

structure is viewed along the b axis. This projection illustrates very clearly that the external shape of a crystal – in this case the prominence of $\{10\bar{1}\}$ – is a function of the packing of the molecules in the crystal lattice.

We are indebted to Professor R. W. Asmussen, Chemical Laboratory B, Technical University of Denmark for his kind interest and support during the final stages of this research.

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Effective Ionic Radii in Oxides and Fluorides*

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(Received 8 May 1968)

An empirical set of 'effective' ionic radii has been compiled by the use of techniques similar to those of Goldschmidt. The actual radius values were derived from: (1) 1000 experimental interatomic distances and (2) an approximately linear relationship between ionic volume and unit cell volume of over 60 isotopic series of oxides and fluorides. These radii take into account electronic spin state and the coordination of both cations and anions and have been found to reproduce closely the experimental interatomic distances in most oxides and fluorides. The choice of absolute values for anion radii and certain deviations from additivity are important and must be taken into consideration.

Introduction

The traditional sets of ionic radii of Goldschmidt, Barth, Lunde & Zachariasen (1926), Pauling (1927), Zachariasen (1931), and Ahrens (1952) have been used with considerable success by chemists, physicists, mineralogists, and crystallographers alike. Ionic radii have been important to the crystal chemist because structure types and cation coordination numbers are determined principally by cation/anion radius ratios. The ability to substitute one cation for another in a particular structure is largely dependent upon matching ionic radii; thus, good values of ionic radii have been important to the chemist synthesizing inorganic compounds. The crystallographer has found radii helpful in comparing experimental interatomic distances with those

calculated for other structures.* These interatomic distances in turn can help the chemist to infer oxidation states.

There are, however, several deficiencies in these traditional sets of radii: (1) they do not reproduce interatomic distances to the accuracy now possible in modern structural analyses; (2) although several papers (Pauling, 1927; Zachariasen, 1931) present techniques for calculating the effect of coordination number on *interatomic distances*, no provision is made for determining

* Goldschmidt's & Pauling's radii and correction factors for coordination number (CN) \neq VI were included in Volume II of *Internationale Tabellen zur Bestimmung von Kristallstrukturen* (1935). Interatomic distances in numerous inorganic compounds were published in Volume III of *International Tables for X-Ray Crystallography* (1962) and in *Tables of Interatomic Distances and Configuration in Molecules and Ions* (1958, 1965).

* Contribution No. 1454.

values of the *radii* in other than octahedral coordination; (3) the effect of variations in electronic spin state on radii has not been included.

This paper presents an extensive table of empirical radii that can be used to closely reproduce average observed cation-anion distances in most oxide and fluoride crystal structures. These radii, which take into consideration both anion and cation coordination and electronic spin state, were derived from over 1000 average interatomic distances. Certain radii were made consistent with regular plots of effective ionic radii (r) or volume (r^3) *vs.* (1) unit cell volumes for over 60 isotopic series of compounds, (2) electron configuration, (3) coordination number (CN), and/or (4) valence.

Background of ionic radii

Crystal chemists have tried for many years to treat atoms and ions as hard spheres and to calculate atomic and ionic radii that would closely reproduce interatomic distances. Approximate additivity of atomic and ionic radii was noted by the earliest investigators (Goldschmidt *et al.*, 1926; Pauling, 1927; Zachariasen, 1931). However, since the additivity of a given set of radii was not found applicable to all bond types, separate tables of radii were derived for ionic, covalent, and metallic bonding. The history of radii determinations for ionic compounds, treated in detail by Pauling (1927), Ahrens (1952), Slater (1964), and Tosi (1964), will be reviewed here only briefly to point out similarities and differences in the methods.

The first attempt at such determinations was by Bragg (1920) who derived a set of atomic radii which reproduced interatomic distances in both ionic and metallic crystals to an average deviation of about 0.06 Å. Bragg & West (1927) later revised these radii so as to be more in accord with Wasastjerna's (1923) conclusion that $r(\text{O}^{2-}) = 1.32$ Å. * Bragg & West arrived at a value of $r(\text{O}^{2-}) = 1.35$ Å from close-packed oxygen structures. Goldschmidt *et al.* (1926) derived a set of radii to be used only in ionic crystals. Goldschmidt's radii were obtained from average interatomic distances using Wasastjerna's radii of $r(\text{O}^{2-}) = 1.32$ Å and $r(\text{F}^-) = 1.33$ Å. Because structural data were scarce, Goldschmidt's table was necessarily limited. However he was able to extend the table to cover radii for which there were no experimental interatomic distances by interpolation or extrapolation of unit-cell dimensions of isotopic series *e.g.* In^{3+} , Y^{3+} , and Tl^{3+} from the C rare earth oxide structure type. If his radii are based on $r(\text{O}^{2-}) = 1.40$ Å, the value generally used by later investigators, they agree well with more recent sets of radii. Goldschmidt was the first to note that radii varied with coordination number and provided a few examples of this variation.

* Throughout this paper a Roman numeral at the upper left of the element will be used to designate CN. Thus, $^{\text{X}}\text{Ba}^{2+}$ refers to the ten-coordinated barium ion. If no symbol for CN is present, six coordination is implied.

Pauling (1927) calculated a set of radii based on an inverse variation with effective nuclear charge in isoelectronic series of the alkali ions. The radii of the alkali ions were determined from interatomic distances in alkali halides assuming $r(\text{O}^{2-}) = 1.40$ Å and $r(\text{F}^-) = 1.36$ Å. Pauling prepared two tables of radii: (1) a univalent set from which radii of ions of any charge could be calculated and (2) a table of ionic octahedral crystal radii (ionic radii for multivalent ions). A correction factor was provided to allow calculation of interatomic distances in crystals where the CN of the cation differed from six. However, the coordination of the anion was neglected. Pauling (1928) noted that additivity in the alkali halides alone was poor and introduced extra terms in the expression for interatomic distance to correct for cation-cation and anion-anion repulsion. With these corrections, calculated and observed distances agreed to within about 0.001 Å.

Subsequently, Zachariasen (1931) derived a set of radii from the best available interatomic distances, assuming $r(\text{K}^+) = 1.33$ Å and $r(\text{Cl}^-) = 1.81$ Å. He calculated univalent radii using Pauling's (1927) method and provided equations with which interatomic distances could be calculated if valence and CN of the cation were known. Zachariasen's radii differed considerably from Pauling's but not from Goldschmidt's corrected radii using $r(\text{O}^{2-}) = 1.40$ Å. Although Zachariasen's radii reproduced interatomic distances quite accurately, they seem to have been used less than some of the other sets of radii. Ahrens' or Pauling's radii were probably preferred because of the simplicity of extracting radii directly from a table rather than of calculation from univalent radii with corrections for valence and CN. However, even Zachariasen's table did not allow direct comparison of cation radii when the cation CN was different from 6, nor did it differentiate between high and low spin ions.

The next extensive list of radii was prepared by Ahrens (1952) who revised Pauling's radii by the use of slightly different values for the alkali ions. His method utilized the regularities found by plotting radii *vs.* ionization potentials. The regular curves obtained by Ahrens were used to estimate the radii of ions for which no values previously existed. Ahrens' table was thus the most complete table for many years and consequently was widely used. However, Ahrens considered only octahedral radii and made no provision for variation of radius with electronic spin state.

More recently, two further sets of radii were introduced. Slater (1964) extended the idea of Bragg (1920) and published a table of atomic radii in which $r(\text{VI}\text{O}^{2-}) = 0.60$ Å, which reproduced interatomic distances in 1200 metallic, covalent, and ionic solids to a deviation of ± 0.12 Å. These radii have not proved to be particularly useful in oxide and fluoride crystal chemistry. Fumi & Tosi (1964) derived a set of ionic radii for the alkali halides based on (1) a correlation between Born repulsive parameters and the ratio r_c/r_a in alkali halides and (2) the minimum in the LiF and NaCl electron

density maps. Their most significant conclusion was that the ratio r_c/r_a is much larger than that found in all the other traditional sets of radii. Fumi & Tosi's cation and anion crystal radii are larger and smaller respectively by ~ 0.2 Å than the traditional radii. These radii will be considered in more detail in the discussion.

The advent of accurate structure analysis by the use of Guinier d -value data, intensities collected with counter diffractometers, and least-squares refinements of crystal structures has provided a wealth of new accurate cell dimensions and interatomic distances. These data have been used in our derivation of an empirical set of 'effective' ionic radii by an extension of Goldschmidt's (1926) method, with the further assumption that the radii of the anions also vary with CN. This derivation uses approximately 1000 interatomic distances in oxides and fluorides, assumes $r(\text{VI O}^{2-}) = 1.40$ Å and $r(\text{VI F}^-) = 1.33$ Å, and takes into consideration both coordination number and electronic spin state of first-row transition metal ions. Low-spin tetrahedrally coordinated ions and high-spin second-row transition-metal ions are not included because of their infrequent occurrence. The term 'effective' ionic radii is used to emphasize the fact that these radii are empirical and include effects of covalency in specific metal-oxygen or metal-fluorine bonds. We feel these radii more closely reproduce interatomic distances in solids than the previous sets of radii and will be more useful to those who wish to compare radii rather than interatomic distances.

Methods of determining 'effective' ionic radii

Assumptions

It has already been shown that interatomic distances (and therefore 'effective' ionic radii) depend on CN (Goldschmidt, 1926), electronic spin state (van Santen & van Wieringen, 1952; Blasse, 1965), covalency (Pauling, 1927), and the presence of strong anion-anion or cation-cation repulsive forces (Pauling, 1928). Changes due to CN variation are of the order of 0.0–0.3 Å; those due to change in magnetic spin state are ~ 0.1 Å. The changes due to covalency effects are unknown but are probably reasonably constant for combinations of cations with anions whose electronegativities are approximately the same. Repulsive forces cause changes in the order of 0.0–0.1 Å.

In deriving the set of 'effective' ionic radii listed in Table 1(a) the following assumptions were made:

(1) The principle of additivity of both cation and anion radii to accurately reproduce interatomic distances is valid if one takes into consideration CN, electronic spin, covalency, and repulsive forces. (Repulsive forces are discussed further in another section.)

(2) The effect of covalency in shortening $M-X$ bonds is comparable in all $M-F$ or $M-O$ bonds (Phillips & Williams, 1965).

(3) With the exceptions noted in assumption 1, radii are independent of structure type.

(4) The radii of both cation and anion vary with coordination number. (The variation in anion radii with CN is discussed in detail in another section.)

(5) Although individual cation-anion distances vary in a polyhedron, the average cation-anion distance over all similar polyhedra in one structure is constant.

(6) With a constant anion, the volume of the unit cells of isostructural series is proportional to the volume of the cations.

Assumption 5 is not basically different from 6 in that it says an ion can be deformed in any fashion but the total volume of the polyhedron will not change.* The test of assumptions 1–6 is the consistency of radii derived from different structures.

The principle of obtaining radii from relative unit volumes for a particular structure type was originated by Grimm & Wolff (1926) and Goldschmidt *et al.* (1926). Goldschmidt estimated the radii of numerous rare earth ions by comparing cell volumes of rare earth oxides with those of Sc_2O_3 and Y_2O_3 for which interatomic distances were known. A similar procedure was used by others to obtain sets of radii applicable to certain structures: Templeton & Dauben (1954) – rare earth fluorides, chlorides, oxychlorides, and oxides; Geller (1957) – oxide perovskites; Geller & Mitchell (1959) – garnets; Roth & Schneider (1960) – rare earth oxides; Sasvári (1960) – rocksalt, rutile, fluorite, and antiferroite compounds; Knox (1961) – fluoride perovskites; and Espinosa (1962) – garnets.

Procedure

As a first approximation, anion radii (O^{2-} and F^-) with CN=III, IV, and VI were determined by subtracting Ahrens' sixfold radii from interatomic distances in simple oxide structures: III – rutile; IV – corundum and *C* rare earth; VI – rocksalt. In a second step, cation radii for various CN's were determined. These radii were in turn used to obtain anion radii with CN=II, III, IV, and VIII. The results are listed in Table 2. The values in parentheses represent anion radii obtained at a later stage by repeating this procedure with appropriate refined cation radii, *e.g.* in quartz $r(\text{II O}^{2-}) = R_{\text{av}}(\text{Si-O}) - r(\text{IV Si}^{4+}) = 1.607 - 0.26 = 1.347$ Å. The consistency of these values can be taken as a measure of their validity.

* The approximate linearity of radii-volume plots has been shown by Bertaut & Forrat (1957) for $\text{A}_3\text{B}_5\text{O}_{12}$ garnets, by Whinfrey, Eckart & Tauber (1960), and Brisse & Knop (1968) for $\text{A}_2\text{B}_2\text{O}_7$ pyrochlores, by Gattow (1963, 1964) for A_2BX_4 compounds, by Pannetier & Courtine (1966) for ABO_4 , by Giglio (1963) for ABX_6 , by Sasvári (1960) for AX_2 and by Roth & Schneider (1960) for A_2O_3 . Sasvári also corrected certain radii of Ahrens to comply with this regularity and derived a set of eight-coordinated radii from the fluorite structures. Although Giglio, Gattow, and Pannetier & Courtine plotted r vs. V , we feel that it is more correct to plot r^3 vs. V or r vs. A (cubic). The excellent linearity in simple oxide structures (rocksalt, rutile, corundum and *C* rare-earth) supports this view.

EFFECTIVE IONIC RADII IN OXIDES AND FLUORIDES

Table 1(a). *Effective ionic radii*

ION	EC	CN	SP	A-IR	CR	'IR'	ION	EC	CN	SP	A-IR	CR	'IR'	
AC+3	6P	6	VI		1.18		CS+1	5P	6	XII		2.02	1.88	
AG+1	4D10	II				.81	CU+1	3D10	II			.60	.46	
		IVSq				1.16			VI		.96			
		V				1.26		CU+2	3D	9	IVSq		.76	
		VI		1.26		1.12			V				.62	
		VII				1.29			VI		(.72)	.79	.65	
		VIII				1.38			VI		.92	1.048	.73	
AG+2	4D	9	VI		.89	1.44		DY+3	4F	9	VI		1.03	
AG+3	4D	8	IVSq						VIII		.89	1.17	1.03	
AL+3	2P	6	IV			.53		ER+3	4F11	VI		1.021	.881	
		V				.62			VIII			1.14	1.00	
		VI		.51		.670		EU+2	4F	7	VI		1.31	1.17
AM+3	5F	6	VI		1.07	1.15			VIII			1.39	1.25	
AM+4	5F	5	VI		.92	1.01	R	EU+3	4F	6	VI	.98	1.090	.950
		VIII				1.09	.95	F -1	2P	6	II		1.21	1.07
AS+3	4S	2	VI	(.58)					III			1.145	1.285	
AS+5	3D10	IV				.475			IV			1.16	1.30	
		VI				.64	.50		VI		1.33	1.17	1.31	
AT+7	5D10	VI						F +7	15	2	VI	.08	1.19	1.33
AU+1	5D10	VI						FE+2	3D	6	IV		.77	.63
AU+3	5D	8	IVSq			.84	.70		VI		HS	.75	.61	
		VI		(.85)					VI		LS	.910	.770	
B +3	1S	2	III			.16	.02	FE+3	3D	5	IV		.63	.49
		IV				.26	.12		VI		HS	.69	.55	
		VI				.23			VI		LS	.64	.55	
BA+2	5P	6	VI		1.34	1.50	1.36	FR+1	6P	6	VI	1.80	.785	.645
		VII				1.53	1.39		VI					
		VIII				1.56	1.42	GA+3	3D10	IV			.61	.47
		IX				1.61	1.47		V				.69	.55
		X				1.66	1.52		VI		.62	.760	.620	
		XII				1.74	1.60	GD+3	4F	7	VI	.97	1.078	.938
BE+2	1S	2	III			.31	.17		VII		(.73)	1.20	1.06	
		IV				.41	.27	GE+2	4S	2	VI			
		VI		.35				GE+4	3D10	IV		.53	.54	.40
BI+3	6S	2	V			1.13	.99	H +1	1S	0	I		-.24	-.38
		VI		(.96)		1.16	1.02		II				-.04	-.18
		VIII				1.25	1.11	HF+4	4F14	VI	.78	.85	.71	
BI+5	5D10	VI			.74				VIII				.97	.83
BK+3	5F	8	VI			1.10	.96	HG+1	6S	1	III		1.11	.97
BK+4	5F	7	VIII			1.07	.93	HG+2	5D10	II			.83	.69
BR-1	4P	6	VI		1.96				IV			1.10	1.10	.96
BR+7	3D10	VI			.39				VI		1.10	1.16	1.02	
C +4	1S	2	III			.06	-.08	HO+3	4F10	VI	.91	1.28	1.14	
		IV				.15P			VII			1.034	.894	
		VI				.16			VIII			1.16	1.02	
CA+2	3P	6	VI		.99	1.14	1.00	I -1	5P	6	VI	2.20		
		VII				1.21	1.07	I +5	5S	2	VI	.62	1.09	.95
		VIII				1.26	1.12	I +7	4D10	VI		.50		
		IX				1.32	1.18	IN+3	4D10	VI	.81	.930	.790	
		X				1.42	1.28		VII			1.063	.923	
		XII				1.49	1.35	IR+3	5D	6	VI		.87	.73
CD+2	4D10	IV				.98	.84	IR+4	5D	5	VI	.68	.77	.63
		V				1.01	.87	K +1	3P	6	VI	1.33	1.52	1.38
		VI		.97		1.09	.95		VII			1.60	1.46	
		VII				1.14	1.00		VIII			1.65	1.51	
		VIII				1.21	1.07		IX			1.69	1.55	
		XII				1.45	1.31		X			1.73	1.59	
CE+3	6S	1	VI		1.07	1.174	1.034		XII			1.74	1.60	
		VIII				1.28	1.14	LA+3	4D10	VI	1.14	1.201	1.061	
		XII				1.43	1.29		VII			1.24	1.10	
CE+4	5P	6	VI		.9	.94	.80		VIII			1.32	1.18	
		VII				1.11	.97		IX			1.34	1.20	
CF+3	6D	1	VI			1.09	.95		X			1.42	1.28	
CL-1	3P	6	VI		1.81				XII			1.46	1.32	
CL+5	3S	2	III			.26	.12	LI+1	1S	2	IV		.73	.59
CL+7	2P	6	IV			.34	.20		VI		.68	.88	.74	
		VI		.27				LU+3	4F14	VI	.85	.988	.848	
CM+3	5F	7	VI			1.12	.98		VIII			1.11	.97	
CM+4	5F	6	VIII			1.09	.95	MG+2	2P	6	IV		.63	.49
CO+2	3D	7	VI			.79	.65		VI		.66	.860	.720	
		LS		.72		.875	.735		VIII			1.03	.89	
		HS				.665	.525	MN+2	3D	5	VI	LS	.81	.67
CO+3	3D	6	VI			.75	.61		VI		HS	.960	.820	
		LS		.63		.87	.73		VIII			1.07	.93	
CR+2	3D	4	VI			.96	.82		VI			.72	.58	
		LS				.755	.615	MN+3	3D	4	V		.72	.58
CR+3	3D	3	VI		.63				VI		LS	.79	.65	
CR+4	3D	2	IV			.58	.44		VI		(.66)	.680	.540	
		VI				.69	.55	MN+4	3D	3	VI		.41	.27
CR+5	3D	1	IV			.490	.350		IV		(.60)	.680	.540	
		VIII				.71	.57	MN+6	3D	1	IV		.41	.27
CR+6	3P	6	IV			.44	.30	MN+7	3P	6	IV		.40	.26
		VI				.52			VI		.46			
CS+1	5P	6	VI		1.67	1.84	1.70	MO+3	4D	3	VI		.81	.67
		IX				1.92	1.78	MO+4	4D	2	VI	.70	.790	.650
		X				1.95	1.81	MO+5	4D	1	VI		.77	.63
								MO+6	4P	6	IV		.56	.42

Table 1(a) (cont.)

ION	EC	CN	SP	A-IR	CR	'IR'	ION	EC	CN	SP	A-IR	CR	'IR'	
MO+6	4P	6	V		.64	.50	S +6	2P	6	VI	.30			
			VI	.62	.74	.60	SB+3	5S	2	IVPY		.91	.77	
			VII	(.16)	.85	.71				V		.94	.80	
N +3	2S	2	VI						VI	(.76)				
N +5	1S	2	III		.02	-.12	SB+5	4D10	VI		.62	.75	.61	
			VI	.13			SC+3	3P	6	VI	.81	1.870	.730 R*	
NA+1	2P	6	IV		1.13	.99			VIII		1.01	.87	R	
			V		1.14	1.00	SE-2	4P	6	VI	1.98P			
			VI	.97	1.16	1.02	SE+4	4S	2	VI	(.50)			
			VII		1.27	1.13	SE+6	3D10	IV			.43	.29	
			VIII		1.30	1.16			VI		.42			
			IX		1.46	1.32	SI+4	2P	6	IV		.40	.26	*
NB+2	4D	3	VI		.85	.71			VI		.42	1.540	.400 R*	
NB+3	4D	2	VI		.84	.70	SM+3	4F	5	VI	1.00	1.104	.964 R	
NB+4	4D	1	VI	(.74)	.83	.69			VIII		1.23	1.09	R	
NB+5	4P	6	IV		.46	.32	SN+2	5S	2	VI	.93			
			VI	.69	.78	.64			VIII		1.36	1.22	R	
			VII		.80	.66	SN+4	4D10	VI	.71	.830	.690 R*		
ND+3	4F	3	VI	1.04	1.135	.995	SR+2	4P	6	VI	1.12	1.30	1.16	
			V		1.26	1.12			VII		1.35	1.21		
			VIII		1.23	1.09			VIII		1.39	1.25		
NI+2	3D	8	VI	.69	.840	.700 R*			X		1.46	1.32		
NI+3	3D	7	VI	LS	.70	.56			XII		1.58	1.44		
			HS		.74	.60	TA+3	5D	2	VI		.81	.67	
NP+2	5F	5	VI		1.24	1.10	TA+4	5D	1	VI		.80	.66	R
NP+3	5F	4	VI	1.10	1.18	1.04	TA+5	5P	6	VI	.68	.78	.64	
NP+4	5F	3	VI	.95					VIII		.83	.69		
			VIII		1.12	.98	TB+3	4F	8	VI	.93	1.063	.923 R	
NP+7	6P	6	VI	.71					VIII		1.18	1.04	R	
O -2	2P	6	II		1.21	1.35	TB+4	4F	7	VI	.81	.90	.76	R
			III		1.22	1.36			VIII		1.02	.88	.88	
			IV		1.24	1.38	TC+4	4D	3	VI		.78	.64	R
			VI	1.40	1.26	1.40	TC+7	4P	6	VI		.56		
			VII		1.28	1.42	TE-2	5P	6	VI	2.21P			
OS+4	5D	4	VI	.69	.770	.630	TE+4	5S	2	III		.66	.52	
P +3	3S	2	VI	(.44)					IV	(.70)				
P +5	2P	6	IV		.31	.17			VI		.56			
			VI		.35		TE+6	4D10	VI		1.02	1.14	1.00	
PA+3	5F	2	VI	1.13			TH+4	6P	6	VI		1.20	1.06	
PA+4	6D	1	VI	.98					VII		1.23	1.09		
			VIII		1.15	1.01			IX		1.00	.86	E	
PA+5	6P	6	VI	.89			TI+2	3D	2	VI		.81	.67	R
			IX		1.09	.95	TI+3	3D	1	VI	(.76)	.67	.53	
PB+2	6S	2	IVPY		1.08	.94	TI+4	3P	6	V		.68	.745	.605 R*
			VI	1.20	1.32	1.18			VI		1.47	1.64	1.50	
			VII		1.45	1.29	TL+1	6S	2	VI		1.74	1.60	R
			IX		1.47	1.33			VIII		1.90	1.76	R	
			XI		1.53	1.39	TL+3	5D10	VI	.95	1.020	.880	R	
			XII		1.63	1.49			VII		1.14	1.00	R	
PB+4	5D10	VI		.84	.915	.775	TM+3	4F12	VI	.87	1.009	.869	R	
			VIII		1.08	.94	U +3	5F	3	VI		1.13	.99	R
PD+1	4D	9	VI		.73	.59	U +4	5F	2	VI	.97	1.20	1.06	R
PD+2	4D	8	IVSQ		.78	.64			VII		1.12	.98		
			VI	(.80)	1.00	.86			VIII		1.14	1.00	R*	
PD+3	4D	7	VI		.90	.76			IX		1.19	1.05		
PD+4	4D	6	VI		.65	.62	U +5	5F	1	VI		.90	.76	
PM+3	4F	4	VI	1.06	1.119	.979			VII		1.10	.96		
PO+4	6S	2	VIII		1.24	1.10	U +6	6P	6	VI		.59	.45	
PO+6	5D10	VI		.67					IV		.62	.48		
PR+3	4F	2	VI	1.06	1.153	1.013			VI	.80	.89	.75		
			VIII		1.28	1.14			VII		1.02	.88		
PR+4	4F	1	VI	.92	.92	.78			VI		.93	.79		
			VIII		1.13	.99	V +2	3D	3	VI	(.88)	.780	.640	R
PT+2	5D	8	VI	(.80)			V +3	3D	2	VI	(.74)	.73	.59	R
PT+4	5D	6	VI	(.65)	.77	.63	V +4	3D	1	VI	(.63)	.495	.355	R
PU+3	5F	5	VI	1.08	1.14	1.00			V		.60	.46	*	
PU+4	5F	4	VI	.93	.94	.80			VI	.59	.68	.54		
			VII		1.10	.96	W +4	5D	2	VI	.70	.790	.650	R
RA+2	6P	6	VI	1.43			W +6	5P	6	IV		.55	.41	*
RB+1	4P	6	VI	(1.47)	1.63	1.49			VI	.62	.72	.58		
			VII		1.70	1.56			VII	.92	1.032	.892	R*	
			VIII		1.74	1.60	Y +3	4P	6	VI		1.155	1.015	R*
			XII		1.87	1.73			VII		1.24	1.10		
RE+4	5D	3	VI	(.72)	.77	.63	YB+3	4F13	VI	.86	.998	.858	R	
RE+5	5D	2	VI		.66	.52			VIII		1.12	.98	R	
RE+6	5D	1	VI		.66	.52			IV		.74	.60	*	
RE+7	5P	6	VI		.54	.40			V		.82	.68		
			IV	.56	.71	.57			VI	.74	.885	.745	R*	
RH+3	4D	6	VI	.68	.805	.665			VI	.79	.86	.72	R	
RH+4	4D	5	VI		.755	.615	ZR+4	4P	6	VI		.92	.78	
RU+3	4D	5	VI		.82	.68			VII		.98	.84		
RU+4	4D	4	VI		.67	.760			VIII					
S -2	3P	6	VI	1.84P										
S +4	3S	2	VI	(.37)										
S +6	2P	6	IV		.26	.12							*	

EC - electron configuration, CN - coordination number, SP - electronic spin, A-IR - Ahrens ionic radii (CN=VI) (Ahrens, 1952), CR - crystal radii based on $r(\text{VI}^{2+}) = 1.19 \text{ \AA}$, 'IR' - effective ionic radii based on $r(\text{VI}^{2+}) = 1.40 \text{ \AA}$.

Table 1(b). References for Table 1(a)*

- AC+3 VI
AG+1 II
PREWITT,C.T. AND R.D.SHANNON, TO BE PUBLISHED. AG FF 0P
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 1,(1963) AG P 0
- AG+1 IVS0
BYSTROM,A. AND L.EVENS, ACTA CHEM,SCAND, 6+613(1950) AG P 02
DONOHUE,J. AND L.WELSHOLZ, J. AM. CHEM. SOC. 66+295(1944) K AG C 0
SCATTURIN,V. AND P.L.BELLON, J. ELFCROCHEM.SOC. 10A,R19(1961) AR 0
- AG+1 V
JOST,K.H., ACTA CRYST. 14,779(1961) (AG P 03)X
- AG+1 VI
RODE,H., Z. ANORG. ALLGEM. CHEM, 267,62(1951) AG SR F6
KIERKEGAARD,P. AND S. HOLMEN, ARKIV KEMI 23,213(1965) AG M0 P 06
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 1,(1963) AG F
ZACHARIASEN,W.H., Z.KRIST. 8,116(1952) AG P 5 04
- AG+1 VII
KIERKEGAARD,P. AND S. HOLMEN, ARKIV KEMI 23,213(1965) AG M0 P 06
- AG+1 VIII
KROGH-MOE,J., ACTA CRYST. 10,77(1965) AG BA 013
WELLS,A.F., Z.KRIST. 95,74(1966) AR C2 (M 02)14
- AG+2 VI
AG+3 IVS0
SCATTURIN,V. AND P.L.BELLON, J. ELFCROCHEM.SOC. 10A,R19(1961) AG+1 AG+3 02
- AL+3 IV
BROWN,H.E. AND S.W.BAILEY, ACTA CRYST. 17,130(1964) K AL C13 08
BURNHAM,C.W., Z.KRIST. 118,37(1963) AL2 ST 05
EULER,F. AND J.A.BRUCE, ACTA CRYST. 19,071(1965) M3 AL5 01p
MACHATSCHKI,F., Z.KRIST. 94,222(1936) AL AS 04
MOONEY,R.C.L., ACTA CRYST. 9,728(1954) AL P 04
SCHWARZENBACH,P., Z.KRIST. 123,151(1966) AL P 04
SMITH,J.V. AND S.W.BAILEY, ACTA CRYST. 16,801(1963) AL-0
WILLIAMS,P.P. AND H.D.MEGAW, ACTA CRYST. 17,882(1965) ALRTV5
LIEBAUF,P., ACTA CRYST. 14,390(1961) LI AL 516 010
MAREZIO,M., ACTA CRYST. 19,396(1966) LI AL 02
- AL+3 V
BERTAUT,F. AND J.MARFESCHAL, COMPT.REND. 257,867(1963) Y AL 03
BURNHAM,C.W. AND M.J.BUERGER, Z.KRIST. 115,269(1961) AL2 ST 05
- AL+3 VI
BURNHAM,C.W., Z.KRIST. 118,37(1963) AL2 ST 05
CROMER,D.T. ET AL., ACTA CRYST. 22,182(1967) M3 AL (S 04)2,12 H2 0
CROMER,D.T. ET AL., ACTA CRYST. 21,383(1966) C5 AL (S 04)2,12 H2 0
EULER,F. AND J.A.BRUCE, ACTA CRYST. 19,071(1965) M3 AL5 01p
FARRELL,E.F. ET AL., AM. MINERALOGIST 48,804(1963) RE AL2 P 04
GIBBS,G.V. AND J.V.SMITH, AM. MINERALOGIST 50,209(1965) M3 AL2 ST3 01p
JACK,K.H. AND V.GUTMANN, ACTA CRYST. 4,286(1951) AL F3
MAREZIO,M. AND J.P. REMEIKA, J. CHEM. PHYS. 44,314(1966) LI AL 02
NARAY-SZABO,ST.V. AND K.SASVARI, Z.KRIST. 99,27(1964) M3 AL F6
NEWMAN,R.E. AND Y.M. DEHAAN, Z.KRIST. 117,235(1962) ALP 03
PEDERSEN,B.F., ACTA CHEM,SCAND. 16,491(1962) AL NR 04
PRANDL,W., Z.KRIST. 123,81(1966) AL2 CA3 (ST 04)3
SADANAGA,I. ET AL., ACTA CRYST. 15,68(1962) AL4 ST 08
- AM+3 VI
SHANNON,R.D. AND C.T.PREWITT, TO BE PUBLISHED. R3 VS V (LA F3)
- AM+4 VI
AM+4 VIII
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 1,(1963) AM 02
- AS+3 VI
AS+5 IV
FINNEY,J.J., AM. MINERALOGIST 48,1(1963) PR FER (AS 04)2 (M 12
FINNEY,J.J., ACTA CRYST. 21,437(1966) CU2 (AS 04) (0 H)3 H2 0
HILMER,W., ACTA CRYST. 9,87(1956) (LI AS 03)X
JOST,K.H. ET AL., ACTA CRYST. 21,408(1966) AS2 05,5/3 H2 0
LIEBAUF,P., ACTA CRYST. 9,11(1956) (M AS 03)X
LUKASZEWICZ,K., BULL. ACAD. POLON. SCI. SER. SCI. CHIM. 11,761(1966) M62 AS2 07
MACHATSCHKI,F., Z.KRIST. 94,222(1936) AL AS 04
MOONEY,R.C.L., ACTA CRYST. 1,163(1954) R1 AS 04
MORL,H. AND T. ITO, ACTA CRYST. 3,1(1950) FE3 AS 04,8 H2 0
PLIETH,K. AND G.SANGER, Z.KRIST. 124,91(1967) ZM2 CU AS2 04
POULSEN,S.J. AND C.CALVO, CAN. J. CHEM. 46,917(1968) CUS AS2 08
SCHULZE+G.E.R., Z. PHYSIK. CHEM. 248,215(1934) B AS 04
SHANNON,R.D. AND C.T.PREWITT, TO BE PUBLISHED. R3 VS V (ZTCOH)
- AS+5 VI
IBERS,J.A., ACTA CRYST. 9,967(1956) K AS F6
JOST,K.H. ET AL., ACTA CRYST. 21,808(1966) AS2 05,5/3 H2 0
- AT+7 VI
AU+1 VI
AU+3 IVS0
EINSTEIN,F.W.B. ET AL., J. CHEM. SOC. 1967,978 AU F3
- AU+3 VI
B +3 III
BLOCK,S. AND A.PERLOFF, ACTA CRYST. 19,297(1965) RA BR 07
IHARA,M. AND J.KROGH-MOE, ACTA CRYST. 20,132(1966) CD RA 07
KROGH-MOE,J., ACTA CRYST. 13,889(1966) CS2 86 01R
KROGH-MOE,J., ACTA CRYST. 15,190(1966) LI2 84 07
KROGH-MOE,J., ACTA CRYST. 18,77(1965) AG2 BA 01
KROGH-MOE,J., ACTA CRYST. 18,108(1965) K RS 08
MAREZIO,M. ET AL., ACTA CRYST. 16,799(1963) CA R2 04
MAREZIO,M. ET AL., ACTA CHEM,SCAND. 16,995(1963) K2 RA 07,4 H2 0
ZACHARIASEN,W.H. ET AL., ACTA CRYST. 16,114(1963) RE2 R 02 (0 H)
- B +3 IV
BLOCK,S. AND A.PERLOFF, ACTA CRYST. 19,297(1965) RA BR 07
CLARK,J.R., AM. MINERALOGIST 49,1549(1964) SR RA 06 (0 H)2,3 H2 0
HOARD,J.L. AND V.BLAIR, J. AM. CHEM. SOC. 57,1945(1935) RR R 24
IHARA,M. AND J.KROGH-MOE, ACTA CRYST. 20,132(1966) CD RA 07
KROGH-MOE,J., ACTA CRYST. 16,995(1963) K2 RA 07,4 H2 0
KROGH-MOE,J., ACTA CRYST. 13,889(1966) CS2 86 010
KROGH-MOE,J., ACTA CRYST. 15,190(1966) LI2 84 07
KROGH-MOE,J., ACTA CRYST. 18,77(1965) AG2 BA 01
MAREZIO,M. ET AL., ACTA CRYST. 16,978(1963) K2 RA 07,4 H2 0
MAREZIO,M. ET AL., ACTA CRYST. 16,978(1963) K2 RA 07,4 H2 0
MAREZIO,M. AND J.P. REMEIKA, J. CHEM. PHYS. 44,334(1966) LI R 02
PANT,A.K. AND D.W.J. CRUCKSHANK, Z.KRIST. 125,286(1967) CA B ST 04,0 H
PERLOFF,A. AND S.BLOCK, ACTA CRYST. 20,278(1966) SR BA 07
PREWITT,C.T. AND R.D.SHANNON, ACTA CRYST. R24,869(1968) R2 03
REMEIKA,J.P. AND M.MAREZIO, J. PHYS. CHEM. SOLIDS 26,208(1965) LI R 02
ZACHARIASEN,W.H., ACTA CRYST. 16,390(1963) H B 02
ZACHARIASEN,W.H., ACTA CRYST. 16,385(1963) H B 02
- B +3 VI
BA+2 VI
MINTA,M.V. AND S.RAMAKESHAN, Z.KRIST. 114,200(1966) RA (CL 04)2,3 H2 0
MIGHELL,A.D. ET AL., ACTA CRYST. 20,191(1966) BA B2 04
SCHNERING+H.G. ET AL., Z. ANORG. ALLGEM. CHEM. 305,201(1960) RA 2N 02
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 1,(1963) BA 0
ZACHARIASEN,W.H., Z.KRIST. 70,139(1940) BA TT ST3 09
- BA+2 VII
HILMER,W., ACTA CRYST. 15,1101(1962) BA 6E 03
SCHNERING+H.G. ET AL., Z. ANORG. ALLGEM. CHEM. 314,144(1963) RA C 0P
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 3,(1965) RA3 NT 04
- BA+2 VIII
BLAND,J.A., ACTA CRYST. 14,875(1961) RA2 TI 04
HILMER,W., ACTA CRYST. 15,1101(1962) BA 6F 03
LANDER,J.J., ACTA CRYST. 4,148(1951) BA NI 02
MANOHARAN,M. AND J.RAMAKESHAN, Z.KRIST. 119,357(1964) BA (0 H)2,8 H2 0
MARDELLI,M. AND G.FAVA, ACTA CRYST. 15,477(1962) BA 52 03,H2 0
RAO,R.V.G.S. ET AL., Z.KRIST. 110,231(1958) CU BA2 (C 0 0 H)6,4 H2 0
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 1,(1963) BA F2
- BA+2 IX
BLOCK,S. AND A.PERLOFF, ACTA CRYST. 19,297(1965) RA BR 07
COLBY,M.Y. AND L.J.B.LACOSTE, Z.KRIST. 90,1(1935) RA C 03
FOSSO, AND G. O. JONSSON, ACTA CHEM,SCAND. 10,298(1956) BA 6E 04
HARRIS,L.A. AND M.L.YAKEL, ACTA CHEM,SCAND. 12,52(1958) RA TF (S2 03)2,2 H2 0
MIGHELL,A.D. ET AL., ACTA CRYST. 20,819(1966) RA R2 DR
- BA+2 X
BLOCK,S. AND A.PERLOFF, ACTA CRYST. 19,297(1965) RA BR 07
BURLEY,G. J. RES. NATL. BUR. STD. 60,23(1958) BA M P 04
NEWMAN,R.E. AND H.D.MEGAW, ACTA CRYST. 13,303(1960) BA AL2 ST2 08
ROBERTSON,C. ET AL., J. RES. NATL. BUR. STD. 70A,395(1965) BA 6E 04
TEMPLETON,D.H. AND C.H. DAUBEN, J. CHEM. PHYS. 41,515(1964) RA T14 04
ZACHARIASEN,W.H., ACTA CRYST. 1,263(1948) RA3 P 0412
- BA+2 XII
EVANS, H.T., JR., ACTA CRYST. 4,377(1951) BA TI 03
HOARD,J.L. AND W. VINCENT, J. AM. CHEM. SOC. 62,3126(1940) BA SI F6,BA 6E F6
SAHL,K., BEITR. MINERAL. PETROG. 9,111(1963) BA 5 04
SCHNERING+H.G. ET AL., Z. ANORG. ALLGEM. CHEM. 353,13(1967) BA2 M F6
SHIRANE,G. ET AL., PHYS. REV. 105,856(1957) BA TI 03
ZACHARIASEN,W.H., ACTA CRYST. 1,263(1948) RA3 P 0412
- BE+2 III
HARRIS,L.A. AND M.L.YAKEL, ACTA CRYST. 22,354(1967) Y2 BE 04
- BE+2 IV
BURGERS,C.A. AND H.LIPSON, Z.KRIST. 82,297(1932) BE 5 04,4 H2 0
BURNS,J.H. AND E.K.GORDON, ACTA CRYST. 20,135(1966) LI2 BE F4
FARRELL,E.F. ET AL., AM. MINERALOGIST 48,804(1963) RE AL2 04
GOLOVASTIKOV,N.L., SOVIET PHYS.-CRYST. 6,733(1962) NA RE P 04
HARRIS,L.A. AND M.L.YAKEL, ACTA CRYST. 20,295(1966) CA12 BEIT 029
MROSE,W.E. AND D.E. APPELMAN, Z.KRIST. 117,16(1962) AL RE ST 04,0 H
SEARSD,R. AND J.H.BURNS, J. CHEM. PHYS. 41,3478(1964) L16 RE F4 ZR F6
SMITH,D.K. ET AL., J. ELECTROCHEM. SOC. 111,78(1964) RE 0
ZACHARIASEN,W.H. ET AL., ACTA CRYST. 16,114(1963) RE2 B 03 (0 H)
- BE+2 VI
BI+3 V
ABRAHAM,S.C. ET AL., J. CHEM. PHYS. 47,4038(1967) B12 BE 0P0
AURIVILLIUS,B. ACTA CHEM,SCAND. 18,2375(1964) R12 02 S 04,H2 0
- BI+3 VI
AURIVILLIUS,B., ACTA CHEM,SCAND. 18,2375(1964) B12 02 S 04,H2 0
AURIVILLIUS,B. AND I.JONSSON, ARKIV KEMI 19,271(1962) R1 0 H CR 04
AURIVILLIUS,B. ET AL., ACTA CHEM,SCAND. 18,1555(1964) R12 GE 05
SEGAL,D.J. ET AL., Z.KRIST. 123,77(1966) B13 ST3 012
ZEMANN,J., HEIDELBERGER BEITR. MINERAL. PETROG. 5,139(1956) B12 M0 06
- BI+3 VIII
AURIVILLIUS,B., ARKIV KEMI 3,153(1951) B1 50 04
MOONEY,R.C.L., ACTA CRYST. 1,163(1954) B1 AS 04
MOONEY-SLATER,R.C.L., Z.KRIST. 117,371(1962) B1 P 04
QURASHI,M.M. AND W.H.BARNES, AM. MINERALOGIST 50,485(1965) B1 V 04
SHANNON,R.D. AND C.T.PREWITT, TO BE PUBLISHED. R3 VS V (ZTCOH)
TOMASHPOL'SKII,Y. ET AL., SOVIET PHYS.-CRYST. 9,715(1965) R1 FE 03
- BI+5 VI
BK+3 VI
PETERSON,J.R. AND B.B.CUNNINGHAM, INORG. NUCL. CHEM. LETTERS 3,327(1967) BK2 03
- BK+4 VIII
PETERSON,J.R. AND B.B.CUNNINGHAM, INORG. NUCL. CHEM. LETTERS 3,327(1967) BK 02
- BR-1 VI
BR+7 VI
C +4 III
CHESSIN,H.W.C.HAMILTON, AND B.POST, ACTA CRYST. 18,689(1965) CA C 03
- C +4 IV
C +4 VI
CA+2 VI
BURGER,M.J., Z.KRIST. 108,288(1956) CA2 NA H ST3 09
CLARK,J.R. ET AL., ACTA CRYST. 15,207(1962) CA B3 05 0 H
CRUCKSHANK,D.W.J., ACTA CRYST. 17,685(1964) CA2 SI 04
GARD,J.A. AND H.F.W. TAYLOR, ACTA CRYST. 13,785(1960) CA8 (ST3 09) (0 H)2
SHANNON,R.D. AND C.T.PREWITT, TO BE PUBLISHED. R3 VS V (ZTCOH)
ITO,T. ET AL., ACTA CRYST. 5,209(1952) K2 CA4 RE AL2 S128.060,H2 0
RIETVELD,H.M., ACTA CRYST. 20,508(1966) CA3 U 06
SMITH,D.K. ET AL., ACTA CRYST. 18,787(1965) CA2 SI 04
STREIBER,H.W. AND F.J.SANS, AM. MINERALOGIST 48,679(1963) CA M6 (C 03)2
TAKEUCHI,Y. AND S.DONNAY, ACTA CRYST. 12,465(1959) CA AL2 ST2 08
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 1,(1963) CA C F3
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 1,(1963) CB CA F3
- CA+2 VII
BAKARIN,V.V. AND N.V.BELOVA, DOKL. AKAD. NAUK SSSR 135,587(1960) CA BE2 (P 04)2
CHISTY,C.L. ET AL., ACTA CRYST. 11,761(1958) CA B3 04 (0 H)3,H2 0
MEGAW,H.D. ACTA CRYST. 5,477(1952) CA3 (SI 03) 0 H2,2 H2 0
POSNER,A.S. ET AL., ACTA CRYST. 11,308(1958) CA10 (P 04)2 F6
PRANDL,W., Z.KRIST. 123,81(1966) AL2 CA3 (ST 04)3
SHANNON,R.D. AND C.T.PREWITT, TO BE PUBLISHED. R3 VS V (ZTCOH)
SWALLOW,A.B. ET AL., ACTA CRYST. 21,397(1966) CA2 FE (P 04)2,H2 0
WEBB,M.C., ACTA CRYST. 21,942(1966) CA2 P2 07
ZACHARIASEN,W.H., Z.KRIST. 73,7(1950) CA TT ST 05
- CA+2 VIII
BERTAUT,F. AND P.BLUM, ACTA CRYST. 9,121(1956) CA T12 04
BURBANK,R.D., ACTA CRYST. 18,88(1965) CA W 04
CLARK,J.R. AND C.T.PREWITT, TO BE PUBLISHED. R3 VS V (ZTCOH)
CRUCKSHANK,D.W.J., ACTA CRYST. 17,685(1964) CA B3 03,10 H)5,2 H2 0
DECKER,B.F. AND J.S.KASPER, ACTA CRYST. 10,332(1957) CA FE2 04

Table 1(b) (cont.)

SILLEN,L.G. AND K.LUNDBORG, Z.ANORG.ALLGEM.CHEM, 259,2(1943) LA2 MO 06	MA6 IV	PALENIK,G.J., INORG.CHEM, 6,507(1967) K2 MN 04
TEMPLETON,D.H. AND C.H.DAUBEN, J.AM.CHEM.SOC, 76,9237(1954) LA2 03		
LA+3 VII		
GUILLEN,M. AND E.F.BERTAUT, COMPT.REND. SFR.A+B 2620,962(1966) LA2 TI 05	MA7 IV	FERRARI,A. ET AL., ACTA CRYST. 21,661(1966) SR (MN 04)2,3 H2 O
LA+3 VIII		JAVANA,A. AND A. ENGELBRECHT, PHYS.REV, 96,649(1954) MN 03 F
BRISSE,F., PH.D.THESIS,DALHOUSIE UNIV.,HALIFAX,N.S.(1967) LA2 H2 07	MOONET,R.C.L., PHYS.REV, 37,1306(1931) K MN 04	
SHANNON,R.D. AND C.T.PREWITT, TO BE PUBLISHED. R VS A (PYROCHLORE)	PALENIK,G.J., INORG.CHEM, 6,507(1967) MN 04	
LA+3 IX		SASVARI,K., Z.KRIST, 99,9(1938) AG MN 04
HUNT,E.B.,JR., ET AL., ACTA CRYST. 7,106(1954) LA2 (S 04)3,9 H2 O	MA7 VI	
ZALKIN,A. ET AL., INORG.CHEM, 5,1466(1966) LA F3	MO+3 VI	HEPWORTH,M.A. ET AL., ACTA CRYST. 10,63(1957) MO F3
LA+3 X		
LONGO,J.M. AND A.W.SLEIGHT, INORG.CHEM, 7,108(1966) LA4 REA 019	MO+4 VI	ANSELL,G.B. AND L.KATZ, ACTA CRYST. 21,482(1966) ZN2 MO3 0A
LA+3 XII		BRANDT,B.G. AND A.C.SKAPSKI, ACTA CHEM.SCAND, 21,661(1967) MO 02
HUNT,E.B.,JR., ET AL., ACTA CRYST. 7,106(1954) LA2 (S 04)3,9 H2 O	IBERS,J.A. AND G.W.SMITH, ACTA CRYST. 17,190(1964) NA CO2,3 MO3 012	
LA+1 IV		WYCKOFF,R.W.G., CRYSTAL STRUCTURES 2,(1964) BR MO 03
BURNS,J.H. AND W.R.BUSING, INORG.CHEM, 4,1510(1965) RB LI F2	WYCKOFF,R.W.G., CRYSTAL STRUCTURES 2,(1964) SA MO 03	
BURNS,J.H. AND E.K.GORDON, ACTA CRYST. 20,195(1965) LI2 RF F4		
EVANS,E.D. AND H.W.ONDIK, ACTA CRYST. 15,1280(1962) LI K2 P3 09,H2 O	MO+5 VI	EDWARDS,A.J. AND R.O.PEACOCK, J.CHEM.SOC, 1961,4253 NA MO F6
GALF,J. AND A.HARDY, ACTA CRYST. 19,432(1965) LI V2 05	KIERKEGAARD,P. AND M.WESTERLUND, ACTA CHEM.SCAND, 16,2217(1964) MO P 05	
KEFFER,C. ET AL., INORG.CHEM, 4,1511(1965) LI3 P 0		
LARSON,A.C., ACTA CRYST. 18,717(1965) LI2 S 04,H2 O	MO+6 IV	ABRAHAMS,S.C., J.CHEM.PHYS, 46,2052(1967) ZN MO 04
LIEBAU,F., ACTA CRYST. 14,389(1961) LI2 S12 05	ABRAHAMS,S.C. AND J.W. REDDY, J.CHEM.PHYS, 43,2533(1965) MN MO 04	
LIEBAU,F., ACTA CRYST. 14,399(1961) LI AL S14 010	ABRAHAMS,S.C. ET AL., J.CHEM.PHYS, 48,2619(1968) CI MO 04	
MAREZIO,M., ACTA CRYST. 18,483(1965) LI GA 02	KIHLBORG,L., ARKIV KEMI 21,357(1963) MO 03	
MAREZIO,M., ACTA CRYST. 19,396(1965) LI AL 02	KIHLBORG,L., ARKIV KEMI 21,365(1963) MO 011 (MON),MO 011 (0-RH)	
MAREZIO,M. AND J.P.REMEIKA, J.CHEM.PHYS, 44,3348(1966) LI R 02	LECIEJEWICZ,J., Z.KRIST, 101,158(1965) P5 MO 04	
REMEIKA,J.P. AND M.MAREZIO, J.PHYS.CHEM.SOLID, 26,2091(1965) LI B 02	SELEBORG,M., ACTA CHEM.SCAND, 20,2195(1966) K2 MO3 010	
SEARSD,R. ET AL., INORG.CHEM, 4,1510(1965) LI6 RF F4 ZR F6	SELEBORG,M., ACTA CHEM.SCAND, 21,499(1967) NA2 MO2 07	
ZACHARIASEN,W.H. AND H.A.PLETTINGER, ACTA CRYST. 14,229(1961) LI2 W 04	SILLEN,L.G. AND K.LUNDBORG, Z.ANORG.ALLGEM.CHEM, 252,21(1943) LA2 MO 06	
ZEMANN,A., ACTA CRYST. 13,863(1960) LI3 P 04		
ZINTL,E. ET AL., Z.ELEKTROCHEM, 40,568(1934) LI2 0		
LA+1 VI		
ABRAHAMS,S.C. AND J.L.BERNSTEIN, J.PHYS.CHEM.SOLID, 28,1445(1967) LI TA 03	MO+6 V	EICK,H.A. AND L.KIHLBORG, ACTA CHEM.SCAND, 20,1698(1966) V2 MO 08
ABRAHAMS,S.C. AND M.J.WILLIAMS, J.CHEM.PHYS, 39,2923(1963) LI CU CL3,2 H2 O	GATEHOUSE,B.M. AND P.LEVERETT, CHEM.COMM, 1967,374 K2 MO3 010	
ABRAHAMS,S.C. ET AL., J.PHYS.CHEM.SOLID, 27,997(1966) LI NR 03	SELEBORG,M., ACTA CHEM.SCAND, 20,2195(1966) K2 MO3 010	
ABRAHAMS,S.C. ET AL., J.PHYS.CHEM.SOLID, 28,1693(1967) LI TA 03		
BRUNTON,G., ACTA CRYST. 21,811(1966) LI U F5	MO+6 VI	GATEHOUSE,B.M. AND P.LEVERETT, CHEM.COMM, 1967,374 K2 MO3 010
BRUNTON,G., J.INORG.NUCL.CHEM, 29,1631(1967) LI4 U FB	KIERKEGAARD,P., ARKIV KEMI 18,551(1962) MO P2 08	
BURNS,J.H., ACTA CRYST. 15,1098(1962) LI SR F6	KIERKEGAARD,P., ARKIV KEMI 18,553(1962) NA MO 02 P 04	
CANNILLO,F. ET AL., ACTA CRYST. 21,200(1966) K NA3 FE2 TI2 (S14 012)2	KIERKEGAARD,P., ARKIV KEMI 19,1(1963) (MO 02)2 P 07	
GALF,J. AND A.HARDY, ACTA CRYST. 19,432(1965) LI V2 05	KIERKEGAARD,P. AND S.HOLMEN, ARKIV KEMI 25,233(1965) AG MO P 06	
GIBBS,G.V. AND F.INOUE, AM.MINERALOGIST, 44,670(1959) CA MG (C 03)2	GELLER,S., ARKIV KEMI 21,357(1963) MO 03	
MAREZIO,M. AND J.P.REMEIKA, J.PHYS.CHEM.SOLID, 26,1277(1965) LI GA 02	KIHLBORG,L., ARKIV KEMI 21,365(1963) MO 011 (MON),MO 011 (0-RH)	
MAREZIO,M. AND J.P.REMEIKA, J.CHEM.PHYS, 44,3143(1966) LI AL 02	KIHLBORG,L., ARKIV KEMI 21,427(1964) MO5 014	
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 1,(1963) LI F	KIHLBORG,L., ARKIV KEMI 21,443(1964) MO18 052	
	KIHLBORG,L., ARKIV KEMI 21,461(1964) MO8 023	
	SELEBORG,M., ACTA CHEM.SCAND, 20,2195(1966) K2 MO3 010	
	SMITH,G.W. AND J.A.IBERS, ACTA CRYST. 19,269(1967) CO MO 04	
LA+3 VI		
BARTRAM,S.F., INORG.CHEM, 5,749(1966) LU6 U 012	MO+6 VII	KIHLBORG,L., ARKIV KEMI 21,427(1964) MO5 014
TEMPLETON,D.H. AND C.H.DAUBEN, J.AM.CHEM.SOC, 76,5237(1954) LU2 03		
LA+3 VIII		
BRISSE,F., PH.D.THESIS,DALHOUSIE UNIV.,HALIFAX,N.S.(1967) LU2 TI2 07		
EULER,F. AND J.A.BRUCE, ACTA CRYST. 19,971(1965) LU3 MF4 012		
SHANNON,R.D. AND C.T.PREWITT, TO BE PUBLISHED. R VS A (PYROCHLORE)		
MO+2 IV		
SMITH,J.V., AM.MINERALOGIST 38,643(1953) CA2 MG S12 07		
MO+2 V		
BAUR,W.H., ACTA CRYST. 9,515(1961) MG F2		
BAUR,W.H., ACTA CRYST. 15,815(1962) FE S 04,4 H2 O		
BRUNTON,G. ET AL., ACTA CRYST. 11,169(1958) CUR MG8 (C 03)4 (O H)24,8 H2 O		
CALVO,C., CAN.J.CHEM, 43,1139(1965) MO2 P2 07		
CORBRIDGE,D.E.C., ACTA CRYST. 9,991(1956) MG H P 03,6 H2 O		
GIBBS,G.V. ET AL., AM.MINERALOGIST, IN PRESS, MOP ST 04		
KASPER,J.S. AND J.S.PRENER, ACTA CRYST. 7,244(1954) MG6 MN 08		
LUKASIEWICZ,K., BULL.ACAD.POLON.SCI.SFR.SCI.CHEM, 11,361(1961) MO2 AS2 07		
RENTZPERIS,P.J. AND C.T.SOLDATOS, ACTA CRYST. 11,686(1954) MG S 04		
STEINFINK,H. AND F.INOUE, AM.MINERALOGIST 44,670(1959) CA MG (C 03)2		
SUTOR,D.J., ACTA CRYST. 25,418(1967) MG H P 04,3H2 O		
TAKEUCHI,Y., ACTA CRYST. 5,574(1952) MO2 B2 05		
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 1,(1963) MG 0		
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 2,(1964) K MN F3		
ZACHARIASEN,W.H., ACTA CRYST. 7,788(1954) MG U 04		
ZEMANN,A. AND J.ZEMANN, ACTA CRYST. 10,409(1957) K2 MO2 (S 04)3		
MO+2 VIII		
GIBBS,G.V. AND J.V.SMITH, AM.MINERALOGIST 50,2023(1965) MG3 AL2 S13 012		
ZEMANN,A. AND J.ZEMANN, ACTA CRYST. 14,835(1961) MG3 AL2 S73 012		
MO+2 VI LS		
MO+2 VI HS		
ABRAHAMS,S.C. AND J.W. REDDY, J.CHEM.PHYS, 43,2533(1965) MN MO 04		
BAUR,W.H., ACTA CRYST. 11,466(1958) MN F2		
GELLER,S. AND J.L.DURAND, ACTA CRYST. 13,325(1960) LI MN P 04		
MOSE,M.E. AND D.E.APPLEMAN, Z.KRIST, 117,16(1962) (MN,F3) BE (P 04) (O H)		
PEACOCK,R. AND M.J.BUEGGER, Z.KRIST, 117,33(1962) CA MN S7E 06		
RENTZPERIS,P.J., NEUES JAHRB.MINERAL.MONATSH, 210(1958) MN S 04		
RENTZPERIS,P.J., Z.KRIST, 119,117(1963) ZN2 MN (O H)2 S12 04		
SCHNEIDER,W., ACTA CRYST. 14,784(1961) K2 MN (S 04)2,4 H2 O		
SHIRANE,G. ET AL., J.PHYS.SOC.JAPAN, 14,1352(1959) MN TT 03		
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 1,(1963) MN 0		
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 2,(1964) K MN F3		
ZALKIN,A. ET AL., J.CHEM.PHYS, 37,697(1962) CS MN F3		
MO+2 VIII		
SHANNON,R.D. AND C.T.PREWITT, UNPUBLISHED DATA. R VS A (GARNET)		
MO+3 V		
ABRAHAMS,S.C. AND J.L.BERNSTEIN, J.CHEM.PHYS, 46,3776(1967) DY MN2 05		
YAKEL,H.L. ET AL., ACTA CRYST. 16,957(1963) Y MN 03		
MO+3 VI LS		
BLASSE,G., J.INORG.NUCL.CHEM, 27,748(1965)		
SHANNON,R.D. AND C.T.PREWITT, TO BE PUBLISHED. R3 VS V (K3 MI11 (C NI6))		
MO+3 VI HS		
COLLIN,R.L. AND W.N.LIPSCOMB, ACTA CRYST. 2,104(1949) H MN 02		
DACHS,H., Z.KRIST, 118,303(1963) MN 0 0 H		
FERT,A., BULL.SOC.FRANC.MINERAL, ACTA CRYST. 8,51(1962) MN P 03		
HASE,W. ET AL., Z.KRIST, 124,428(1967) MN2 03		
HEPWORTH,M.A. AND K.H.JACK, ACTA CRYST. 10,345(1957) MN F3		
NORRESTRAM,R., ACTA CHEM.SCAND, 21,287(1967) MN2 03		
ROTH,R.G., S.J.SCHNEIDER, J.RES.NATL.BUR.STD, 64A,309(1966) R3 VS V (MN2 03)		
SHANNON,R.D., INORG.CHEM, 6,1474(1967) R3 VS V (PEROVSKITE)		
SHANNON,R.D. AND C.T.PREWITT, TO BE PUBLISHED. R VS A (MN2 03)		
MO+4 VI		
ABRAHAMS,S.C. AND J.L.BERNSTEIN, J.CHEM.PHYS, 46,3776(1967) DY MN2 05		
BODE,H. AND W.WENDT, Z.ANORG.ALLGEM.CHEM, 269,165(1952) RB2 MN F6		
KASPER,J.S. AND J.S.PRENER, ACTA CRYST. 7,244(1954) MG6 MN 08		
SHANNON,R.D. AND C.T.PREWITT, TO BE PUBLISHED. R3 VS V (RUTILE)		
WADSLAY,A.D., ACTA CRYST. 8,165(1955) ZN MN3 07,3 H2 O		

Table 1(b) (cont.)

ANDERSSON,S., ACTA CHEM. SCAND. 18:2359(1964) N83 O7 F	PB-2 VII	HAMILTON,W.C., ACTA CRYST. 10:103(1957) PB (N 03)2
BODE,H. AND M. DORREN, ACTA CRYST. 11:88(1958) NI P2		SAHL,K., BEITR. MINERAL. PETROG. 9:111(1963) PB 5 O4
BATEHOUSE,B.W. AND A.D. WADSLLEY, ACTA CRYST. 17:1545(1964) N82 O5		
KATZ,L. AND H.D. MEGAW, ACTA CRYST. 22:639(1967) K NB 03		
MOROSIN,B. AND A. ROSENZWEIG, ACTA CRYST. 18:874(1965) GA NB 04		
PEDERSEN,B.F., ACTA CHEM. SCAND. 18:1921(1962) AL NB 04		
SKAPSKI,A.C. AND D. ROGERS, CHEM. COMM. (1965) 611 SB NB 04		
SLEIGHT,A.W., TO BE PUBLISHED. H62 NB 2 F		
NB+5 VII		
BROWN,G.W. AND L.A. WALKER, ACTA CRYST. 20:220(1966) K2 NR F7		
HOARD,J.L., J. AM. CHEM. SOC. 61:3252(1939) K2 NB F7		
ND+3 VI		
TEMPLETON,D.H. AND C.H. DAUBEN, J. AM. CHEM. SOC. 76:5237(1954) ND2 O3		
ND+3 VIII		
HILLIGAN,W.O. AND L.W. VERNON, J. PHYS. CHEM. 56:145(1952) ND V O4		
SHANNON,R.D. AND C.T. PREWITT, TO BE PUBLISHED. R VS A (PYROCHLORE)		
ND+3 IX		
BURNS,J.H., INORG. CHEM. 4:881(1965) NA ND F4		
NI+2 VI		
BALZ,D. AND K. PLIETH, Z. ELEKTROCHEM. 59:505(1955) K2 NI F4		
BAUR,W.H., ACTA CRYST. 11:488(1958) NI P2		
BILLY,C. AND M.H. HAENDLER, J. AM. CHEM. SOC. 79:1049(1957) NI F2		
DYER,L.D. ET AL., J. AM. CHEM. SOC. 76:1499(1954) NA NI O3		
KEELING,R.O., JR., ACTA CRYST. 10:209(1957) NI W O4		
LANDER,J.J., ACTA CRYST. 4:186(1951) BA NI O2		
O'CONNOR,B.H. AND D.H. DALE, ACTA CRYST. 21:705(1966) NI 5 O4.6 H2 O		
SCHNERING,H.G., Z. ANORG. ALLGEM. CHEM. 353:131(1967) NA2 NI F6		
SHIRANE,G. ET AL., J. PHYS. SOC. JAPAN 14:1352(1959) NI TT O3		
VAN NIEKERK,J.N., F. R. SCHODING, ACTA CRYST. 6:609(1953) NI(C) H3 C O 0.2.4 H2 O		
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 1, (1963) NI O		
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 2, (1964) K NI F3		
NI+3 VI L5		
BLASSE,G., J. INORG. NUCL. CHEM. 27:748(1965) X3 NI F6		
SHANNON,R.D., INORG. CHEM. 6:1474(1967) R3 VS V (PEROVSKITE)		
NI+3 VI HS		
BLASSE,G., J. INORG. NUCL. CHEM. 27:749(1965)		
NP+2 VI		
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 1, (1963) NP O		
NP+3 VI		
SHANNON,R.D. AND C.T. PREWITT, TO BE PUBLISHED. R3 VS V (LA F3)		
NP+4 VI		
NP+4 VIII		
SHANNON,R.D. AND C.T. PREWITT, TO BE PUBLISHED. R VS A (FLUORITE)		
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 1, (1963) NP O2		
NP+7 VI		
O -2 II		
O -2 III		
O -2 IV		
O -2 VI		
O -2 VIII		
OS+4 VI		
SHANNON,R.D. AND C.T. PREWITT, TO BE PUBLISHED. R3 VS V (RUTILE)		
P +3 VI		
P +5 IV		
CRUICKSHANK,D.W.J., ACTA CRYST. 17:671(1964) NA P O3 N H3		
CRUICKSHANK,D.W.J., ACTA CRYST. 17:672(1964) NA P O7.10 H2 O		
CRUICKSHANK,D.W.J., ACTA CRYST. 17:674(1964) NA5 P O11		
CRUICKSHANK,D.W.J., ACTA CRYST. 17:675(1964) (N H6) P O4 O12		
CRUICKSHANK,D.W.J., ACTA CRYST. 17:679(1964) P2 O5		
CRUICKSHANK,D.W.J., ACTA CRYST. 17:681(1964) RR P O5		
FELDMANN,H. AND S. GOSSE, J. CHEM. PHYS. 41:1910(1964) CUS P O4 (O H3)		
BELLERS, AND J.L. DURAND, ACTA CRYST. 13:325(1960) LI MN P O4		
JARCHOW,O.H., ACTA CRYST. 17:1253(1964) NA2 H2 P4 O12		
KEFFER,C. ET AL., INORG. CHEM. 6:119(1967) L13 P O4		
KIERKEGAARD,P., ARKIV KEMI, 18:521(1961) M2 P O8		
KIERKEGAARD,P., ARKIV KEMI, 18:553(1961) NA MO O2 P O4		
KIERKEGAARD,P. AND S. HOLMEN, ARKIV KEMI 23:213(1965) A4 MO P O6		
KIERKEGAARD,P. AND M. WESTERLUND, ACTA CHEM. SCAND. 1A:2217(1964) MO P O5		
KRSTANOVIC,I., Z. KRIST. 121:315(1965) Y P O4		
PAULING,L. AND J. SHERMAN, Z. KRIST. 96:481(1957) AL P3 O9		
SCHWARZENBACH,D., Z. KRIST. 123:161(1966) AL P O4		
WEBB,N.C., ACTA CRYST. 21:942(1966) CAP P2 O7		
ZEMANN,J., ACTA CRYST. 13:865(1960) L13 P O4		
P +5 VI		
PA+3 VI		
PA+4 VI		
PA+4 VIII		
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 1, (1963) PA O2		
PA+5 VI		
PA+5 IX		
BROWN,D. ET AL., J. CHEM. SOC. 1967:1429 K2 PA F7		
PB+2 IVPY		
BOUCHER,M.L. AND D.R. PEACOCK, Z. KRIST. 126:99(1968) PB ST O3		
BYSTROM,A. AND L. LEVRS, ACTA CHEM. SCAND. 4:613(1950) A2 P O2		
KAT,M.I., ACTA CRYST. 14:80(1961) PB O		
PB+2 VI		
MAGNELI,A., ARKIV KEMI, MINERAL. GEOL. 15B:3(1942) PB 5B P O6		
MOLLER,C.K., ACTA CHEM. SCAND. 8:81(1954) PB (N H4) 2 (S O4) 2		
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 2, (1964) CS PR F3		
PB+2 VIII		
FINNEY,J.J., AM. MINERALOGIST 48:1(1963) PB FE2 (AS O4) 2 (O H) 2		
LECIEJEWICZ,J., Z. KRIST. 121:196(1965) PR MO O4		
KAT,M.I., ACTA CRYST. 14:80(1961) PB O		
QUARENTI,S. AND R. DEPIERI, ACTA CRYST. 19:207(1965) PB CR O4		
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 1, (1963) PB F2		
PB+2 IX		
COLBY,M.Y. AND L.J.B. LACOSTE, Z. KRIST. 84:299(1932) PB C O3		
PB+2 XI		
NARAY-SZABO,I. AND G. ARGAY, ACTA CHIM. ACAD. SCI. HUNG. 40:283(1964) PB CR O4		
PB+2 XII		
ROGERS,D.B. AND R.D. SHANNON, FALL A.C.S. MTC., ATLANTIC CITY (1968) PD CO O2		
PD+2 IV50		
WASER,J. ET AL., ACTA CRYST. 6:661(1953) PD O		
PD+2 VI		
BARTLETT,N. AND R. WATLAND, ACTA CRYST. 11:747(1958) PD F2		
PD+3 VI		
HEPWORTH,M.A. ET AL., ACTA CRYST. 10:63(1957) PD F3		
PD+4 VI		
SLEIGHT,A.W., TO BE PUBLISHED. R VS A (PYROCHLORE)		
PM+3 VI		
TEMPLETON,D.H. AND C.H. DAUBEN, J. AM. CHEM. SOC. 76:5237(1954) PM2 O3		
PM+4 VIII		
SHANNON,R.D. AND C.T. PREWITT, TO BE PUBLISHED. R VS A (FLUORITE)		
PM+6 VI		
PR+3 VI		
FERT,A., BULL. SOC. FRANC. MINERAL. CRIST. 85:257(1962) PR2 O3		
TEMPLETON,D.H. AND C.H. DAUBEN, J. AM. CHEM. SOC. 76:5237(1954) PR2 O3		
PR+3 VIII		
SHANNON,R.D. AND C.T. PREWITT, TO BE PUBLISHED. R VS A (PYROCHLORE)		
PR+4 VI		
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 2, (1964) BA PR O3		
PR+4 VIII		
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 1, (1963) PR O2		
PT+2 VI		
PT+4 VI		
BORLINGER,C.O., ARKIV KEMI, MINERAL. GEOL. 15B:2(1942) K2 PT (O H) 6		
HOEKSTRA,H.R. AND S. SEGEL, INORG. CHEM. 7:141(1968) TL2 PT2 O7		
MELLOR,D.P. AND N.C. STEPHENSON, AUSTR. J. RES. 44A:6(1951) K2 PT F6		
SHANNON,R.D., SOLID STATE COMM. IN PRESS. R3 VS V (PT P2)		
PU+3 VI		
SHANNON,R.D. AND C.T. PREWITT, TO BE PUBLISHED. R3 VS V (LA F3)		
PU+4 VI		
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 2, (1964) BA PU O3		
PU+4 VIII		
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 1, (1963) PU O2		
RA+2 VI		
RB+1 VI		
HOPPE,R. AND H. SABROWSKY, Z. ANORG. ALLGEM. CHEM. 339:144(1965) RR 5C O2		
PLYUKHIN,V.V. AND N.V. BELOV, SOVIET PHYS.-CRYST. 6:685(1962) RB 8E2 F5		
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 1, (1963) RB F		
RB+1 VII		
CORBRIDGE,D.E.C., ACTA CRYST. 9:308(1956) RB P O3		
CRUICKSHANK,D.W.J., ACTA CRYST. 17:661(1964) (RR P O3)		
RB+1 VIII		
ANDERSSON,S. AND A.D. WADSLLEY, ACTA CRYST. 15:194(1962) RB2 T16 O13		
BURNS,J.H. AND W.R. BUSING, INORG. CHEM. 4:1510(1965) RB L1 F2		
CRUICKSHANK,D.W.J., ACTA CRYST. 17:661(1964) (RB P O3)		
RB+1 XII		
ELLINGER,F.H. AND W. H. ZACHARIASEN, J. PHYS. CHEM. 58:405(1954) RB AM O2 C O3		
HOARD,J.L. AND V. BALTAR, J. AM. CHEM. SOC. 57:1965(1935) RA 8 F4		
RE+4 VI		
SHANNON,R.D. AND C.T. PREWITT, TO BE PUBLISHED. R3 VS V (RUTILE)		
RE+5 VI		
DONOHUE,P.C. ET AL., INORG. CHEM. 4:1152(1965) CN2 RE2 O7		
RE+6 VI		
WYCKOFF,R.W.G., CRYSTAL STRUCTURES 2, (1964) RE O3		
RE+7 IV		
KREBS,B. ET AL., CHEM. COMM. (1968) 263 RE2 O7		
MORROW,J.C., ACTA CRYST. 13:443(1960) K RE O4		
RE+7 VI		
KREBS,B. ET AL., CHEM. COMM. (1968) 263 RE2 O7		
RH+3 VI		
HEPWORTH,M.A. ET AL., ACTA CRYST. 10:63(1957) RH F3		
SHANNON,R.D., INORG. CHEM. 6:1474(1967) R3 VS V (PEROVSKITE)		
SHANNON,R.D. AND C.T. PREWITT, TO BE PUBLISHED. R3 VS V (CORUNDUM)		
RH+4 VI		
SHANNON,R.D. AND C.T. PREWITT, TO BE PUBLISHED. R3 VS V (RH O2)		
RU+3 VI		
HEPWORTH,M.A. ET AL., ACTA CRYST. 10:63(1957) RU F3		
SHANNON,R.D. AND C.T. PREWITT, TO BE PUBLISHED. R3 VS V (PEROVSKITE)		
RU+4 VI		
COTTON,F.A. AND J.T. WAQUE, INORG. CHEM. 5:317(1965) RU O2		
DONOHUE,P.C. ET AL., INORG. CHEM. 4:306(1965) BA RU O3		
SHANNON,R.D. AND C.T. PREWITT, TO BE PUBLISHED. R VS A (PYROCHLORES)		
SHANNON,R.D. AND C.T. PREWITT, TO BE PUBLISHED. R3 VS V (RUTILE)		
S -2 VI		
S +4 VI		
S +6 IV		
BAUR,W.H., ACTA CRYST. 17:863(1964) MG 5 O4.4 H2 O		
BAUR,W.H., ACTA CRYST. 17:1167(1964) MG 5 O4.7 H2 O		
BAUR,W.H., ACTA CRYST. 17:1361(1964) FE 5 O4.7 H2 O		
CROMEY,D.T. ET AL., ACTA CRYST. 21:583(1966) CS AL (S O4) 2.12 H2 O		
GRAEBER,E.J. ET AL., AM. MINERALOGIST 50:1929(1965) K FF (S O4) 2		

Table 1(b) (cont.)

U +4 VIII BRUNTON G., ACTA CRYST. 21,814(1966) LI U F5 BRUNTON G., J. INORG. NUCL. CHEM. 29,1631(1967) L14 U F8 DURIF, A., ACTA CRYST. 9,533(1956) U GE 04 LARSON A. C., ET AL., ACTA CRYST. 17,555(1964) U F4 WYCKOFF, R. W. G., CRYSTAL STRUCTURES 1, (1963) U O2 ZACHARIASEN W. H., ACTA CRYST. 2,390(1949) NA2 U F6	Y +3 VI BARTRAM, S. F., INORG. CHEM. 5,749(1966) Y6 U 012, LUG U 012 BERTAUF, F., AND J. HARESCHAL, COMPT. REUD. 257,867(1958) Y AL 03 FERT, A., BULL. SOC. FRANC. MINERAL. CRIST. 85,267(1962) Y2 03 HARRIS, L. A., AND H. L. YAKEL, ACTA CRYST. 22,354(1967) Y2 BE 04 MULLER-BUSCHBAUM, H., Z. ANORG. ALLGEM. CHEM. 359,138(1969) SR Y2 04 PATON, W. B., AND C. T. PREWITT, TO BE PUBLISHED. R VS A (PTROCHLORE) SHANNON, R. D., AND C. T. PREWITT, TO BE PUBLISHED. R VS A (PTROCHLORE)
U +4 IX ZACHARIASEN W. H., ACTA CRYST. 2,390(1949) U2 F9	Y +3 VIII BAGLIO, J. A., AND G. GASHUROV, ACTA CRYST. 824,292(1968) Y V 04 BATT, A., AND B. POST, ACTA CRYST. 15,1268(1962) Y3 FF5 012 BRISSE, F., PH.D. THESIS, DALHOUSIE UNIV., HALIFAX, N.S. (1967) Y2 M2 07 CUNNINGHAM, J. A., ET AL., INORG. CHEM. 6,499(1967) Y (CS H7 02) 3, H2 0 EULER, F., AND J. A. BRUCE, ACTA CRYST. 19,971(1965) Y3 M5 012 GELLER, S., AND M. A. GILLES, ACTA CRYST. 10,239(1957) Y3 FF5 012 KRSTANOVIC, I., Z. KRIST. 121,315(1965) Y P 04 MILLIGAN, M. O., AND L. W. VERNON, J. PHYS. CHEM. 56,145(1952) Y V 08 ZALKIN, A., AND D. H. TEMPLETON, J. AM. CHEM. SOC. 75,2453(1953) Y F3
U +5 VI ROSENZWEIG, A., AND D. T. CROMER, ACTA CRYST. 23,865(1967) CS U F6 ZACHARIASEN W. H., ACTA CRYST. 2,390(1949) K2 U F6 ZACHARIASEN W. H., ACTA CRYST. 2,390(1949) NA2 U F6	Y +3 IX FRICKE, R., AND W. DURRWACHTER, Z. ANORG. ALLGEM. CHEM. 259,309(1949) Y (O H) 3
U +5 VII LOOPSTRAB, O., ACTA CRYST. 17,651(1964) U3 08 ZACHARIASEN W. H., ACTA CRYST. 2,296(1949) U F5	YB+3 VI FERT, A., BULL. SOC. FRANC. MINERAL. CRIST. 85,267(1962) YB 03 TEMPLETON, D. H., AND C. H. DAUBEN, J. AM. CHEM. SOC. 76,5237(1954) TB2 03
U +6 II ZACHARIASEN W. H., ACTA CRYST. 7,793(1954) K3 U 02 F5	YB+3 VIII EULER, F., AND J. A. BRUCE, ACTA CRYST. 19,971(1965) YB3 M5 012 MILLIGAN, M. O., AND L. W. VERNON, J. PHYS. CHEM. 56,145(1952) YB V 04 SHANNON, R. D., AND C. T. PREWITT, TO BE PUBLISHED. R VS A (PTROCHLORE)
U +6 IV ROSS, M., ET AL., AM. MINERALOGIST 49,1603(1964) CU (U O2 P O4) 2, R H2 0	ZN+2 IV ANSELL, G. B., AND L. KATZ, ACTA CRYST. 21,482(1966) ZN2 M03 08 CALVO, C., J. PHYS. CHEM. SOLIDS 24,141(1963) ZN3 P 04 COREY, R. B., AND R. W. G. WYCKOFF, Z. KRIST. 86,8(1933) ZN (O H) 2 PREWITT, C. T., ET AL., Z. KRIST. 119,117(1963) ZN 2N 51 04 RENTZEPERIS, P. J., Z. KRIST. 119,117(1963) ZN2 MN (O H) 2 SI 04 SCHNERING, H. G., AND R. HOPPE, Z. ANORG. ALLGEM. CHEM. 312,87(1961) SR ZN 02
U +6 VI DEBETSP, C., ACTA CRYST. 21,589(1966) U 03 LOOPSTRAB, O., ACTA CRYST. 17,651(1964) U3 08 SIEGEL, S., ET AL., ACTA CRYST. 20,292(1966) U 03	SCHNERING, H. G., ET AL., Z. ANORG. ALLGEM. CHEM. 305,281(1960) RA ZN 02 SMITH, P., ET AL., Z. KRIST. 119,375(1964) ZN4 0 (R O2) 6 SPITSBERGER, U., ACTA CRYST. 13,197(1960) RA ZN 02 STEPHENS, J. S., AND C. CALVO, CAN. J. CHEM. 45,2303(1967) ZN3 (P O4) 2
V +2 VI MONTGOMERY, H., ET AL., ACTA CRYST. 22,775(1967) V (N H) 2 (C O4) 2, H2 0 WYCKOFF, R. W. G., CRYSTAL STRUCTURES 1, (1963) V O	ZN+2 V ABRAHAMS, S. C., J. CHEM. PHYS. 46,2052(1967) ZN M0 04 COCO, G., ET AL., Z. KRIST. 123,321(1966) ZN2 (O H) P 04 HANKE, K., NATURWISS. 54,1991(1967) ZN TE 03 MONTGOMERY, H., AND E. C. LINGAFELTER, ACTA CRYST. 16,748(1963) ZN (CS H7 02) 2 H2 0 PLIETH, K., AND G. SANGER, Z. KRIST. 124,91(1967) ZN2 CU AS2 04 STEPHENS, J. S., AND C. CALVO, CAN. J. CHEM. 45,2303(1967) ZN3 (P O4) 2
V +3 VI HEPNORTH, M. A., ET AL., ACTA CRYST. 10,63(1957) V F3 NEWMAN, R. E., AND Y. M. DEHMAN, Z. KRIST. 117,235(1962) V2 03 SHANNON, R. D., INORG. CHEM. 6,1478(1967) R3 VS V (PEPOVSKITE) WYCKOFF, R. W. G., CRYSTAL STRUCTURES 2, (1964) CE V 03	ZN+2 VI ABRAHAMS, S. C., J. CHEM. PHYS. 46,2052(1967) ZN M0 04 ANSELL, G. B., AND L. KATZ, ACTA CRYST. 21,482(1966) ZN2 M03 04 BATES, C. H., ET AL., SCIENCE 137,993(1962) ZN 0 BAUR, W. H., ACTA CRYST. 11,488(1956) ZN F2 BYSTRON, A., ET AL., ARKIV KEMI, MINERAL. GEOL. 150B4(1962) ZN 5B2 06 CALVO, C., CAN. J. CHEM. 43,1197(1965) ZN2 P2 07 CALVO, C., J. PHYS. CHEM. SOLIDS 24,141(1963) ZN3 (P O4) 2 GILGLOM, R., ACTA CRYST. 11,789(1958) NA2 ZN (S O4) 2, H2 0 SCHNERING, H. G., Z. ANORG. ALLGEM. CHEM. 353,131(1967) BA2 7N F6 WYCKOFF, R. W. G., CRYSTAL STRUCTURES 2, (1964) AG 7N F3 WYCKOFF, R. W. G., CRYSTAL STRUCTURES 2, (1964) K ZN F3
V +4 VI ANDERSSON, G., ACTA CHEM. SCAND. 10,623(1956) V O2 KIERKEGAARD, P., AND J. LONGO, UNPUBLISHED DATA, V O2 SHANNON, R. D., AND C. T. PREWITT, TO BE PUBLISHED. R3 VS V (RUTILE) WYCKOFF, R. W. G., CRYSTAL STRUCTURES 2, (1964) CA V 03	ZR+4 VI BRISSE, F., PH.D. THESIS, DALHOUSIE UNIV., HALIFAX, N.S. (1967) LA2 ZR2 07 JONA, F., ET AL., PHYS. REV. 105,849(1957) PB ZR 03 SHANNON, R. D., AND C. T. PREWITT, TO BE PUBLISHED. R VS A (PYROCHLORE) WYCKOFF, R. W. G., CRYSTAL STRUCTURES 2, (1964) BA ZR 03 WYCKOFF, R. W. G., CRYSTAL STRUCTURES 2, (1964) SR ZR 03
V +5 IV CHRIST, C. L., AND C. CALVO, CAN. J. CHEM. 45,2287(1967) CO2 V2 07 BAGLIO, J. A., AND G. GASHUROV, ACTA CRYST. 824,292(1968) Y V 04 DONALDSON, D. M., AND W. H. BARNES, AM. MINERALOGIST 40,580(1955) PR MN (V O4) (O H) EVANS, H. T., JR., Z. KRIST. 114,257(1960) K V 03 EVANS, H. T., JR., Z. KRIST. 114,257(1960) N H V 03 MILLIGAN, M. O., AND L. W. VERNON, J. PHYS. CHEM. 56,145(1952) M V 04 PATSCHEKE, E., ET AL., CHEM. PHYS. LETTERS 2,47(1968) ER V 04 SHANNON, R. D., AND C. T. PREWITT, TO BE PUBLISHED. R3 VS V (ZIRCON)	ZR+4 VII LUNDGREN, G., ARKIV KEMI 13,59(1958) ZR4 (O H) 6 (CR O4) 2, H2 0 SMITH, D. K., AND H. W. NEWKIRK, ACTA CRYST. 10,963(1956) ZR 02
V +5 V CHRIST, C. L., ET AL., ACTA CRYST. 7,801(1954) K V O3, H2 0 EVANS, H. T., JR., AND S. BLOCK, INORG. CHEM. 5,1808(1966) K V3 08 GALY, J., AND A. HARDY, ACTA CRYST. 19,432(1965) LI V2 05	ZR+4 VIII BODE, H., AND G. TEUFER, ACTA CRYST. 9,929(1956) K2 ZR F6 BURNS, J. H., ET AL., ACTA CRYST. 824,230(1968) NA7 ZR6 F3 KRSTANOVIC, I., R., ACTA CRYST. 11,896(1958) ZR 51 04 LARSON, A. C., AND D. T. CROMER, ACTA CRYST. 14,128(1961) ZR (E O3) 4 SEARS, D. R., AND J. H. BURNS, J. CHEM. PHYS. 41,3478(1964) L76 RE FQ ZR F8 SINGER, J., AND D. T. CROMER, ACTA CRYST. 12,712(1959) ZR (S O4) 2, H2 0 TEUFER, G., ACTA CRYST. 15,1187(1962) ZR 02 WYCKOFF, R. W. G., CRYSTAL STRUCTURES 1, (1963) ZR 02
V +5 VI CAUGHLAN, C. N., ET AL., INORG. CHEM. 5,2131(1966) V O (O C H3) 3 EVANS, H. T., JR., AND S. BLOCK, INORG. CHEM. 5,1808(1966) K V3 08 EVANS, H. T., JR., AND S. BLOCK, INORG. CHEM. 5,1808(1966) CS V3 08 SMALLON, A. G., ET AL., ACTA CRYST. 21,397(1966) CA3 V10 O28, 17 H2 0	
W +4 VI SHANNON, R. D., AND C. T. PREWITT, TO BE PUBLISHED. R3 VS V (RUTILE)	
W +6 IV ABRAHAMS, S. C., AND J. L. BERNSTEIN, J. CHEM. PHYS. 45,2745(1966) SC2 (W O) 3 BURBANK, R. D., ACTA CRYST. 18,88(1965) CA W 04 TEMPLETON, D. H., AND A. ZALKIN, ACTA CRYST. 16,762(1963) FU2 (W O) 3 ZACHARIASEN W. H., AND H. A. PLETINGER, ACTA CRYST. 19,229(1961) L12 W O4 ZALKIN, A., AND D. H. TEMPLETON, J. CHEM. PHYS. 40,301(1964) CA W 04	
W +6 VI KEELING, R. O., JR., ACTA CRYST. 10,209(1957) NI W 04 KIERKEGAARD, P., ACTA CHEM. SCAND. 12,1715(1958) W O P2 07 LOOPSTRAB, O., AND P. BOLDRINI, ACTA CRYST. 21,158(1966) W O3 ULKU, D., Z. KRIST. 124,192(1967) FE W 04	

* This is not intended to be an exhaustive list of references for each ion. For example, there are many references in the literature to certain ions in the usual coordinations such as $V^{1+}Al^{3+}$ and some of these have been omitted to save space. For those ions and coordinations which occur rarely such as $IVCr^{5+}$ or VZn^{2+} , the list is apt to be more complete.

Table 2. Anion radii for different coordination numbers

O ²⁻		F ⁻	
CN	Radius, Å	CN	Radius, Å
II	1.35 (1.349 ± 5)	II	1.285 (1.285 ± 9)
III	1.36 (1.357 ± 10)	III	1.29 (1.300 ± 12)
IV	1.38 (1.378 ± 4)	IV	1.31
VI	1.40 (1.396 ± 9)	VI	1.33
VIII	1.42		

In the next step appropriate anion radii were subtracted from average distances in cation-anion polyhedra. Approximately 1000 average interatomic dis-

tances in oxides and fluorides were taken from more than 700 structure determinations. Values of radii for the trivalent rare-earth ions determined in this way agreed quite well with those of Templeton & Dauben (1954). Since our method was similar to theirs, the Templeton & Dauben values, quoted to three decimal places, were used without revision. Since anion coordination is frequently not discussed in structure papers, the following system (see also Holser, 1959) was used to determine the proper values for a compound $P_a Q_b R_x$: $pP + qQ = rR$, where P and Q are the CN's of the cations and R is the CN of the anion.

Table 1(b) lists, by ion according to CN and spin, (where applicable) all the references from which data were taken to construct Table 1. With most references, the source of data is indicated by a chemical formula, compound type, or radius plot (see below). Structure determinations from 1930 through early 1968 were covered in the literature search. In general, many qualitative judgements were made as to the weight given to a particular interatomic distance. More recent structure determinations not involving film methods, those reporting low R values, and those made on well-characterized crystals were given the most weight. The set of values thus obtained was considered to be a first approximation.

The next step was to plot ionic volume, r^3 , vs. unit cell volume, V , for more than 60 isotopic series. According to assumption 6 these plots should be linear. Fig. 1 shows the plot for the rutile MO_2 structure (Shannon, 1968). This example is chosen because the rutile structure covers a wide range of cation radii,

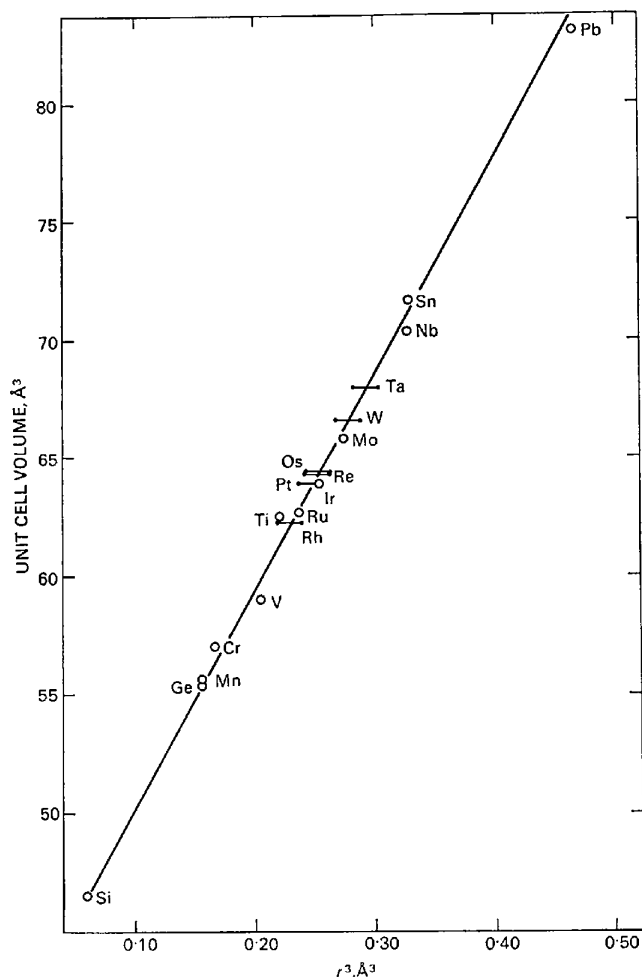


Fig. 1. Cell volume vs. r^3 for compounds with the rutile structure. Circles represent data from structure refinements, and the horizontal lines are for compositions where only the cell volumes are known (after Shannon, 1968).

0.39–0.78 Å, and unit-cell volumes are accurately known. The radii were adjusted to provide linearity and consistency with crystal structure data. The radii were further adjusted to be consistent with both crystallographic data and unit-cell volume data over those structures containing common ions. A severe limitation, however, was found to be the accuracy of many reported cell dimensions. Numerous examples which first appeared to deviate from linearity were found to fall in line with other data after cell dimensions were redetermined with least-squares refinement using Guinier camera data.

No structure data are available for many ions. In such cases, a reliable estimated value can often be obtained from plots of radii vs. cell volume (Fig. 1), radii vs. oxidation state, and radii vs. electron configuration (Figs. 3 & 4). Examples of radii determined by radii-volume plots are Ni^{3+} and Co^{3+} LS [perovskite (Shannon, 1967)], Rh^{4+} , Pt^{4+} , Re^{4+} , Os^{4+} , W^{4+} , and Ta^{4+} [rutile (Rogers, Shannon, Sleight & Gillson, 1969)] (Fig. 1), and Rh^{3+} [perovskites (Shannon, 1967) and corundum (Prewitt, Shannon, Rogers & Sleight, to be published)]. The accuracy of these values depends on the accuracy of the cell dimensions and on the linearity of the plot.

Plots of radii vs. CN (Fig. 2) and radii vs. oxidation state are generally found to be regular. This is consistent with the equations given by Zachariasen (1931) and Pauling (1927). Consequently, when the values of radii as determined by structural data appeared to be inconsistent with these regular curves, the sources of data were investigated; if these appeared questionable, the value of the radius was made consistent with the radii plots and marked in Table 1(a) with an E , e.g. Nb^{3+} .

The variation in radii of the first-row transition metal ions with the number of e_g and t_{2g} electrons has been discussed qualitatively by van Santen & van Wieringen (1952), calculated theoretically by Hush & Pryce (1958), and plotted experimentally by Liehr (1960), Knox (1961), Blasse (1965), and Pearson (1968). Similar plots were made for our data, Figs. 3 and 4. By use of these plots, hypothetical values of radii were determined for the low spin ions, Mn^{2+} , Ni^{3+} , Fe^{3+} , Mn^{3+} and Co^{3+} . Low-spin radii for Fe^{2+} and Co^{2+} were taken from radii vs. volume plots for the pyrite structure; these radii were consistent with the above electron configuration plots.

As a final step, the anion radii with CN II, III, IV, VI, and VIII were recalculated using interatomic distances from the simple oxide structures and the final refined set of cation radii. These values, given in parentheses in Table 2 with their estimated standard deviations do not differ significantly from the original values. It was not possible to calculate average values for $\text{VI}^{\text{III}}\text{O}_2^-$ because of the lack of examples. No calculations for IVF^- or VIF^- were made because of a problem with highly symmetric structures discussed in another section.

Results

Table 1(a) presents three sets of radii. The first is that of Ahrens (A-IR). The second column contains crystal radii as defined by Fumi & Tosi (CR). This column was derived from column three but it is based on $r(\text{VI}F^-) = 1.19 \text{ \AA}$ and an assumed difference between six-coordinated oxygen and fluorine radii of 0.07 \AA as

was found for the ionic radii. The third column contains the radii obtained in this work for various coordination numbers and spin states. Except for the radii of S^{2-} , Se^{2-} , and Te^{2-} , which are included in column one and marked with *P*, Pauling's radii are omitted because Ahrens' radii are taken from revised values of Pauling. Each row in Table 1 (a) contains the ion, the electron configuration (EC), coordination number (Roman nume-

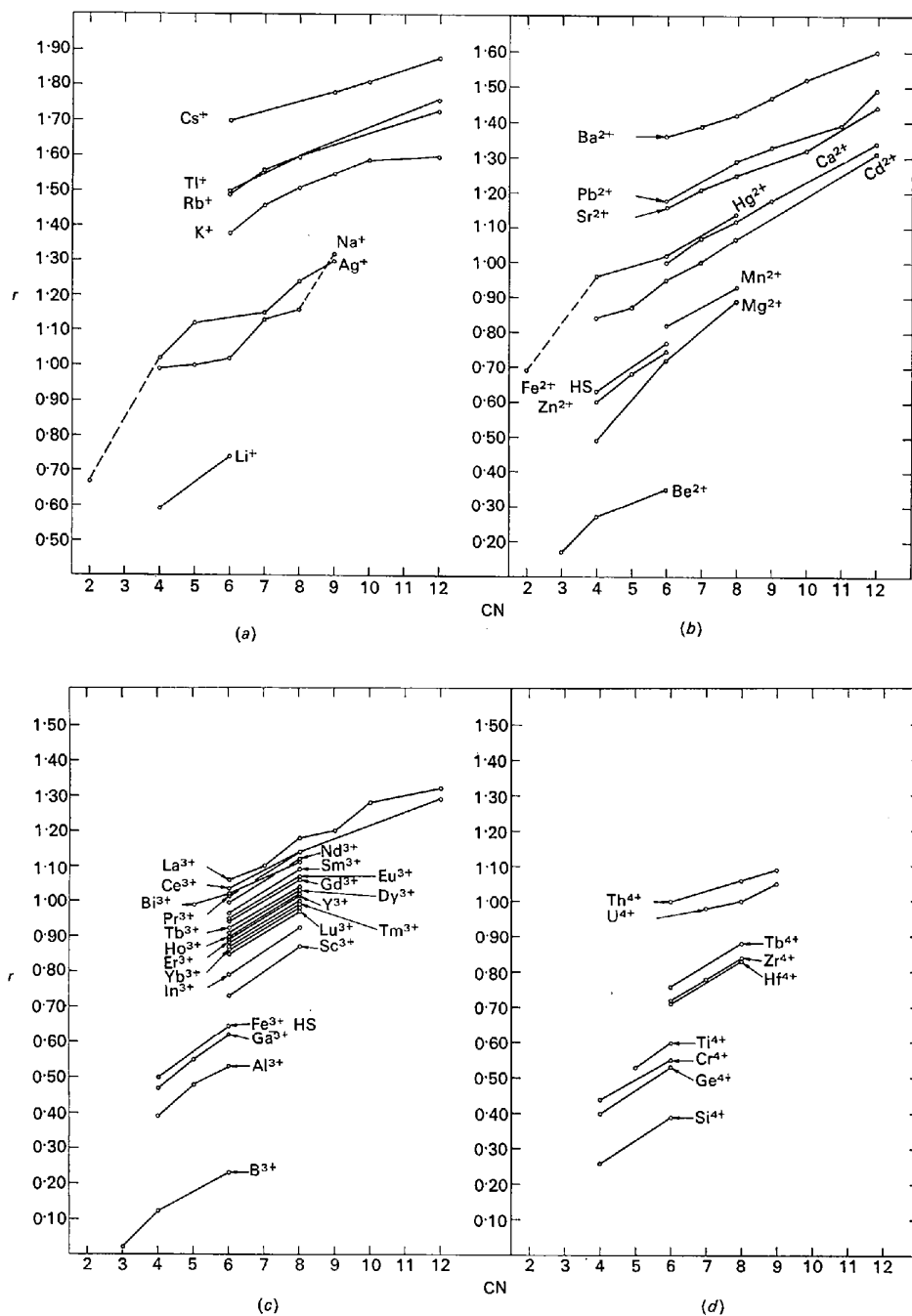


Fig. 2. 'Effective' ionic radius vs. CN for some common cations.

ral), spin state (HS or LS), three values of ionic radii, and finally a symbol giving some indication of the reliability (? , *E*, *R*, *, or no symbol). The values indicated by a question mark are considered doubtful because of one or more reasons: uncertainty as to oxidation state,

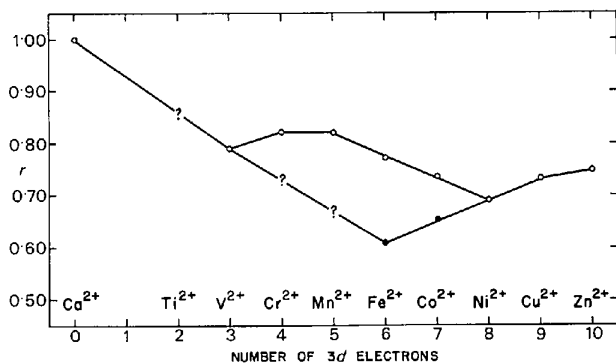


Fig. 3. 'Effective' ionic radius vs. number of 3d electrons for divalent transition-metal ions.

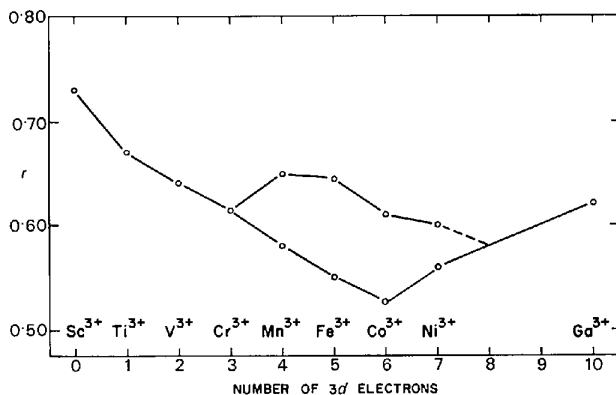


Fig. 4. 'Effective' ionic radius vs. number of 3d electrons for trivalent transition-metal ions.

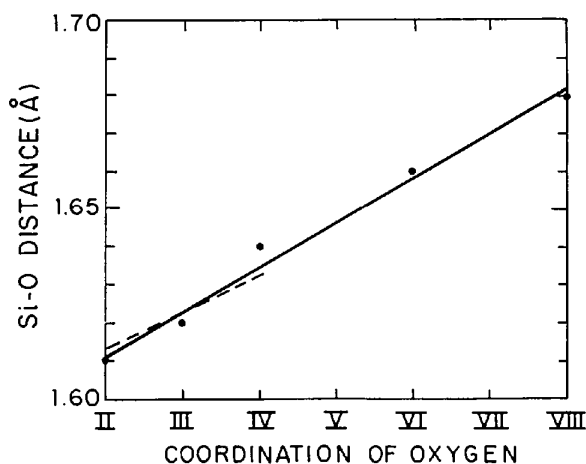


Fig. 5. Si-O distance vs. oxygen coordination. The dashed line represents the variation of Si-O distances reported by Smith & Bailey (1963).

CN, or composition of the compounds studied, or deviation from radii vs. CN, or radii vs. valence plots. The values estimated from radii vs. CN, radii vs. oxidation state, or radii vs. electron configuration plots are followed by the letter *E*. Values of radii taken from radii vs. volume plots are marked by *R*. Finally, those values for which at least 5 structural determinations resulted in radii differing by no more than ± 0.01 Å are marked with an asterisk.

Although many different types of coordination exist for a given CN, for simplicity we have chosen to differentiate only the common types of four coordination: square planar (IVSQ), square pyramidal (IVPY), and tetrahedral (IV).

Table 3 compares observed and calculated interatomic distances in more than 100 compounds with the use of radii from Zachariasen, Pauling, Ahrens, and Table 1(a). The first three columns in Table 3 contain calculated interatomic distances of Zachariasen, Pauling, and Ahrens corrected for cation coordination using the correction factors listed by Pauling (1960) and Zachariasen (1931). The agreement between observed and calculated distances is seen to be much improved in most cases where CN of the cation and/or anion is different from VI.

When the distances calculated from Table 1(a) differ significantly from the observed distances, a reason for the discrepancy can usually be found. One of these reasons is that interatomic distances in highly symmetric structures are generally shorter than expected and another is that it is often difficult to establish exact coordination numbers for some ions. These effects are discussed further in later sections of this paper. Other reasons are that some radii are based on insufficient data and/or that a structure solution and refinement may be, to some degree, in error. In addition there are undoubtedly some unexplained departures from additivity which are reflected in deviations of the order of ± 0.01 Å.

Discussion

Change of anion radius with CN

Although the dependence of interatomic distance on CN was noted by Goldschmidt (1927) and the idea of increases of cation radii with CN has been mentioned by several investigators (Pauling, 1927; Zachariasen, 1931; Geller, 1957; Sasvári, 1960), the possibility that anion radii may also depend upon CN appears to have been considered by only a few authors (Slaughter, 1966; Jeffrey & Slaughter, 1963). The effect of CN on anion radii is not great, but it is noticeable when comparing interatomic distances in structures containing a series of *M*-O distances where the CN of O²⁻ varies (Tables 3 and 4). This is probably the principal cause of the variations in Si-O distances noted by Smith & Bailey (1963) in their survey of silicate structures.*

* This effect was recently discovered independently by Gibbs & Brown (1968).

Fig. 5 shows how the average Si-O distance would vary with average oxygen coordination in silicates although most silicates fall in the range ${}^{\text{II}}\text{O}-{}^{\text{IV}}\text{O}$ as indicated by the dashed line which is taken from the Smith & Bailey work.

The change in anion radii with CN is much smaller in magnitude [$r({}^{\text{VI}}\text{O}^{2-}) - r({}^{\text{II}}\text{O}^{2-}) = 0.05 \text{ \AA}$] than the change in radii with cation CN [$r({}^{\text{VIII}}\text{Cd}^{2+}) - r({}^{\text{IV}}\text{Cd}^{2+})$

$= 0.26 \text{ \AA}$; $r({}^{\text{VIII}}\text{Mg}^{2+}) - r({}^{\text{IV}}\text{Mg}^{2+}) = 0.41 \text{ \AA}$]. One explanation for this effect involves electronic polarizabilities of cations and anions. Intuitively, one might expect the change in radius of an ion with CN to be roughly proportional to its electronic polarizability. A comparison of cation and anion polarizabilities from various sources made by Tessman, Kahn & Shockley (1953) shows generally that polarizabilities of

Table 4. Comparison of observed and calculated interatomic distances in oxides and fluorides with varying coordination

Distance	CN of O^{2-}	Compound	$R_{\text{obs.}}$	$R_{\text{calc.}}$	Distance	CN of O^{2-}	Compound	$R_{\text{obs.}}$	$R_{\text{calc.}}$
${}^{\text{IV}}\text{Al-O}$	II	$\text{LiAlSi}_4\text{O}_{10}$	1.720	1.74	${}^{\text{VI}}\text{Sc-O}$	II	$\text{Sc}_2(\text{WO}_4)_3$	2.063	2.08
		AlPO_4	1.739	"			III	$\gamma\text{-ScOOH}$	2.10
	III	KAlSi_3O_8 (microcline)	1.741	1.75		$\text{Sc}(\text{OH})_3$		2.08	"
		$\text{NaAlSi}_3\text{O}_8$ (low albite)	1.737	"		IV	Sc_2O_3	2.11	2.11
${}^{\text{VI}}\text{Al-O}$	IV	Al_2SiO_5 (sillimanite)	1.770	"	V	CaSc_2O_4	2.122	2.12	
		LiAlO_2	1.761	1.77	VI	KScO_2	2.12	2.13	
	II	$\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	1.881	1.88	${}^{\text{IV}}\text{Si-O}$	II	LiScO_2	2.11	"
		$\text{CsAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	1.882	"			RbScO_2	2.12	"
III	Al_2SiO_5 (kyanite)	1.905	1.89	SiO_2 (quartz)		1.607	1.610		
IV	$\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	1.886	1.91	SiO_2 (low cristobalite)		1.605	"		
${}^{\text{VI}}\text{Cd-O}$	II	Al_2O_3	1.91	1.91	SiO_2 (coesite)	1.613	"		
		LiAlO_2	1.90	1.93	Al_2SiO_5 (sillimanite)	1.615	"		
	III	$3\text{CaSO}_4 \cdot 8\text{H}_2\text{O}$	2.30	2.30	$\text{LiAlSi}_4\text{O}_{10}$	1.609	"		
		$\text{Cd}_2\text{V}_2\text{O}_7$	2.31	2.31	III	$\text{Sc}_2\text{Si}_2\text{O}_7$	1.622	1.620	
${}^{\text{VI}}\text{Co}^{2+}\text{-O}$	VI	CdO	2.348	2.35	ZrSiO_4	1.612	"		
		CoSO_4	2.07	2.085	Al_2SiO_5 (kyanite)	1.628	"		
	III	CoMoO_4	2.082	2.095	Al_2SiO_5 (andalusite)	1.629	"		
		$\text{Co}(\text{NH}_2)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	2.094	"	$\text{Zn}_2\text{Mn}(\text{OH})_2\text{SiO}_4$	1.626	"		
${}^{\text{VI}}\text{Cr}^{3+}\text{-O}$	VI	CoO	2.133	2.135	$\text{AlBeSiO}_4\text{OH}$	1.625	"		
		Cr_5O_{12}	1.972	1.965	$\text{NaAlSi}_3\text{O}_8$	1.618	"		
	III	$\text{KCr}_3\text{O}_{12}$	1.97	1.975	KAlSi_3O_8	1.612	"		
		HCrO_2	1.979	"	$\text{Li}_2\text{Si}_2\text{O}_5$	1.631	"		
${}^{\text{VI}}\text{Fe}^{2+}\text{-O}$	IV	Cr_2O_3	1.99	1.995	$\text{Ca}_2\text{NeHSi}_3\text{O}_9$	1.630	"		
		FeWO_4	2.104	2.13	$\text{CaMnSi}_2\text{O}_6$	1.623	"		
	III	$\text{FeGe}(\text{OH})_6$	2.14	"	IV	$\gamma\text{-Ca}_2\text{SiO}_4$	1.644	1.640	
		$\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$	2.140	2.15	Mg_2SiO_4	1.625	"		
${}^{\text{VI}}\text{Ga}^{3+}\text{-O}$	VI	Fe_2SiO_4	2.172	"	MgFeSiO_4	1.638	"		
		FeO	2.155	2.170	Fe_2SiO_4	1.634	"		
	III	GaNbO_4	1.997	1.98	$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$	1.649	"		
		$\beta\text{-Ga}_2\text{O}_3$	2.00	"	$\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	1.635	"		
${}^{\text{IV}}\text{Ge-O}$	IV	$\alpha\text{-Ga}_2\text{O}_3$	2.00	2.00	${}^{\text{VI}}\text{Si-F}$	II	$(\text{NH}_4)_2\text{SiF}_6$	1.674	1.685
		LiGaO_2	2.00	2.02			$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SiF}_6$	1.664	"
	III	GeO_2	1.739	1.75		III	Na_2SiF_6	1.695	1.700
		BaGe_4O_9	1.740	1.76		IV	K_3SiF_7	1.70	1.710
${}^{\text{VI}}\text{Ni}^{2+}\text{-O}$	IV	$\text{Na}_2\text{O} \cdot \text{GeO}_2 \cdot 6\text{H}_2\text{O}$	1.769	"	$(\text{NH}_4)_3\text{SiF}_7$	1.71	"		
		$\text{Na}_2\text{Sn}_4\text{Ge}_{10}\text{O}_{30}(\text{OH})_4$	1.752	"	${}^{\text{VI}}\text{Tl}^{4+}\text{-O}$	II	$\text{Na}_2\text{Tl}_6\text{O}_{13}$	1.957	1.955
	BaGeO_3	1.785	1.78	$\text{Rb}_2\text{Tl}_6\text{O}_{13}$			1.983	"	
	III	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	2.063	2.06		III	$\text{Tl}_2\text{Ti}_2\text{O}_6$	1.970	1.965
NiWO_4		2.08	"	Tl_2O_2		1.959	"		
${}^{\text{IV}}\text{P}^{5+}\text{-O}$	VI	NiO	2.084	2.08	IV	NiTiO_3	1.99	1.985	
		MoPO_4	1.528	1.52	MnTiO_3	1.99	"		
	III	AlPO_4	1.515	"	V	BaTi_4O_9	1.98	"	
		P_2O_5	1.54	"	$\text{Na}_2\text{Tl}_3\text{O}_7$	1.992	1.995		
${}^{\text{VI}}\text{P}^{5+}\text{-O}$	III	$\text{Na}_2\text{H}_2\text{P}_4\text{O}_{12}$	1.542	1.53					
		NaPO_3NH_3	1.528	"					

anions are larger than those of most cations, in distinct contrast to the relative change in anion and cation radii with CN. However, Ruffa (1964) has shown in TiO_2 and other compounds with high Madelung potentials that the polarizability of the cation may be considerably greater than that of the anion. Thus, the possibility still exists that there may be some correlation between change in radius with CN and polarizability.

An alternative explanation for this effect depends on the anion-anion repulsive forces described by Pauling (1928). In most of the oxides for which reliable radii have been determined, the cation/anion radius ratio, ρ , is considerably less than 1. When this condition holds, anion-anion forces can be large. As ρ becomes small and as the anion CN diminishes from VI to II, the nearest neighbor anion interactions become more important. The increase in anion-anion forces prevents the anion from deforming as much as might be expected from polarizability considerations. The cations in such structures, however, cannot approach each other closely and cation-cation repulsion is probably less than anion-anion forces. Consequently, the cation is easily able to expand into the void between the anions - thus shortening considerably the cation-anion distance.

Absolute values of radii

The question of absolute values for anion and cation radii is still not resolved. Although it has been possible to devise sets of radii which are almost additive, the values of anionic radii have been determined by approximate methods. This question of the relative sizes of anion and cation radii is very important because it determines the physical picture we have of ionic solids. Traditionally this has been a picture of anion-close-packed solids.

Values of anion radii have been chosen from: (1) molar refractivities of salts in solution (Wasastjerna, 1923); (2) anion-anion distances in close-packed solids (Bragg & West, 1927); (3) Born repulsive coefficients determined from isothermal compressibilities and thermal expansion coefficients (Fumi & Tosi, 1964) and (4) electron density distribution in alkali halides (Witte & Wölfel, 1955; Schoknecht, 1957; and Meisalo & Inkinen, 1967). The traditional sets of radii were based on (1) and (2). The first values of ionic radii were determined by Wasastjerna who used the ratio of the cube root of the molar refractivities of the free ions to determine $r_c:r_a$ in the alkali halides. He arrived at $r(\text{VI F}^-) = 1.33 \text{ \AA}$ and $r(\text{VI O}^{2-}) = 1.32 \text{ \AA}$. Bragg & West noted that observed O-O distances in silicates were roughly 2.7 \AA and concluded that $r(\text{O}^{2-}) = 1.35 \text{ \AA}$. Used with available sets of interatomic distances in common oxides, these values led to small $r_c:r_a$ and resulted in the concept of anion close-packed oxides. Many solid state phenomena such as diffusion, mechanical deformation, kinetics of transformations, and solid state reactions have been interpreted on this basis.

More recent evidence, however, indicates that the ratio $r_c:r_a$ may be considerably larger than indicated by

the traditional sets of radii. Comparative calculations of wave functions of free ions and ions in a crystal by Petrashen, Abarenkov & Kristofel (1960) showed a tightening of electron clouds in anions and a relaxation of cation electrons in solids. Analysis of electron density distributions in NaCl (Witte & Wölfel, 1955), LiF (Krug, Witte & Wölfel, 1955) and KBr (Meisalo & Inkinen, 1967), indicated anion radii and cation radii smaller and larger respectively than traditional ionic radii. Fumi & Tosi on the basis of calculations of Born repulsive parameters from compressibility and thermal expansion data present convincing evidence that $r_c:r_a$ is larger than in the traditional sets of radii. They found $r(\text{VI F}^-) = 1.15\text{--}1.20 \text{ \AA}$ with an estimated error of 0.05 \AA . Assuming a constant difference of $r(\text{VI O}^{2-}) - r(\text{VI F}^-) = 0.07 \text{ \AA}$, then $r(\text{VI O}^{2-}) = 1.22\text{--}1.27 \text{ \AA}$. These values are more in agreement with the shortest nonbonding O-O distances in many oxides. As shown in Table 5 these range from 2.15 \AA in the NaNO_3 structure to greater than 3 \AA in the antiferite structures. Perhaps the most surprising distance in this group is that of the 2.16 \AA shared edges of the SiO_6 octahedra in the rutile form of SiO_2 (stishovite). Although extremely high pressure must be used to synthesize stishovite, it is difficult to reconcile this short O-O distance with an $r(\text{III O}^{2-}) = 1.36 \text{ \AA}$, especially since Fig. 1 shows there is nothing unusual about the cell volume of stishovite. Furthermore, with smaller anions one is not forced to assume negative radii for III C^{4+} in the carbonate ion and III N^{5+} in the nitrate ion. Although there is intrinsically no objection to negative radii so long as one does not assume a hard sphere model, it is esthetically more pleasing to have positive radii. However, even with Fumi & Tosi's crystal radii it is not possible to achieve a complete set of positive radii. The O-H and F-H distances in hydrogen-bonded compounds result in negative radii of -0.04 and -0.24 \AA for II H^+ and I H^+ . Although the value for $r(\text{II H}^+)$ falls within the estimated error of the crystal radii and would still allow a completely positive set of radii, this is not possible for I H^+ . One is forced to the interpretation that an I H^+ -O bond results in a highly deformed oxygen ion in which the proton penetrates the electron cloud of the oxygen ion. On the basis of the above considerations, the

Table 5. Shortest oxygen-oxygen distances in some simple oxides

Compound	Structure type	O-O
NaNO_3	calcite	2.15 \AA
SiO_2	rutile	2.16
CaCO_3	calcite	2.22
Al_2SiO_5	andalusite	2.25
$\text{B}_2\text{O}_3(\text{II})$	$\text{B}_2\text{O}_3(\text{II})$	2.36
S_3O_9	S_3O_9	2.37
$\text{B}_2\text{O}_3(\text{I})$	$\text{B}_2\text{O}_3(\text{I})$	2.38
Al_2O_3	corundum	2.52
SiO_2	quartz	2.60
BeO	wurtzite	2.70
MgO	rocksalt	2.98
Li_2O	antiferite	3.27

Fumi & Tosi crystal radii (CR) are probably more satisfactory than the traditional sets of radii.

Pauling (1928) noted a correlation between radius ratios and the relative stability of certain structures. Values of ρ for structures with tetrahedral cation coordination were generally of the order of 0.2–0.4 whereas values of ρ for octahedral cation coordination were of the order of 0.4–0.7. There were exceptions, but in general the radius ratio was found to provide some indication of the type of prevalent coordination of anions about the cation in ionic crystals. Phillips & Williams (1965) noted that the critical radius ratios were not satisfactory in predicting CN changes but their analysis involved highly covalent rather than ionic crystals.

It is clear that any new set of radii should provide a correlation between radius ratios and CN at least as satisfactory as Pauling's table of ionic radii. Table 6 gives values of ρ calculated by means of an average radius of 1.38 Å for oxygen for numerous cations with CN III, IV, VI, and VIII. As long as ρ falls within ± 0.02 of the limits defined by Pauling (1960) the radius ratio is in boldface. It will be noted that values of ρ calculated from ionic radii (IR) do not fall within the expected limits for most of the small ions, e.g. $^{VI}Al^{3+}$, $^{VI}As^{5+}$, $^{III}B^{3+}$, $^{IV}B^{3+}$, $^{IV}S^{6+}$, $^{IV}Si^{4+}$, and $^{VI}Si^{4+}$, whereas values of ρ calculated from crystal radii (CR) give poor agreement for $^{IV}Ga^{3+}$, $^{IV}Li^{+}$, $^{VI}Mn^{2+}$, $^{IV}Zn^{2+}$, and $^{IV}Mo^{6+}$. Since ions with strong covalent mixing (Ga^{3+} and Zn^{2+}) prefer four coordination *via* sp^3 hybridization, even though $\rho > 0.414$, it is felt that crystal radii predicts CN on the basis of radius ratio as well as effective ionic radii.

Perhaps the most important conclusion to be drawn from the above arguments is that specific values from this or any other set of radii should not be used too rigidly to derive a physical picture of ionic solids. Currently available information on electron density

distributions in solids is not sufficient to establish absolute values of radii. Furthermore, if one assumes that the radius of an ion, say oxygen, is the distance from the oxygen nucleus to the minimum in electron density between the oxygen ion and a cation, this radius may vary depending on the type of cation, *i.e.* on the covalency of the bond. If, however, the crystal radii in Table 1(a) are more accurate than the ionic radii, certain concepts of the structures of ionic solids are no longer valid. For example, oxides should not be thought of as close-packed arrangements of anion spheres whose interstices are partly filled with cations. Instead, the cation–anion bonds should be considered as the important factors determining crystal structure and close-packed anion arrangements as merely the result of the structure attaining a lowest-energy configuration.

Interatomic distances in highly symmetric oxides and fluorides

Agreement between observed and calculated distances from Table 1(a) over a wide variety of compounds with varying cation and anion coordination was shown to be quite good. However, the compounds with rock-salt, fluorite, and perovskite structures show rather poor agreement (Table 7). A possible source of error could be the cation radii. However, the value of $r(^{VIII}Ca^{2+})$ taken from more than 15 Ca–O distances which agree to within 0.02 Å results in $R_{calc} - R_{obs} = 0.06$ Å for CaF_2 . Therefore, it is felt that the lack of agreement of interatomic distances between symmetric and unsymmetric structures is significant. The effect appears to be greater for the fluorides than for oxides and greater for smaller cations than for larger cations. The smaller observed interatomic distances are qualitatively explained by minimization of anion–anion repulsive forces. The regular polyhedra result in the maximum distances between all cations and anions and,

Table 6. *Radius ratios for oxides*

Ion	CN	IR	CR	Ion	CN	IR	CR
Al^{3+}	IV	0.28	0.42	Mg^{2+}	VI	0.52	0.69
	VI	0.38	0.54	Mn^{2+}	VI	0.59	0.79
As^{5+}	IV	0.24	0.38	Mo^{6+}	IV	0.30	0.45
	VI	0.36	0.52		VI	0.43	0.60
B^{3+}	III	0.02	0.12	Ni^{2+}	VI	0.51	0.66
	IV	0.09	0.21	P^{5+}	IV	0.12	0.25
Be^{2+}	III	0.12	0.25	S^{6+}	IV	0.09	0.21
	IV	0.20	0.33	Sc^{3+}	VI	0.53	0.70
Ca^{2+}	VIII	0.81	1.01	Si^{4+}	IV	0.19	0.32
Ce^{4+}	VIII	0.70	0.90		VI	0.30	0.43
Co^{2+}	VI	0.53	0.71	Sn^{4+}	VI	0.50	0.67
Cr^{3+}	VI	0.44	0.61	Ti^{4+}	VI	0.44	0.60
Fe^{2+}	VI	0.56	0.73	W^{6+}	IV	0.30	0.44
Fe^{3+}	IV	0.36	0.52		VI	0.42	0.58
	VI	0.47	0.63	Y^{3+}	VI	0.65	0.83
Ga^{3+}	IV	0.34	0.49		VIII	0.74	0.93
	VI	0.45	0.61	Zn^{2+}	IV	0.43	0.60
Ge^{4+}	IV	0.29	0.44		VI	0.54	0.71
	VI	0.39	0.55	Zr^{4+}	VI	0.52	0.69
In^{3+}	VI	0.57	0.75				
Li^{+}	IV	0.43	0.59				
	VI	0.54	0.71				

therefore, the least repulsion interactions. The greater polarizabilities of the oxide ion and larger cations result in deformation of these ions into voids and consequent reductions in repulsive effects.

Table 7. Calculated and observed interatomic distances in highly symmetric oxides and fluorides

Rocksalt			
MO	R_{Calc}^{M-O}	R_{Obs}^{M-O}	ΔR
VI-VI			
NiO	2.10	2.084	0.016
MgO	2.12	2.105	0.015
CoO	2.135	2.133	0.002
FeO	2.17	2.155	0.015
MnO	2.22	2.222	-0.002
CdO	2.35	2.348	+0.002
CaO	2.40	2.405	-0.005
SrO	2.56	2.58	-0.02
BaO	2.76	2.762	-0.002
MF			
VI-VI			
LiF	2.07	2.008	0.062
NaF	2.35	2.31	0.04
AgF	2.48	2.46	0.02
KF	2.71	2.673	0.037
CsF	3.03	3.00	0.03
Fluorite			
MO ₂			
VIII-IV			
CeO ₂	2.35	2.34	0.01
UO ₂	2.38	2.37	0.01
ThO ₂	2.44	2.42	0.02
MF ₂			
VIII-IV			
CdF ₂	2.38	2.333	0.053
CaF ₂	2.43	2.37	0.06
HgF ₂	2.45	2.40	0.05
SrF ₂	2.56	2.51	0.05
BaF ₂	2.73	2.69	0.04
MBO ₃ Perovskite			
VI-VI or X II-VI			
BaCeO ₃	2.25	2.198	0.052
SrCeO ₃	2.25	2.135	0.115
CeCrO ₃	2.015	1.933	0.082
KNbO ₃	3.00	2.84	0.16
KNbO ₃	2.04	2.011	0.029
BaMoO ₃	2.05	2.02	0.03
SrMoO ₃	2.05	1.987	0.063
BaPbO ₃	2.175	2.136	0.039
BaSnO ₃	2.09	2.058	0.032
CaSnO ₃	2.09	1.96	0.13
SrSnO ₃	2.09	2.016	0.074
BaZrO ₃	2.12	2.096	0.024
SrZrO ₃	2.12	2.05	0.07
MBF ₃			
VI-VI or XII-VI			
KCoF ₃	2.065	2.035	0.030
RbCoF ₃	2.065	2.03	0.035
TlCoF ₃	2.065	2.064	0.001
CsMnF ₃	2.15	2.13	0.02
CsMnF ₃	3.25	3.13	0.12
KFeF ₃	2.10	2.06	0.04

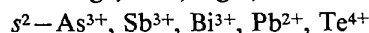
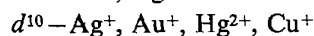
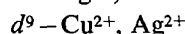
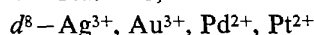
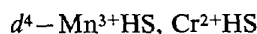
Table 7 (cont.)

	R_{Calc}^{M-O}	R_{Obs}^{M-O}	ΔR
RbFeF ₃	2.10	2.087	0.013
KMgF ₃	2.05	1.986	0.064
KMnF ₃	2.15	2.095	0.055
KNiF ₃	2.03	2.006	0.024
CsPbF ₃	2.51	2.405	0.105
KZnF ₃	2.075	2.027	0.048
AgZnF ₃	2.075	1.99	0.085

Unusual and irregular coordination

When the distances in polyhedra are almost equal, it is easy to determine the coordination. In this case there is usually a clear cut-off point for which peripheral anions may be considered as bonded to the central atom. However, in many cases there is a gradual increase in near-neighbor distances up to very large interatomic distances for the large alkali and alkaline earth ions in network structures such as silicates; consequently, the CN of these ions is frequently uncertain. The curves of radii *vs.* CN reflect this uncertainty [Figs. 2(a) and 2(b)]. For the purposes of this paper a break of 0.02-0.05 Å was sought as the cut-off point in the interatomic distances. When there was no such break, the distances were tabulated as questionable values. It seems likely that the slopes of radii *vs.* CN plots should be regular. The deviation from regularity is particularly noticeable for Na⁺, Ag⁺, K⁺, Cs⁺, Pb²⁺, Sr²⁺, and Ba²⁺. The lack of regularity is attributed either to an insufficient number of examples of a particular coordination and/or to the difficulty in determining the CN.

Several other groups of ions exhibit irregular coordination which frequently does not result in consistent interatomic distances. Also, the radii derived from these distances do not fall on the regular curves of radii *vs.* CN. These are the ions with the following electron configurations:



A detailed discussion of the stereochemistry of d^4 , d^8 , d^9 , and d^{10} ions is given by Orgel (1960). Ions with d^8 configuration frequently occur in square planar coordination. This coordination is usually clearly recognized, *e.g.* PdO, AuF₃. The ions with d^4 and d^9 configurations have the familiar Jahn-Teller distortion exemplified by Cu²⁺. These ions are characterized by four ligands at one distance and two ligands at a different distance, either closer or further away. When the difference is slight, the coordination is pseudo-octahedral; when the difference is large, square-planar or two-coordinated structures result. In the cupric oxides and fluorides the distances of the fifth and sixth neighbors range from just slightly larger than the other four

to distances almost outside the bonding sphere. In the case of cupric compounds we have calculated the average distance of all six neighbors for octahedral coordination and the four near neighbors for square-planar coordination and have listed the radii in Table I as both IVSQ and VI.

Ions with the d^{10} configuration have been observed with linear two coordination. Orgel has related this behavior to the small separation in energy of the d^{10} and d^9s states and predicts linear coordination of Cu^+ , Ag^+ , Au^+ , and Hg^{2+} . Two-coordinated radii are tabulated for Cu^+ , Ag^+ , and Hg^{2+} .

Another group represents the ions with a lone pair of electrons: As^{3+} , Sb^{3+} , Bi^{3+} , Pb^{2+} , and Te^{4+} . The oxides formed with these ions are considered to be highly covalent. For example in PbO the lone pair acts as a ligand and results in a coordination of four neighbors in a plane on one side of the Pb^{2+} ion and the lone pair on the other side at the apex of the pyramid. This configuration has been designated in Table 1(a) as IVPY.

Summary

The goal of this work has been to provide radii which will be *useful* to anyone interested in the structures of oxides and fluorides. The set of empirical radii derived here is primarily intended to be used in calculating expected interatomic distances in oxide and fluoride crystal structures. Although the absolute values of radii were considered, one cannot reliably assign specific numbers to specific ions. Certain effects such as anion-anion repulsion, irregular coordination, and metal-metal bonding cause deviations from predicted interatomic distances which have been largely ignored because these effects are difficult to include in a simple table of radii. These 'high-order' effects probably are of greater importance in structures with larger anions than in those containing oxide or fluoride ions and must be left to future work.

Note added in proof: - Prof. B. Reuter, who has just completed a refinement of the structure of the ordered spinel, MgV_2O_4 , has suggested a value of $r(\text{IVMg}^{2+}) = 0.58 \text{ \AA}$. Because the original value of 0.49 \AA came from a single structure refinement and because this new value is more consistent with Fig. 2(b), the new value is preferred.

We would like to acknowledge the interest of Professor M. J. Buerger whose encouragement in the early stages of this work provided much of the incentive for its completion. We would also like to thank Professors W. H. Baur and A. Pabst for critically reviewing the manuscript prior to publication.

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Stereochemistry and Crystal Structure of a Cobalt(III) Sulphito Complex: *trans*-Sulphiteisothiocyanate-bis(ethylenediamine)cobalt(III) Dihydrate

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(Received 14 May 1968)

The crystal structure of $\text{Co(en)}_2\text{SO}_3\text{NCS}\cdot 2\text{H}_2\text{O}$ has been determined from three-dimensional X-ray data and refined by the full-matrix least-squares method to a residual of 0.078. The compound crystallizes in the monoclinic system, space group $P2_1/c$ with four molecules in the unit cell of dimensions $a = 9.13 \pm 0.02$, $b = 6.59 \pm 0.02$, $c = 22.88 \pm 0.06$ Å, $\beta = 95.5 \pm 0.5^\circ$. The coordination around the metal atom is octahedral, the sulphito group being bonded through sulphur to the metal and in *trans* configuration. The Co-N(NCS) distance is not significantly different from the Co-N(en) distances. Some important dimensions are: Co-S, 2.203 ± 0.006 Å; mean Co-N(en), 1.962 ± 0.010 Å; mean S-O, 1.485 ± 0.012 Å; mean O-S-O, $110.3 \pm 0.7^\circ$; Co-N(NCS), 1.974 ± 0.018 Å.

Introduction

Recently, the infrared and visible absorption spectra of a series of sulphito-bis(ethylenediamine)cobalt(III) complexes were measured by Baldwin (1961). These spectra, together with measurements of conductivity in aqueous solution and a study of chemical reactions, were interpreted by Baldwin in terms of possible structures for these complexes. For $\text{Co(en)}_2\text{SO}_3\text{NCS}\cdot 2\text{H}_2\text{O}$ it was postulated that the sulphito group is bonded through sulphur, the bond possibly involving $d\pi-d\pi$ bonding, and that the compound had the *cis* configuration. Kinetic studies of sulphito complexes of Co^{III} have also been made recently, indicating that the sulphito group has a marked *trans* labilizing effect (Tewari, Gaver, Wilcox & Wilmarth, 1967).

We undertook the structure determination of this compound in order to establish whether the postulated structure was correct, and, if so, to compare the dimensions of the sulphito group coordinated to Co^{III} , with the dimensions found for this group in $\text{PdSO}_3(\text{NH}_3)_3$ (Spinnler & Becka, 1967). Furthermore, we considered that a comparison between the different Co-N distances in this compound would be of interest

in relation to the kinetics of reaction of sulphito complexes. In an earlier communication (Baggio & Becka, 1967) we described the main features of the structure as obtained from least-squares refinement with individual isotropic temperature factors. In this paper we give the details of the structure and structure determination with individual anisotropic temperature factors for Co, the atoms of SO_3 , and the atoms of NCS.

Experimental

Preparation

$\text{Co(en)}_2\text{SO}_3\text{NCS}\cdot 2\text{H}_2\text{O}$ was prepared by the method reported by Baldwin (1961), and crystals suitable for X-ray studies were obtained by recrystallization. The chemical and physical properties of the sample were in good agreement with those reported previously. Chemical analysis of a sample gave the following percentage composition for C, N and H: C, 17.37; N, 19.21; H, 5.75, the theoretical composition being: C, 16.59; N, 19.83; H, 5.66.

Crystal data

Name of substance: *trans*-sulphiteisothiocyanate-bis(ethylenediamine)cobalt(III) dihydrate. Chemical formulae: structural, $\text{Co(en)}_2\text{SO}_3\text{NCS}\cdot 2\text{H}_2\text{O}$; alpha-

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