorter. Now inter-bond angles at three-connected phosphorus are generally below 100°, while those at four-connected phosphorus are usually quite close to tetrahedral. In a cage molecules such as P_4O_{10}, it is impossible, with the observed P–O bridging bond length, to accommodate both tetrahedral P^V and a limiting contact P...P distance: since the stretching of bonds is energetically the most expensive escape, the observed structure represents a compromise between the departures from the ideal P...P distance and the ideal OPO angles. No such problem arises at P^{III} since the OPO angle is already much smaller. Similarly in the continuous forms of $(P_2O_5)_n$, no such constraints apply.

Arsenic(III) oxide exists in both a molecular, As_4O_6, and a continuous form, which occur [32] naturally as arsenolite and claudetite, respectively. The molecular form has [33] an angle of 126° associated with an As...As distance of 3.21 Å, essentially identical with the 3.22 Å expected. The continuous form has [34] an As...As distance of 3.16 Å, subtending an angle of 123° at oxygen. The structure of anhydrous arsenic(V) oxide is unknown: the hydrate $As_2O_5 \cdot 5/3H_2O$ is better described as $H_5As_3O_{10}$, and will be discussed below under chain-forming arsenates.

Silicates and Germanates

There exists a wide range of silicates and germanates containing double tetrahedra, $M_2O_7^{-6}$ (M = Si or Ge), and the important structural data for these are set out in Table IV, along with those for a few triple tetrahedra. In addition to the species listed in the table, $Sc_2Ge_2O_7$ is known [35] to be isostructural with $Sc_2Si_2O_7$; $Na_2Cd_3Si_3O_{10}$ to contain [36] the same anion as $Na_2Ca_3Si_3O_{10}$, and $La_2Ge_2O_7$ to contain [37] the $Ge_3O_{10}^{-8}$ ion as found in $Gd_4(GeO_4)Ge_3O_{10}$: furthermore the mineral rosenhahnite $Ca_3Si_3O_9 \cdot H_2O$ contains [39] the ion $[(HO)O_2SiOSi(O_2)OSiO_2(OH)]^{-6}$. The ions whose structures have been accurately determined fall into two categories, those which are bent at bridging oxygen and those

TABLE III. Oxides of Phosphorus and Arsenic.

Compound	Space Group	r(M–O)/A	<(MOM)/°	$r(M...M)_{obs}$/A	$r(M...M)_{calc}$/A	Ref.
P_4O_6	–[h]	1.638	126.4	2.924 $(P^{III}...P^{III})$	2.90	[a]
P_4O_8	C2/c	1.596	121.2	2.781 $(P^V...P^V)$	2.90	[a]
		1.668 1.576 [i]	124.4	2.870 $(P^V...P^{III})$	2.90	
		1.633	130.1	2.962 $(P^{III}...P^{III})$	2.90	
P_4O_9	$R\bar{3}c$	1.590	122.8	2.793 $(P^V...P^V)$	2.90	[b]
		1.633	126.8	2.920 $(P^V...P^{III})$	2.90	
P_4O_{10}	–[h]	1.604	123.5	2.826 $(P^V...P^V)$	2.90	[b]
P_4O_{10}	R3c	1.62	123.5	2.85 $(P^V...P^V)$	2.90	[c]
P_2O_5-II	Fdd2	1.65	133.7	2.91 $(P^V...P^V)$	2.90	[d]
P_2O_5-III	Pnma	1.59	143.4	3.02 $(P^V...P^V)$	2.90	[e]
As_4O_6 (Arsenolite)	–[h]	1.80	126	3.21 $(As^{III}...As^{III})$	3.22	[f]
As_2O_3 (Claudetite)	$P2_1/c$	1.80	123	3.16 $(As^{III}...As^{III})$	3.22	[g]

[a] B. Beagley, D. W. J. Cruickshank, T. G. Hewitt and K. H. Jost, *Trans. Faraday Soc.*, *65*, 1219 (1969). [b] B. Beagley, D. W. J. Cruickshank, T. G. Hewitt and A. Haaland, *Trans. Faraday Soc.*, *63*, 836 (1967). [c] D. W. J. Cruickshank, *Acta Cryst.*, *17*, 677 (1964). [d] H. C. J. de Decker, *Rev. Trav. Chim.*, *60*, 413 (1941). [e] D. W. J. Cruickshank, *Acta Cryst.*, *17*, 679 (1964). [f] Ref. 33. [g] Ref. 34. [h] Vapour-phase determination by electron diffraction. [i] The authors ([a] above) refer darkly to a "strange quirk of the X-ray data".

TABLE IV. Silicates and Germanates Containing Double and Triple Tetrahedra.

Compound	Formula	Space-Group	$r(M–O)/Å$	$r(M...M)/Å$	$<(\mathrm{MOM})_{\mathrm{obs}}/^\circ$	$<(\mathrm{MOM})_{\mathrm{calc}}/^\circ$	Ref.
Hemimorphite	$Zn_4(OH)_2Si_2O_7\cdot H_2O$	Imm2	1.627	3.145	150.3	144.6	a
Paracelsian	$BaAl_2OSi_2O_7$	$P2_1/c$	1.65	3.24	158	140	b
Barrylite	$BaBe_2Si_2O_7$	$Pna2_1$	1.567	2.971	143.0	163.0	c
Tilleyite	$Ca_5Si_2O_7(CO_3)_2$	$P2_1/c$	1.65	3.27	164	140	d
Bertrandite	$Be_4Si_2O_7(OH)_2$	$Cmc2_1$	1.62	3.06	142	146	e
Lawsonite	$CaAl_2Si_2O_7(OH)_2\cdot H_2O$	Cmcm	1.65	3.05	135	140	f
Ilvaite	$CaFe_3Si_2O_7(OH)_2$	Pnma	1.63	2.98	132	144	g
Epidote	$Ca_2(Al, Fe)Al_2O_2H(SiO_4)Si_2O_7$	$P2_1/m$	1.72	3.26	143	129	h
Zoisite	$Ca_2Al_3(SiO_4)Si_2O_7(O_2H)$	Pnma	1.67	3.26	155	136	i
Barysilite	$MnPb_8(Si_2O_7)_3$	$R\bar{3}c$	1.69	3.10	133	133	j
–	$Pb_3Si_2O_7{\equiv}PbPb_8(Si_2O_7)_3$	$R\bar{3}c$	1.666	2.958	125.2	137.0	k
Hardystonite	$Ca_2ZnSi_2O_7$	$P\bar{4}2_1m$	1.649	3.084	138.4	140.1	l
Fresnoite	$Ba_2(TiO)Si_2O_7$	P4bm	1.626	3.088	143.5	144.8	m
Perrierite	$Mg_2La_4Ti_3O_8(Si_2O_7)_2$	$P2_1/c$	1.637	3.248	165.6	142.5	n
Mg-Chevnikite	$Mg_2Nd_4Ti_3O_8(Si_2O_7)_2$	$P2_1/c$	1.621	3.177	157.4	146.0	n
Co-Chevnikite	$Co_2Nd_4Ti_3O_8(Si_2O_7)_2$	$P2_1/c$	1.634	3.204	157.3	143.1	n
–	$Pr_2Si_2O_7$(low T)	$P4_1$	1.67	3.05	132	136	o
–	$Pr_2Si_2O_7$(high T)	$P2_1/c$	1.619	2.948	131.1	144.0	o
–	$Nd_2Si_2O_7$	$P2_12_12_1$	1.613	2.954	132.6	147.9	p
–	$Sm_2Si_2O_7$(low T)	$P4_1$	1.649	2.985	129.7	141.1	q
			1.644	3.049	136.0	141.1	
–	$Gd_2Si_2O_7$	$Pna2_1$	1.672	3.287	158.7	136.0	p
–	$Er_2Ge_2O_7$	$P4_12_12$	1.756	3.256	136.0	128.3	r
Thortveitite	$Sc_2Si_2O_7$	C2/m	1.605	3.210	180.0	149.9	s
–	$Er_2Si_2O_7$	$P2_1/c$	1.632	3.264	180.0	143.5	p
–	$Yb_2Si_2O_7$	C2/m	1.626	3.252	180.0	144.8	p
Kentrolite	$Pb_2(Mn, Fe)_2O_2Si_2O_7$	$C222_1$	1.646	3.292	180.0	140.7	t
–	$K_2Pb_2Si_2O_7$	$P\bar{3}$	1.61	3.22	180.0	149	u
–	$K_2Pb_2Ge_2O_7$	$P\bar{3}$	1.61	3.21	180	159	v
–	$Na_2Ca_3Si_3O_{10}$	C2/c	1.716	3.130	131.6	129.2	w
–	$Gd_4(GeO_4)Ge_3O_{10}$	P1	1.81	3.13	120	122	x
Zunyite	$Al_{12}(OH)_{18}AlO_4(Si_5O_{16})Cl$	$F\bar{4}3m$	1.63	3.26	180	144	y

[a] W. S. McDonald and D. W. J. Cruickshank, *Z. Krist.*, *124*, 180 (1967). [b] V. V. Bakakin and N. V. Belov, *Kristallografiya*, *5*, 864 (1960). [c] K. K. Abrashev, V. V. Ilyukhin and N. V. Belov, *Kristallografiya*, *9*, 816 (1964). [d] J. V. Smith, *Acta Cryst.*, *6*, 9 (1953). [e] L. P. Solov'eva and N. V. Belov, *Kristallografiya*, *9*, 551 (1964). [f] I. M. Rumanova and T. I. Skipetrova, *Doklady Akad. Nauk. S.S.S.R.*, *124*, 324 (1959). [g] N. V. Belov and M. I. Mokeeva, *Tr. Inst. Krist. Akad. Nauk. S.S.S.R.*, *9*, 47 (1954). [h] T. Ito, N. Morimoto and R. Sadanaga, *Acta Cryst.*, *7*, 53 (1954). [i] E. G. Fesenko, I. M. Rumanova and N. V. Belov, *Kristallografiya*, *1*, 171 (1956). [j] J. Lajzerowicz, *Acta Cryst.*, *20*, 357 (1966). [k] W. Petter, A. B. Harnik and U. Keppler, *Z. Krist.*, *133*, 445 (1971). [l] S. J. Louisnathan, *Z. Krist.*, *130*, 427 (1969). [m] P. B. Moore and S. J. Louisnathan, *Z. Krist.*, *130*, 438 (1969). [n] C. Calvo and R. Faggiani, *Amer. Mineral*, *59*, 1277 (1974). [o] J. Felsche, *Z. Krist.*, *133*, 364 (1971). [p] Ref. 39. [q] Y. I. Smolin, Y. F. Shepelev and I. K. Butikova, *Kristallografiya*, *15*, 214 (1970). [r] Ref. 35. [s] Y. I. Smolin, Y. F. Shepelev and A. P. Titov, *Kristallografiya*, *17*, 857 (1972). [t] O. Gabrielson, *Arkiv. Mineral. Geol.*, *3*, 141 (1963). [u] I. Naráy-Szabó and A. Kalman, *Silikat-technik*, *12*, 316 (1961). [v] G. Bassi and J. Lajzerowicz, *Bull. Soc. Fr. Mineral. Crist.*, *88*, 342 (1965). [w] Ref. 36. [x] Y. I. Smolin, Y. F. Shepelev and I. K. Butikova, *Kristallografiya*, *16*, 911 (1971). [y] Ref. 40.

which are linear. However, the linear and non-linear classes are not essentially different: the mean value of $|r(M....M)_{obs} - r(M....M)_{calc}|$ in the bent species is 0.094 Å, while the value for all the compounds in Table IV is 0.10 Å. The linearity in some of the lanthanide disilicates may be apparent only: thus in both $Er_2Si_2O_7$ and $Yb_2Si_2O_7$ ($\theta = 180°$), the temperature factors for the bridging oxygens are [39] much higher than for any other oxygen atom, while in $Gd_2Si_2O_7$ ($\theta = 158.7°$) and $Nd_2Si_2O_7$ ($\theta = 132.6°$) the central-oxygen temperature factors are comparable with those of the other oxygens: it is possible that the SiOSi bending potentials in the erbium and ytterbium compounds have two minima with a shallow barrier, so that the thermally averaged structure appears to be linear with a large temperature factor. However, whatever the true position of the bridging oxygen in these species the Si...Si distance is unaffected. Smolin and Shepelev ascribe [39] the variations in Si–O bond order, and hence in bond length to the different polarisations of the anion by the several cations: this variation in r(Si–O), taken together with r(Si...Si), gives rise to the observed variations in the SiOS angle. In zunyite [40], the $Si_5O_{16}^{-12}$ anion has the constitution $Si(OSiO_3)_4^{-12}$, and the SiOSi bridges are linear by symmetry.

Silicates containing single and double rings are listed in Table V: in addition to the single-ring species listed, the compounds $Ca_2BaSi_3O_9$, $BaTiGe_3O_9$ and $Sr_3Ge_3O_9$ all appear [41, 42] to contain M_3O_3 rings. With very few exceptions the Si...Si distances in the single-ring compounds are very close to the 3.10 Å anticipated from the hard-atom model, and the correspondence of observed an calculated angles SiOSi is also in general good. The anion $Si_6O_{15}^{-6}$ consists [43] of two crystallographically independent Si_3O_3 rings with coincident triads, joined together by three SiOSi bridges: the Si...Si distances within the two rings are 2.98 Å and 3.03 Å respectively, while the inter-ring distance is 3.06 Å.The Si_8 anions $Si_8O_{20}^{-8}$ and $Si_8O_{18}(OH)_2^{-6}$ consist of [44–46] approximately cubic arrays of silicon atoms with oxygen briges along each edge and a single terminal oxygen on each silicon: again the mean Si...Si distances in the three examples of this type, 3.13, 3.12 and 3.13 Å respectively, are very close to the 3.10 Å expected. In millarite [47], the $Si_{12}O_{30}^{-12}$ anion consists of two Si_6O_6 rings joined together via six SiOSi briges: the Si...Si distance within the rings is 3.24 Å and between them 3.11 Å. Osumilite $(Na,K,Ca)(Mg,Fe^{II})_2(Al,Fe^{II},Fe^{III})_3(Si,Al)_{12}O_{30}\cdot H_2O$ appears [48] to be isostructural with millarite. Eudialite, $Na_{12}Ca_6Zr_3Fe_3(Si_3O_9)_2(Si_9O_{27})_2$ contains [49] both Si_3O_3 rings and Si_9O_9 rings: in the smaller rings, Si...Si is 3.00 Å and in the larger 2.98 Å.

Silicates and germanates containing long chain $(MO_3)_n^{-2n}$ are listed in Table VI: they may be classified into orthorhombic, monoclinic and triclinic series. These pyroxenes and related species conform very closely to the predictions of the hard atom model, as may be seen from the mean values of $|\delta_\theta| = |{<}(MOM)_{obs} - {<}(MOM)_{calc}|$ and of $|\delta_r| = |r(M...M)_{obs} - r(M...M)_{calc}|$. Mean values of $|\delta_\theta|$ are for the orthorhombic, monoclinic and triclinic series, 6.3°, 3.4°, and 6.1° respectively, with an overall mean of 5.2°, while the corresponding mean values of $|\delta_r|$ are 0.076 Å, 0.033 Å and 0.047 Å, with an overall mean of 0.055 Å. In addition to those species listed in Table VI, $MgGeO_3$, $MnGeO_3$ and $CoGeO_3$ are isostructural [50] with hypersthene, and $FeGeO_3$ is isostructural [51] with clinoenstatite: however calculation of r(Ge...Ge) is not thought to be worthwhile until accurate atomic coordinates are available. Similarly, Li_2SiO_3 is isostructural [52] with Na_2SiO_3, and $BaSiO_3$ (high-temperature form) with [53] $BaGeO_3$. Three phases of composition $LiAl(SiO_3)_2$ have been structurally characterised: spodumene, $LiAl(SiO_3)_2$-I, is a monoclinic pyroxene (C2/c) in which r(Si...Si) is [54] 3.01 Å and <(SiOSi) is 138°: the high temperature form β-spodumene, $LiAl(SiO_3)_2$-II, on the other hand is [55, 56] a stuffed keatite, crystallising in $P4_12_12$ and $P4_32_12$, in which there are three independent Si...Si distances of 3.183 Å, 3.186 Å and 3.143 Å subtending angles at the bridging oxygens of 150.7°, 154.0° and 143.6° respectively: the expected minimum values are 140.9°, 142.9° and 139.1° respectively. A further high temperature form, $LiAl(SiO_3)_2$-III is [57] a stuffed high quartz, crystallising in $P6_222$ and $P6_422$, in which the aluminium and silicon atoms are distributed at random in the positions (3c): the (Al, Si)...(Al, Si) distance is 3.181 Å, which may be compared with the expected r(Si...Si), 3.10 Å and r(Al...Al), 3.32 Å; the observed angle <(Al, Si)O(Al, Si) is 151.6°. Non-pyroxene chains are formed in sillimanite [58] and andalusite [59], Al_2SiO_5. The chains in sillimanite have the backbone $(AlOSiO)_n$ with both aluminium and silicon having four-coordination; the other half of the aluminium atoms are in six-coordinated sites; the mean Si...Al distance is 3.104 Å (expected 3.21 Å) and the Al...Al distance is 3.27 Å (expected 3.32 Å). In andalusite, the chain-forming aluminium atoms are five-coordinate, with r(Al...Si) = 3.05 Å. Mullite (composition range $(Al_2O_3)_2\cdot SiO_2$–$(Al_2O_3)_3(SiO_2)_2$) is similar [59] to sillimanite (Al_2SiO_5; $Al_2O_3\cdot SiO_2$), but with aluminium and silicon disordered in the tetrahedral sites.

The silicate framework in vlasovite, $Na_2ZrSi_4O_{11}$, consists [60] of chains whose links are based on Si_4O_4 rings: there are three independent Si...Si distances of 3.061 Å, 3.049 Å and 3.024 Å (mean 3.045 Å) subtending angles at bridging oxygen of 146.1°, 141.5° and 137.9° respectively: the values of $|\delta_\theta|$ are 5.2°, 5.9° and 8.3° (mean 6.5°). Cavansite, $Ca(VO)Si_4O_{10}\cdot 4H_2O$, is similar [61]. Litidionite, $CuNaKSi_4O_{10}$ contains [62] tubular chains of tetrahedra, which may be regarded as arising from the notional condensation of two vlasovite-type chains: the mean Si...Si distance observed is 3.064 Å, very close to the 3.10 Å expected; <(SiOSi) is found to be 142.5°, and the calculated value is 144.8°. Tubular chains are found also in narsarsukite, $Na_2(TiO)Si_4O_{10}$ in which <(SiOSi) is 139.9°, r(Si...Si) is 3.055 Å and $<(SiOSi)_{calc}$ is 144.8°. In $K_4Si_8O_{18}$, which contains [64] double chains of Si_4O_{10} rings, there are seven independent SiOSi angles ranging from 133.5° to 148.0° (mean 141.5°): however the Si...Si distances all lie in the range 3.003 Å to 3.099 Å, (mean 3.065 Å) all very close to the expected 3.10 Å. In natrolite, $Na_2Al_2Si_3O_{10}\cdot 2H_2O$, the aluminium and silicon

TABLE V. Silicates Containing Single and Double Rings.

Compound	Formula	Space Group	r(Si–O)/Å	r(Si...Si)/Å	<(SiOSi)$_{obs}$/°	<(SiOSi)$_{calc}$/°	Ref.
Single rings							
Benitoite	$BaTi(Si_3O_9)$	P$\bar{6}$c2	1.65	2.91	124	140	a
Wadeite	$K_2Zr(Si_3O_9)$	P6_3/m	1.59	2.96	137	154	b
Catapleite	$Na_2Zr(Si_3O_9)\cdot 2H_2O$	P6_3/mmc	1.73	2.96	118	127	c
Margarosanite	$Ca_2Pb(Si_3O_9)$	P$\bar{1}$	1.677	2.930	121.8	135.1	d
Pectolite	$Ca_2Na(HSi_3O_9)$	P$\bar{1}$	1.651	3.095	139.2	139.7	e
–	$K_4(H_4Si_4O_{12})$	P2_1/c	1.63	3.07	141	144	f
Papagoite	$Ca_2Cu_2Al_2(Si_4O_{12})(OH)_6$	C2/m	1.571	2.941	138.8	161.2	g
			1.611	3.041	141.4	148.4	
Taramellite	$Ba_2(Fe,Ti,Mg)_2(Si_4O_{12})(OH)_2$	Pmmn	1.619	3.236	176.0	146.4	h
			1.667	2.985	127.1	136.8	
			1.651	3.060	135.9	139.7	
Tugtupite	$Na_4BeAl(Si_4O_{12})Cl$	I$\bar{4}$	1.629	3.082	142.2	142.2	i
Kainosite	$Ca_2Ln_2(Si_4O_{12})CO_3\cdot H_2O$	Pnma	1.606	3.129	153.9	149.7	j
			1.606	3.129	153.9	149.7	
			1.646	3.097	140.4	140.7	
Nenadkevichite	$(Na,K)_2(Nb,Ti)_2(O,OH)_2$-$(Si_4O_{12})\cdot 4H_2O$	Pbam	1.610	3.212	172.1	148.6	k
			1.621	3.131	150.0	146.0	
Beryl	$Be_3Al_2(Si_6O_{18})$	P6/mcc	1.70	3.12	133	132	l
Dioptase	$Cu_6(Si_6O_{18})\cdot 6H_2O$	R$\bar{3}$	1.54	2.99	155	ca. 180	m
Lovozerite	$Na_2Zr(H_3Si_6O_{18})\cdot \frac{1}{2}NaOH$	C2	1.595	3.089	151.1	152.7	n
Scawtite	$Ca_7(Si_6O_{18})CO_3\cdot 2H_2O$	C2/m	1.658 (×2)	3.167	145.5	138.4	o
			1.638 (×4)	3.085	140.7	142.3	
Double rings							
–	$(Nien_3)_3(Si_6O_{15})\cdot 26H_2O$	P6_3	1.643	3.021	133.9	141.3	p
–	$(Cuen_2)_4(Si_8O_{20})\cdot 38H_2O$	P$\bar{1}$	1.618	3.131	151.5	146.7	q
–	$(Coen_3)_2[Si_8O_{18}(OH)_2]16\cdot 4H_2O$	P2_1/c	1.618	3.124	149.9	146.7	r
Ekanite	$KTh(Ca,Na)_2Si_8O_{20}$	P4/mcc	1.601	3.127	151.8	151.0	s
Millarite	$KCa_2Be_2Al(Si_{12}O_{30})\cdot \frac{1}{2}H_2O$	P6/mcc	1.644	3.106	141.7	141.1	t
			1.631	3.240	166.7	143.7	

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TABLE VI. Pyroxenes and their Analogues.

Compound	Formula	Space Group	r(M–O)/Å	r(M...M)/Å	<(MOM)$_{obs}$/°	<(MOM)$_{calc}$/°	$\lvert\delta_\theta\rvert$/°	$\lvert\delta_r\rvert$/Å	Ref.
Orthorhombic									
Enstatite[d]	$MgSiO_3$	Pbca	1.654	3.047	134.2	139.1	4.9	0.053	a
			1.675	3.011	128.0	135.4	7.4	0.089	
Protoenstatite	$MgSiO_3$	Pbcn	1.65	3.15	145	140	5	0.05	b
–	$MgZn(SiO_3)_2$	Pbca	1.639	3.057	137.7	142.1	4.4	0.043	c
			1.659	3.025	131.5	138.2	6.7	0.075	
–	$ZnSiO_3$	Pbca	1.629	3.071	141.0	144.2	3.2	0.029	c
			1.642	3.052	136.7	141.4	4.7	0.048	
Hypersthene[d]	$Mg_{0.93}Fe_{1.07}(SiO_3)_2$	Pbca	1.648	3.064	136.8	141.3	4.5	0.036	e
–	$Na_4ZnCd(SiO_3)_4$	Fdd2	1.692	3.190	141.0	132.7	8.3	0.090	f
Stokesite	$CaSn(SiO_3)_3 \cdot 2H_2O$	Pnna	1.632	3.223	161.8	143.5	18.3	0.123	g
			1.633	3.064	139.5	143.3	3.8	0.036	
Ramsayite	$Na_2Ti_2O_3(SiO_3)_2$	Pbcn	1.665	2.985	127.4	137.2	9.8	0.115	h
–	Na_2SiO_3	Cmc2$_1$	1.672	3.075	133.7	135.9	2.2	0.025	i
–	Na_2GeO_3	Cmc2$_1$	1.85	3.02	110	117	7	0.14	j
–	$CuGeO_3$	Cmc2$_1$	1.82	2.94	108	120	12	0.22	k
–	$BaGeO_3$	P2$_1$2$_1$2$_1$	1.90	3.06	107	112	5	0.10	l
–	$MnGeO_3$	Pbca	1.803	3.175	123.4	122.4	1.0	0.015	m
			1.791	3.242	129.7	123.8	5.9	0.082	
–	$(BiO)_2GeO_3$	Cmc2$_1$	1.797	3.377	140.0	123.1	16.9	0.217	n
Monoclinic									
Clinoenstatite	$MgSiO_3$	P2$_1$/c	1.65	3.07	137	140	3	0.03	o
			1.72	3.05	125	129	4	0.05	
–	$(Ca_{0.10}Mg_{0.34}Fe_{0.56})SiO_3$	P2$_1$/c	1.64	3.07	139	142	3	0.03	o
			1.66	3.07	135	138	3	0.03	
Diopside	$CaMg(SiO_3)_2$	C2/c	1.68	3.11	136	135	1	0.01	p
Johannsenite	$CaMn(SiO_3)_2$	C2/c	1.688	3.133	136.3	133.3	3.0	0.033	q
Jadeite	$NaAl(SiO_3)_2$	C2/c	1.632	3.060	139.3	143.5	4.2	0.040	r
–	$NaIn(SiO_3)_2$	C2/c	1.649	3.120	142.2	140.1	2.1	0.020	s
–	$ZnSiO_3$	C2/c	1.626	3.071	141.6	144.8	3.2	0.029	c
Searlesite	$NaBSi_2O_5OH$	P2$_1$	1.615	3.095	146.8	147.4	0.6	0.005	t
			1.621	3.034	138.7	145.9	7.2	0.066	
			1.617	3.047	140.8	146.9	6.1	0.053	
–	$CoGeO_3$	C2/c	1.793	3.096	119.4	123.6	4.2	0.064	u
–	$CdGeO_3$	C2/c	1.83	3.19	121	119	2	0.03	v
Alamosite	$PbSiO_3$	P2/c	1.635	3.09	148	143	5	0.01	w

Triclinic

Foshagite	$Ca_4(SiO_3)_3(OH)_2$	$P\bar{1}$	1.617	3.194	162.0	146.9	15.1	0.094	x
Rhodonite	$(Mn,Ca)SiO_3$	$P\bar{1}$	1.649	3.062	136.4	140.1	3.7	0.038	y
Bustamite	$CaMn(SiO_3)_2$	$P\bar{1}$	1.614	3.184	161	147.6	13.4	0.084	
			1.653	3.054	135	138.2	4.3	0.046	z
			1.659	3.087	137	138.2	1.2	0.013	
Nambulite	$(Li,Na)Mn_4(Si_5O_{14}OH)$	$P\bar{1}$	1.652	3.089	138.7	139.5	0.8	0.011	aa
Babingtonite	$Fe^{II}Fe^{III}Ca_2(Si_5O_{14}OH)$	$P\bar{1}$	1.641	3.058	137.5	141.7	4.2	0.042	bb

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atoms are [65] fully ordered in four-coordinate sites, being linked into complex rings of five tetrahedra: the SiOSi angle is 143.4° and r(Si...Si) is 3.095 Å: the mean Si...Al distance is 3.17 Å, close to the 3.21 Å expected. The alumino-germanate $Na_2Al_2Ge_3O_{10} \cdot 2H_2O$ is [66] isostructural as is [67] scolecite, $CaAl_2Si_3O_{10} \cdot 3H_2O$.

Phosphates and Arsenates

Pertinent structural data for phosphates and arsenates containing double and triple tetrahedra are set out in Table VII. A number of diphosphates $M^{II}_2P_2O_7$ occur in two polymorphs, a low-temperature α-phase and a high temperature β-phase: the α-phases generally have r(P...P) close to the 2.90 Å expected but in β-$Mg_2P_2O_7$ [68], β-$Cu_2P_2O_7$ [69] and β-$Zn_2P_2O_7$ [70], the POP fragment is linear, although in each example the central oxygen atom undergoes large amplitude thermal motion. Similarly $Mg_2As_2O_7$ is apparently linear at the bridging oxygen, but this atom is in fact disordered [71]: nevertheless r(As...As) at 3.342 Å is substantially larger than the 3.22 Å expected. $Co_2As_2O_7$, although crystallising in $C\bar{1}$, appears [72] to be very similar the C2/m structure of thortveitite $Sc_2Si_2O_7$, so that again the AsOAs fragment is linear or very nearly so. In ZrP_2O_7, while the value of r(P...P) may not be very precise [73], the POP group must be linear, from a consideration of the special positions occupied in Pa3: the bridging oxygen occupied positions (4b) at (½, ½, ½) *etc.* and phosphorus occupies (8c) at (x, x, x), $(\bar{x}, \bar{x}, \bar{x})$ *etc.* with $x = 0.39$, $a = 8.20$ Å. Isostructural with ZrP_2O_7 are compounds MP_2O_7 (M = Si, Sn, Pb, Ti, Hf [73], U [74], Th [75]) but for none of these has x been determined. In addition to this cubic phase of SiP_2O_7 [73], two monoclinic phases have been studied, and data for these are listed in Table VII. Excluding the linear or apparently-linear species, which are undoubtedly anomalous and incompletely understood, the mean value of $|\delta_\theta|$ for the compounds in Table VII is 5.4°, and the mean value of $|\delta_r|$ is 0.058 Å indicating remarkably good agreement with the hard atom model.

Cyclic oligophosphates again display configurations in remarkable accord with the predictions of the hard atom model: the data are recorded in Table VIII, and for these compounds the mean value of $|\delta_\theta|$ is 2.6°, and the mean value of $|\delta_r|$ is 0.030 Å. In addition to these oligophosphates, two cyclic phosphimates have been examined: in sodium cyclotriphosphimate tetrahydrate [76] $Na_3(NHPO_2)_3 \cdot 4H_2O$, <PNP is 122.7° (calc. 119.0°) and r(P...P) is 2.954 Å, while in cyclotetraphosphimic acid dihydrate [77], $H_4(NHPO_2)_4 \cdot 2H_2O$ ($\equiv (H_3O^+)_2H_2(NHPO_2)_4^{-2}$), r(P...P) is 2.960 Å, associated with <PNP = 126°: the value expected from the hard atom model is 122°.

Structural data for linear polyphosphates and polyarsenates are recorded in Table IX. With the exception of one of the P...P distances in $Cd(PO_3)_2$ [78], the POP fragments have structures closely in accord with those expected; the mean values of $|\delta_\theta|$ and $|\delta_r|$ are 3.9° and 0.042 Å respectively. $Hg(PO_3)_2$ is [78] isostructural with $Cd(PO_3)_2$, and $Mg(NH_4)(PO_3)_3$ and $Co(NH_4)(PO_3)_3$ are [79] isostructural with $Ni(NH_4)(PO_3)_3$. In $H_5As_3O_{10}$, two thirds of the arsenic atoms are [80] tetrahedrally coordinated, and the remainder are octahedral.

Beryllates and Aluminates

Rather few condensed beryllates and aluminates have been structurally characterised. In euclase, $AlBe(SiO_4)OH$, the anion consists [81] of chains of composition $[Be_2(OH)_2(SiO_4)_2]_n^{-6n}$ in which the $(BeOBeO)_m$ backbone carries bridging SiO_4 groups: the Be...Be and Be...Si distances are 2.78 Å and 2.88 Å respectively (expected values 2.78 Å and 2.94 Å); the observed BeOBe and SiOBe angles are 118° and 124° respectively, comparable with the 118° and 129° calculated. Väyrynenite, $(Mn,Fe)Be(PO_4)OH$, has [81] a structure similar to euclase, but with PO_4 groups acting as bridges along the $(BeOBeO)_m$ chain. In this mineral the Be...Be and Be...P distances are 2.74 Å and 2.76 Å respectively (expected 2.78 Å and 2.84 Å); the observed values of <BeOBe and <BeOP are 113° and 120° respectively, and the corresponding calculated values are 116° and 126°.

The compound $Ba[AlO(OH)_2]_2$ contains [82] chains of $AlO_2(OH)_2$ tetrahedra: the Al...Al distance is 3.197 Å (hard atom value [2] 3.32 Å) associated with an AlOAl angle of 134.4° (calculated value 146.2°) indicative of some steric compression: in $K_2[Al_2O(OH)_6]$ the Al...Al distance is [83] 3.155 Å and the AlOAl angle is 131.5° (calculated 147.1°). $Ca_{17}Na_2(Al_6O_{18})_2$ contains [84] $(AlO)_6$ rings in which the aluminium atoms are four-coordinate: the Al...Al distance is 3.423 Å, associated with an AlOAl angle of 154.8° (calculated 141.2°). The phase of composition $11CaO \cdot 7Al_2O_3 \cdot CaF_2$ contains [85] a network of linked AlO_4 tetrahedra: r(Al...Al) is 3.28 Å and <(AlOAl) is 137° (calculated 141°).

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TABLE VII. Phosphates and Arsenates containing Double and Triple Tetrahedra.

Compound	Space Group	r(M–O)/Å	r(M...M)/Å	$<(MOM)_{obs}/°$	$<(MOM)_{calc}/°$	$\|\delta_\theta\|/°$	$\|\delta_r\|/Å$	Ref.
$Na_4P_2O_7$	$P2_12_12_1$	1.637	2.936	127.5	124.7	2.8	0.036	a
$Na_4P_2O_7\cdot 10H_2O$	C2/c	1.612	2.924	130.2	128.2	2.0	0.024	b
$Na_2(H_2P_2O_7)\cdot 6H_2O$	C2/c	1.598	2.964	136.1	130.3	5.8	0.064	c
$K_4P_2O_7\cdot 3H_2O$	$P2_1/c$	1.636	2.969	130.3	124.8	5.5	0.069	d
$K_3(HP_2O_7)\cdot 3H_2O$	$P2_1/c$	1.615	2.956	132.8	128.5	4.3	0.056	e
$KAlP_2O_7$	$P2_1/c$	1.607	2.827	123.2	128.9	5.7	0.073	f
SiP_2O_7-III	$P2_1/c$	1.589	2.979	139.2	131.7	7.5	0.079	g
SiP_2O_7-IV	$P2_1/c$	1.59	2.91	132	132	0	0.01	h
α-$Mg_2P_2O_7$	$P2_1/c$	1.591	3.026	144.0	131.4	12.6	0.126	i
α-$Ca_2P_2O_7$	$P2_1/c$	1.597	2.895	130.0	130.4	0.4	0.005	j
α-$Sr_2P_2O_7$	Pnma	1.598	2.905	130.7	130.3	0.4	0.005	k
α-$Co_2P_2O_7$	$P2_1/c$	1.583	3.003	143.1	132.7	10.4	0.103	l
α-$Ni_2P_2O_7$	$P2_1/c$	1.602	2.981	137.0	129.7	7.3	0.081	m
α-$Cu_2P_2O_7$	C2/c	1.58	3.10	157	133	24	0.20	n
α-$Zn_2P_2O_7$	Cc	1.582	3.041	148.0	132.9	15.1	0.141	o
		1.603	3.003	139.0	129.5	9.5	0.103	
β-$Mg_2P_2O_7$	C2/m	1.557	3.114	180	137.3	42.7	0.214	p
β-$Ca_2P_2O_7$	$P4_1$	1.603	2.991	137.8	129.5	8.3	0.091	q
		1.627	2.955	130.5	126.1	4.4	0.055	
β-$Cu_2P_2O_7$	C2/m	1.542	3.084	180	140.2	39.8	0.184	r
β-$Zn_2P_2O_7$	C2/m	1.569	3.138	180	135.1	44.9	0.238	s
$Mn_2P_2O_7$	C2/m	1.571	3.142	180	134.7	45.3	0.242	r
$Cd_2P_2O_7$	$P\bar{1}$	1.625	2.972	132.3	126.3	6.0	0.072	t
ZrP_2O_7	Pa3	1.56	3.12	180	137	43	0.22	u
$Na_4As_2O_7$	C2/c	1.783	3.141	123.5	129.1	5.6	0.079	v
$Mg_2As_2O_7$	C2/m	1.671	3.342	180	149.0	31.0	0.122	w
$Na_5P_3O_{10}$-I	C2/c	1.64	2.87	122	124	2	0.03	x
$Na_5P_3O_{10}$-II	C2/c	1.64	2.87	122	124	2	0.03	y
$Zn_2(HP_3O_{10})\cdot 6H_2O$	$P\bar{1}$	1.613	2.912	129.0	128.0	1.0	0.012	z
		1.607	2.915	130.2	128.9	1.3	0.015	
$Zn_5(P_3O_{10})_2\cdot 17H_2O$	$P\bar{1}$	1.612	2.936	131.2	128.2	3.0	0.036	aa
		1.611	2.901	128.4	128.3	0.1	0.001	
$K_4(P_3O_9NH_2)\cdot 4H_2O$	$P\bar{1}$	1.60	2.92	132	130	2	0.02	bb
		1.62	2.92	129	127	2	0.02	

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TABLE VIII. Cyclic Phosphates.

Compound	Space Group	r(P–O)/Å	r(P...P)/Å	<(POP)$_{obs}$/°	<(POP)$_{calc}$/°	$\lvert\delta_\theta\rvert$/°	$\lvert\delta_r\rvert$/Å	Ref.
$Na_3(P_3O_9)$	Pnma	1.615	2.889	126.9	127.7	0.8	0.011	a
$Na_3(P_3O_9)\cdot H_2O$	Pnma	1.620	2.861	124.1	127.0	2.9	0.039	b
$Na_3(P_3O_9)\cdot 6H_2O$	$P\bar{1}$	1.613	2.866	125.4	128.0	2.6	0.034	c
$LiK_2(P_3O_9)\cdot H_2O$	$P2_1/c$	1.613	2.908	128.7	128.0	0.7	0.008	d
$Sr_3(P_3O_9)_2\cdot 7H_2O$	Pnma	1.617	2.896	127.3	127.5	0.2	0.004	e
$Ba_3(P_3O_9)_2\cdot 6H_2O$	$P\bar{1}$	1.612	2.886	127.0	128.2	1.2	0.014	f
		1.610	2.882	127.0	128.5	1.5	0.018	
$Ba_2Zn(P_3O_9)_2\cdot 10H_2O$	C2/c	1.620	2.895	126.6	127.0	0.4	0.005	g
$Cd_3(P_3O_9)_2\cdot 10H_2O$	$P2_1/c$	1.601	2.908	131.1	129.8	1.3	0.008	h
$Ag_3(P_3O_9)\cdot H_2O$	$P\bar{1}$	1.612	2.885	127.1	128.2	1.1	0.015	i
$(NH_4)_4(P_4O_{12})$	Cmca	1.615	2.933	130.5	127.7	2.8	0.033	j
$Na_4(P_4O_{12})\cdot 4H_2O$	$P2_1/c$	1.609	2.953	133.2	128.6	4.6	0.053	k
$Na_4(P_4O_{12})\cdot 4H_2O$	$P\bar{1}$	1.597	2.978	137.6	130.4	7.2	0.078	l
		1.605	2.908	129.9	129.2	0.7	0.008	
$Mg_2(P_4O_{12})$	C2/c	1.590	2.929	134.2	131.6	2.6	0.029	m
		1.595	2.986	138.8	130.8	8.0	0.086	
$Ca(NH_4)_2(P_4O_{12})\cdot 2H_2O$	$P2_1/c$	1.609	2.912	129.7	128.6	1.1	0.012	n
$SrK_2(P_4O_{12})$	$I\bar{4}$	1.598	2.869	127.7	130.3	2.6	0.031	o
$Cu_2(P_4O_{12})$	C2/c	1.590	2.959	137.0	131.6	5.4	0.059	p
$Al_4(P_4O_{12})_3$	$I\bar{4}3d$	1.51	2.87	144	148	4	0.03	q
$Tl_4(P_4O_{12})$	$P\bar{4}2_1c$	1.63	2.99	133	126	7	0.09	r
$Na_4(NH_4)(P_5O_{15})\cdot 4H_2O$	$P\bar{1}$	1.605	2.915	130.5	129.2	1.3	0.015	s
$Na_6(P_6O_{18})\cdot 6H_2O$	Ccmb	1.615	2.903	128.1	127.7	0.4	0.003	t

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TABLE IX. Linear Polyphosphates and Polyarseantes.

Compound	Space Group	r(M–O)/Å	r(M...M)/Å	$<(MOM)_{obs}/°$	$<(MOM)_{calc}/°$	$\|\delta_\theta\|/°$	$\|\delta_r\|/Å$	Ref.
$NaPO_3$	$P2_1/c$	1.62	2.86	124	127	3	0.04	a
		1.59	2.96	136	131	5	0.06	
$NaPO_3$	$P2_1/c$	1.57	2.93	139	136	3	0.03	b
		1.59	2.93	135	132	3	0.03	
KPO_3	$P2_1/c$	1.61	2.91	130	129	1	0.01	c
		1.60	2.92	132	130	2	0.02	
$RbPO_3$	$P2_1/c$	1.62	2.92	129	128	1	0.02	d
$AgPO_3$	$P2_1/c$	1.60	2.83	125	131	6	0.07	a
		1.59	2.93	134	132	2	0.03	
$Cd(PO_3)_2$	Pbca	1.56	3.06	157	137	20	0.16	e
		1.57	2.82	128	135	7	0.08	
$Pb(PO_3)_2$	$P2_1/c$	1.561	2.946	141.5	136.5	5.0	0.046	f
$Yb(PO_3)_3$	$P2_1/c$	1.59	2.96	137	131	6	0.06	g
$Bi(PO_3)_3$	$P2_1/c$	1.593	2.951	135.8	131.1	4.7	0.051	h
$CuLi(PO_3)_3$	$P2_12_12_1$	1.590	2.912	132.8	131.6	1.2	0.012	i
$Na_2H(PO_3)_3$	$P\bar{1}$	1.610	2.925	130.7	128.5	2.2	0.025	j
$Ni(NH_4)(PO_3)_3$	R3	1.61	2.89	128	128	0	0.01	k
$CuNa_2(PO_3)_4$	C2/c	1.589	2.927	134.0	131.7	2.3	0.027	l
$CdBa(PO_3)_4$	$P2_1/c$	1.590	2.951	136.3	131.6	4.7	0.051	m
$CoK_2(PO_3)_4$	Cc	1.594	2.971	137.9	130.9	7.0	0.071	n
$CuK_2(PO_3)_4$	Cc	1.596	2.963	136.7	130.6	6.1	0.063	n
$BiH(PO_3)_4$	$P\bar{1}$	1.588	2.925	133.9	131.9	2.0	0.025	o
$Ba_2Cu(PO_3)_6$	$P2_1/c$	1.593	2.921	133.1	131.1	2.0	0.021	p
$LiAsO_3$	C2/c	1.766	3.188	129.0	131.5	2.5	0.032	q
$NaAsO_3$	$P\bar{1}$	1.773	3.205	129.3	130.5	1.2	0.015	r
$H_5As_3O_{10}$	$P\bar{1}$	1.691^t 1.871^o	3.225	129.7	129.4	0.5	0.005	s
		1.688^t 1.833^o	3.142	126.3	132.3	6.0	0.078	

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