

Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides

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The effective ionic radii of Shannon & Prewitt [*Acta Cryst.* (1969), B25, 925–945] are revised to include more unusual oxidation states and coordinations. Revisions are based on new structural data, empirical bond strength–bond length relationships, and plots of (1) radii *vs* volume, (2) radii *vs* coordination number, and (3) radii *vs* oxidation state. Factors which affect radii additivity are polyhedral distortion, partial occupancy of cation sites, covalence, and metallic character. Mean $\text{Nb}^{5+}\text{--O}$ and $\text{Mo}^{6+}\text{--O}$ octahedral distances are linearly dependent on distortion. A decrease in cation occupancy increases mean $\text{Li}^+\text{--O}$, $\text{Na}^+\text{--O}$, and $\text{Ag}^+\text{--O}$ distances in a predictable manner. Covalence strongly shortens $\text{Fe}^{2+}\text{--X}$, $\text{Co}^{2+}\text{--X}$, $\text{Ni}^{2+}\text{--X}$, $\text{Mn}^{2+}\text{--X}$, $\text{Cu}^+\text{--X}$, $\text{Ag}^+\text{--X}$, and M--H^- bonds as the electronegativity of X or M decreases. Smaller effects are seen for $\text{Zn}^{2+}\text{--X}$, $\text{Cd}^{2+}\text{--X}$, $\text{In}^{3+}\text{--X}$, $\text{Pb}^{2+}\text{--X}$, and $\text{Tl}^+\text{--X}$. Bonds with delocalized electrons and therefore metallic character, *e.g.* Sm--S , V--S , and Re--O , are significantly shorter than similar bonds with localized electrons.

Introduction

A thorough and systematic knowledge of the relative sizes of ions in halides and chalcogenides is rapidly being developed by crystal chemists as a result of (1) extensive synthesis within certain structure types, *e.g.* rocksalt, spinel, perovskite and pyrochlore; (2) preparation of new compounds with unusual oxidation states and coordination numbers; and (3) the abundance of accurate crystal structure refinements of halides, chalcogenides, and molecular inorganic compounds. A set of effective ionic radii which showed a number of systematic trends with valence, electronic spin state, and coordination was recently developed (Shannon & Prewitt, 1969, hereafter referred to as SP 69). This work has since been supplemented and improved by studies of certain groups of ions: rare earth and actinide ions (Peterson & Cunningham, 1967, 1968); tetrahedral oxyanions (Kálmán, 1971); tetravalent ions in perovskites (Fukunaga & Fujita, 1973); rare earth ions (Greis & Petzel, 1974); and tetravalent cations (Knop & Carlow, 1974).

Further, the relative sizes of certain ions or ion pairs were studied by Khan & Baur (1972): NH_4^+ ; Ribbe & Gibbs (1971): OH^- ; Wolfe & Newnham (1969): $\text{Bi}^{3+}\text{--La}^{3+}$; McCarthy (1971): $\text{Eu}^{2+}\text{--Sr}^{2+}$; Silva, McDowell, Keller & Tarrant (1974): No^{2+} . These authors' results have been incorporated here into a comprehensive modification of the Shannon–Prewitt radii.

In this paper the revised list of effective ionic radii, along with the relations between radii, coordination number, and valence is presented. The factors responsible for the deviation of radii sums from additivity such as polyhedral distortion, partial occupancy of cation sites, covalence, and metallic behavior (electron delocalization) will be discussed.

Procedure

The same basic methods used in SP 69 were employed in preparing the revised list of effective ionic radii (Table 1). Some of the same assumptions were made:

(1) Additivity of both cation and anion radii to reproduce interatomic distances is valid if one considers coordination number (CN), electronic spin, covalency, repulsive forces, and polyhedral distortion.*

(2) With these limitations, radii are independent of structure type.

(3) Both cation and anion radii vary with coordination number.

(4) With a constant anion, unit-cell volumes of isostructural series are proportional (but not necessarily linearly) to the cation volumes.

Other assumptions made in SP 69 have been modified:

(1) The effects of covalency on the shortening of M--F and M--O bonds are *not* comparable.

(2) Average interatomic distances in similar polyhedra in one structure are *not* constant but vary in a predictable way with the degree of polyhedral distortion (and anion CN). Both of these modified assumptions will be discussed in detail later.

The anion radii used in SP 69 were subtracted from available average distances. Approximately 900 distances from oxide and fluoride structures were used, and Table 2 lists their references according to CN and spin. These references generally cover from 1969 to 1975. The cation radii were derived to a first approximation from these distances, and then adjusted to be consistent with both the experimental interatomic distances and radii–unit cell volume (r^3 *vs* V) plots, as in

* Polyhedral distortion was not considered in SP 69.

SP 69. Although such r^3 vs V plots are not always linear (Shannon, 1975), their regular curvilinear nature still allows prediction of radii. This system is particularly accurate for radii in the middle of a series, and least reliable for large polarizable cations like Cs^+ , Ba^{2+} , and Tl^{3+} . Radii-volume plots were used by Knop & Carlow (1974) and Fukunaga & Fujita (1973) to derive radii of tetravalent cations. These radii were used along with experimental interatomic distances in deriving the final radii. Greis & Petzel (1974) derived rare earth radii in eight- and nine-coordination using accurate cell dimensions for rare earth trifluorides and distances calculated using the structural parameters of YF_3 and LaF_3 . These radii were used in Table 1 after applying small corrections ($+0.030 \text{ \AA}$ to IXLa^{3+} , IXCe^{3+} , IXPr^{3+} , and IXNd^{3+} ; $+0.025 \text{ \AA}$ to all other Greis & Petzel IXRE^{3+} radii, and 0.015 \AA to all

VIIIRe^{3+} radii) for consistency with experimental interatomic distances and radii-CN plots.

Where structural data were not available or not accurate, plots of (1) radii vs unit cell volumes, (2) radii vs CN and (3) radii vs oxidation state, or combinations of these were used to obtain estimated values. Fig. 1 shows examples of radii-valence plots used to provide consistency between experimental radii and those anticipated from the regular nature of these plots. Cations whose final radii values were derived from both estimated values and experimental interatomic distances are: VIOS^{3+} , VIOS^{6+} , VIOS^{7+} , VIRe^{4+} , VIRe^{5+} , VIRe^{6+} , VIRe^{7+} , VIIRh^{4+} , VIIU^{4+} , VIIU^{5+} , and VIIU^{6+} .

Fig. 2(a)-(e) shows plots of radii vs CN. Generally, it was assumed that radii-CN plots for two different ions do not cross. Radii for IVCu^+ , VICu^+ , IXRb^+ , VNI^{2+} , VIIEr^{3+} , VIYYb^{3+} , VIITb^{3+} , XIINd^{3+} , IVCr^{4+} ,

Table 1. Effective ionic radii

CR crystal radius, IR effective ionic radius, R from r^3 vs V plots, C calculated, E estimated, ? doubtful, * most reliable, M from metallic oxides.

ION	EC	CN	SP	CR	*IR*	ION	EC	CN	SP	CR	*IR*	ION	EC	CN	SP	CR	*IR*
AC+3 6P 6 VI			1.26	1.12	R	CL-1 3P 6 VI			1.67	1.81	P	GD+3 4F 7 VII			1.14	1.00	
AG+1 4D10 II			.81	.67		CL+5 3S 2 IIIPY			.26	.12		GE+2 4S 2 VI			1.193	1.053	R
IV			1.14	1.00	C	CL+7 2P 6 IV			.22	.08	*	GE+4 3D10 IV			1.247	1.107	RC
IVSQ			1.16	1.02		VI			.41	.27	A	VI			.87	.73	A
V			1.23	1.09	C	CM+3 5F 7 VI			1.11	.97	R	VI			.930	.390	*
VI			1.29	1.15	C	CM+4 5F 6 VI			.99	.85	R	VI			.670	.530	R*
VII			1.36	1.22		VIII			1.09	.95	R	H +1 1S 0 I			-.24	-.38	
VIII			1.42	1.28		CO+2 3D 7 IV	HS		.72	.58		II			-.04	-.18	
AG+2 4D 9 IVSQ			.93	.79		V			.81	.67	C	HF+4 4F14 IV			.72	.58	R
VI			1.08	.94		VI	LS		.79	.65	R	VI			.85	.71	R
AG+3 4D 8 IVSQ			.81	.67		HS			.885	.745	R*	VII			.90	.76	
VI			.89	.75	R	CO+3 3D 6 VI	LS		1.04	.90		VIII			.97	.83	
AL+3 2P 6 IV			.53	.39	*	VI			.685	.565	R*	HG+1 6S 1 III			1.11	.97	
VI			.62	.48		HS			.75	.61		II			1.33	1.19	
V			.675	.535	R*	CO+4 3D 5 IV	HS		.54	.40		HG+2 5D10 VI			.83	.69	
AM+2 5F 7 VII			1.35	1.21		VI			.67	.53	R	IV			1.10	.96	
VIII			1.40	1.26		LS			.87	.73	E	VI			1.16	1.02	
IX			1.45	1.31		HS			.94	.80	R	VIII			1.28	1.14	R
AM+3 5F 6 VI			1.115	.975	R	CR+3 3D 3 VI			.755	.615	R*	HO+3 4F10 VI			1.041	.901	R
VIII			1.23	1.09		CR+4 3D 2 IV			.55	.41		VIII			1.155	1.015	R
AM+4 5F 5 VI			.99	.85	R	VI			.69	.55	R	IX			1.212	1.072	R
VIII			1.09	.95		CR+5 3D 1 IV			.485	.345	R	X			1.26	1.12	
AS+3 4S 2 VI			.72	.58	A	VI			.63	.49	EA	I -1 5P 6 VI			2.06	2.20	A
AS+5 3D10 IV			.675	.535	R*	VIII			.71	.57		I +5 5S 2 IIIPY			.58	.44	*
VI			.60	.46	C*	CR+6 3P 6 IV			.40	.26		VI			1.09	.95	
AT+7 5D10 VI			.76	.62	A	VI			.58	.44	C	I +7 4D10 IV			.56	.42	
AU+1 5D10 VI			1.51	1.37	A	CS+1 5P 6 VIII			1.81	1.67		VI			.67	.53	
AU+3 5D 8 IVSQ			.82	.68		IX			1.88	1.74		IN+3 4D10 IV			.76	.62	
VI			.99	.85	A	IX			1.92	1.78		VI			.940	.800	R*
AU+5 5D 6 VI			.71	.57		X			1.95	1.81		VIII			1.06	.92	RC
8 +3 1S 2 III			.55	.41	*	XI			1.99	1.85		IR+3 5D 6 VI			.82	.68	E
IV			.55	.41	*	XII			2.02	1.88		IR+4 5D 5 VI			.765	.625	R
VI			.41	.27	C	CU+1 3D10 II			.60	.46		IR+5 5D 4 VI			.71	.57	EM
BA+2 5P 6 VI			1.49	1.35		IV			.74	.60	E	K +1 3P 6 IV			1.51	1.37	
VII			1.52	1.38		VI			.91	.77	E	VI			1.52	1.38	
VIII			1.56	1.42	C	CU+2 3D 9 IV			.71	.57		VII			1.60	1.46	
IX			1.61	1.47		IVSQ			.71	.57	*	VIII			1.65	1.51	
X			1.66	1.52		V			.79	.65	*	IX			1.69	1.55	
XI			1.71	1.57		VI			.87	.73		X			1.73	1.59	
XII			1.75	1.61	C	CU+3 3D 8 VI	LS		.68	.54		XI			1.78	1.64	
BE+2 1S 2 III			.30	.16		D +1 1S 0 II			.04	-.10		LA+3 4D10 VI			1.172	1.032	R
IV			.41	.27	*	DY+2 4F10 VI			1.21	1.07		VII			1.24	1.10	
VI			.59	.45	C	VIII			1.27	1.13		VIII			1.300	1.160	R
BI+3 6S 2 V			1.10	.96	C	VI			1.33	1.19		IX			1.356	1.216	R
VI			1.17	1.03	R*	UY+3 4F 9 VI			1.052	.912	R	X			1.41	1.27	
VII			1.31	1.17	R	VII			.11	.97		XI			1.50	1.36	C
BI+5 5D10 VII			.90	.76	E	VIII			1.167	1.027	R	LI+1 1S 2 IV			.730	.590	*
BK+3 5F 8 VI			1.10	.96	R	IX			1.223	1.083	R	VI			.90	.76	*
BK+4 5F 7 VI			.97	.83	R	ER+3 4F11 VI			1.030	.890	R	VIII			1.06	.92	C
VIII			1.07	.93	R	VII			1.085	.945		LU+3 4F14 VI			1.001	.861	R
BR-1 4P 6 VI			1.82	1.66	P	VIII			1.144	1.004	R	VII			1.117	.977	R
BR+3 4P 2 IVSQ			.73	.59		IX			1.202	1.062	R	IX			1.172	1.032	R
BR+5 4S 2 IIIPY			.45	.31		EU+2 4F 7 VI			1.31	1.17		VI			.71	.57	
BR+7 3D10 IV			.39	.25		V			1.34	1.20	V	VI			.80	.66	
VI			.53	.39	A	VIII			1.39	1.25		VII			.860	.720	*
C +4 1S 2 III			.06	-.08		IX			1.44	1.30		VIII			1.03	.89	C
IV			.29	.15	P	X			1.49	1.35		HS			.80	.66	
VI			.16	.02		EU+3 4F 6 VI			1.087	.947	R	VI	HS		.89	.75	C
CA+2 3P 6 VI			1.14	1.00		VII			1.15	1.01		LS			.81	.67	E
VII			1.20	1.06	*	VIII			1.206	1.066	R	HS			.970	.830	R*
VIII			1.26	1.12	*	IX			1.260	1.120	R	VI			1.04	.90	C
IX			1.32	1.18		F -1 2P 6 VI			1.145	1.005		VIII			1.10	.96	R
X			1.37	1.23	C	III			1.16	1.30		VI			.72	.58	
XI			1.48	1.34	C	IV			1.17	1.31		LS			.72	.58	R
CD+2 4D10 IV			.92	.78		VI			1.19	1.33		HS			.785	.645	R*
V			1.01	.87		F +7 1S 2 VI			.22	.08	A	VI			.53	.39	R
VI			1.09	.95		FE+2 3D 6 IV	HS		.77	.63		VI			.670	.530	R*
VII			1.17	1.03	C	IVSQ			.78	.64		HS			.67	.53	R
VIII			1.24	1.10	C	VI			.75	.61	E	MN+6 3D 1 IV			.75	.61	R
IX			1.45	1.31		VI	HS		.920	.780	R*	MN+7 3P 6 IV			.39	.25	
CE+3 6S 1 VI			1.15	1.01	R	VIII			1.06	.92	C	VI			.60	.46	A
VII			1.21	1.07	E	FE+3 3D 5 IV	HS		.63	.49	*	VI			.83	.69	E
VIII			1.283	1.143	R	V			.72	.58		MO+4 4D 2 VI			.790	.650	RM
IX			1.336	1.196	R	VI	LS		.69	.55	R	MO+5 4D 1 IV			.60	.46	R
X			1.39	1.25	C	HS			.785	.645	R*	VI			.75	.61	R
XI			1.48	1.34	C	FE+4 3D 4 VI	HS		.92	.78		VI			.55	.41	R*
CE+4 5P 6 VI			1.01	.87	R	FE+6 3D 2 IV			.725	.585	R	VI			.64	.50	
VIII			1.11	.97	R	FR+1 6P 6 VI			.94	1.80	A	VI			.73	.59	R*
X			1.21	1.07		GA+3 3D10 IV			.61	.47	*	VII			.87	.73	
XI			1.14	.99		VI			.69	.55		N -3 2P 6 IV			1.32	1.18	
CF+3 6D 1 VI			1.09	.95	R	VI			.69	.55		N +3 2S 2 VI			.30	.16	A
CF+4 5F 8 VI			.961	.821	R	VI			.760	.620	R*	N +5 1S 2 III			.044	-.104	A
VIII			1.06	.92		GD+3 4F 7 VI			1.078	.938	R	VI			.27	-.13	A

Table 1 (cont.)

ION	EC	CN	SP	CR	'IR'	ION	EC	CN	SP	CR	'IR'	ION	EC	CN	SP	CR	'IR'
Na+1 2P 6 IV				1.13	.99	PR+3 4F 2 VI				1.13	.99 R	TC+4 4D 3 VI				.785	.645 RM
V				1.14	1.00	VIII				1.266	1.126 R	TC+5 4D 2 VI				.74	.60 ER
VI				1.16	1.02	IX				1.317	1.179 R	TC+7 4P 6 VI				.51	.37
VII				1.26	1.12	PR+4 4F 1 VI				.99	.85 R	TE-2 5P 6 VI				2.07	2.21 P
VIII				1.32	1.18	VIII				1.10	.96 R	TE+4 5S 2 III				.66	.52
IX				1.38	1.24 C	PT+2 5D 8 IVSQ				.74	.60	VI				.80	.66
X				1.53	1.39	IX				.94	.80 A	VI				1.11	.97
NB+3 4D 2 VI				.86	.72	PT+4 5D 6 VI				.765	.625 R	TE+6 4D10 IV				.57	.43 C
NB+4 4D 1 VI				.82	.68 RE	PT+5 5D 5 VI				.71	.57 ER	VI				.70	.56 *
VIII				.93	.79	PU+3 5F 5 VI				1.14	1.00 R	TH+4 6P 6 VI				1.08	.94 C
NB+5 4P 6 VI				.78	.64 C	PU+4 5F 4 VI				1.00	.86 R	VIII				1.19	1.05 RC
VI				.83	.69 C	PU+5 5F 3 VI				.88	.74 E	IX				1.23	1.09 *
VIII				.88	.74	PU+6 5F 2 VI				.85	.71 R	X				1.27	1.13 E
ND+2 4F 4 VIII				1.43	1.29	RA+2 6P 6 VIII				1.62	1.48 R	XI				1.32	1.18 C
IX				1.49	1.35	XII				1.84	1.70 R	XII				1.35	1.21 C
ND+3 4F 3 VI				1.123	.983 R	RB+1 4P 6 VI				1.66	1.52	TI+2 3D 2 VI				1.00	.86 E
VIII				1.249	1.109 R*	VII				1.70	1.56	TI+3 3D 1 VI				.810	.670 RM
IX				1.303	1.163 R	VIII				1.75	1.61	TI+4 3P 6 IV				.56	.42 C
X				1.41	1.27 E	IX				1.77	1.63 E	V				.65	.51 C
NI+2 3D 8 IV				.69	.55	X				1.80	1.66	VI				.745	.605 R*
IVSQ				.63	.49	XI				1.83	1.69	VIII				.88	.74 C
V				.77	.63 E	XII				1.86	1.72	TL+1 6S 2 VI				1.64	1.50 R
VI				.830	.690 R*	XIV				1.97	1.83	VIII				1.73	1.59 R
NI+3 3U 7 VI	LS			.70	.56 R*	RE+4 5D 3 VI				.77	.63 RM	XII				1.84	1.70 RE
HS				.74	.60 E	RE+5 5D 2 VI				.72	.58 E	TL+3 5D10 IV				.89	.75
LS				.62	.48 R	RE+6 5D 1 VI				.69	.55 E	VI				1.025	.885 R
NI+4 3D 6 VI				1.24	1.1 E	RE+7 5P 6 IV				.52	.38	VIII				1.12	.98 C
ND+2 5F14 VI				1.24	1.10	VI				.67	.53	TM+2 4F13 VII				1.17	1.03
NP+2 5F 5 VI				1.01	.87 R	RH+3 4D 6 VI				.805	.665 R	VI				1.23	1.09
NP+3 5F 4 VI				1.24	1.01	RH+4 4D 5 VI				.74	.60 RM	VIII				1.020	.880 R
NP+4 5F 3 VI				1.12	.98 R	RH+5 4D 4 VI				.69	.55	VIII				1.134	.994 R
NP+5 5F 2 VI				.89	.75	RU+3 4D 5 VI				.82	.68	IX				1.192	1.05 R
NP+6 5F 1 VI				.86	.72 R	RU+4 4D 4 VI				1.760	.620 RM	U +3 5F 3 VI				1.165	1.025 R
NP+7 6P 6 VI				.85	.71 A	RU+5 4D 3 VI				.705	.565 ER	U +4 5F 2 VI				1.03	.89
O -2 2P 6 II				1.21	1.35	RU+7 4D 1 IV				.52	.38	VII				1.09	.95 E
II				1.22	1.36	RU+8 4P 6 IV				.50	.36	IV				1.14	1.00 R*
III				1.24	1.38	S -2 3P 6 VI				1.170	1.84 P	IX				1.19	1.05
IV				1.26	1.40	S +4 3S 2 VI				.51	.37 A	XII				1.31	1.17 E
V				1.28	1.42	S +6 2P 6 IV				.26	.12 *	U +5 5F 1 VI				.90	.76
VI				1.18	1.32	VI				.63	.29 C	VI				.98	.84 E
VII				1.20	1.34	SB+3 5S 2 IVPV				.90	.76	U +6 6P 6 II				.59	.45
VIII				1.21	1.35 E	V				.94	.80	IV				.66	.52
IX				1.23	1.37 E	VI				.90	.76 A	VI				.87	.73 *
OS+4 5D 4 VI				.770	.630 RM	SB+5 4D10 VI				.74	.60 *	VII				.95	.81 E
OS+5 5D 3 VI				.715	.575 E	SC+3 3P 6 VI				.885	.745 R*	VIII				1.00	.86
OS+6 5D 2 V				.63	.49	VIII				1.010	.870 R*	V +2 3D 3 VI				.93	.79
OS+7 5D 1 VI				.685	.545 E	SE-2 4P 6 VI				1.84	1.98 P	V +3 3D 2 VI				.70	.56 RM
OS+8 5P 6 IV				.53	.39	SE+4 4S 2 VI				.64	.50 A	V +4 3D 1 V				.67	.53
P +3 3S 2 VI				.58	.44 A	SE+6 3D10 IV				.42	.28 *	VI				.72	.58 R*
P +5 2P 6 IV				.31	.17 *	SI+4 2P 6 VI				.56	.42 C	VIII				.86	.72 E
V				.29	.15	VI				.60	.46 *	V +5 3P 6 IV				.495	.355 RM
VI				.52	.38 C	SM+2 4F 6 VII				1.36	1.22	V				.60	.46 *
PA+3 5F 2 VI				1.18	1.04 E	VIII				1.41	1.27	VI				.68	.54
PA+4 6D 1 VI				1.04	.90 R	IX				1.32	1.18	W +4 5D 2 VI				.80	.66 RM
VIII				1.15	1.01	SM+3 4F 5 VI				1.098	.958 R	W +5 5D 1 VI				.76	.62 R
VI				.92	.78	VII				1.16	1.02 E	W +6 5P 6 IV				.56	.42 *
VIII				1.05	.91	VIII				1.219	1.079 R	VI				.65	.51
IX				1.09	.95	IX				1.272	1.132 R	VI				.74	.60 R
PB+2 6S 2 IVPV				1.12	.98 C	XI				1.38	1.24 C	XE+8 4D10 IV				.54	.40
VI				1.33	1.19	SN+4 4D10 IV				.69	.55 R	VI				.62	.48
VII				1.37	1.23 C	V				.76	.62 C	Y +3 4P 6 VI				1.040	.900 R*
VIII				1.43	1.29 C	VI				.830	.690 R*	VII				1.159	1.019 R*
IX				1.49	1.35 C	VII				.89	.75	IX				1.215	1.075 R
X				1.54	1.40 C	VIII				.95	.81 C	YB+2 4F14 VI				1.16	1.02
XI				1.59	1.45 C	SR+2 4P 6 VII				1.32	1.18	VII				1.22	1.08 E
XII				1.63	1.49	VIII				1.35	1.21	VIII				1.28	1.14
PB+4 5D10 IV				.79	.65 E	IX				1.40	1.26	YB+3 4F13 VI				1.008	.868 R*
V				.87	.73 E	IX				1.45	1.31	VII				1.065	.925 E
VI				.915	.775 R	X				1.50	1.36 C	VIII				1.125	.985 R
VIII				1.08	.94 R	XII				1.58	1.44 C	IX				1.182	1.042 R
PD+1 4D 9 II				.73	.59	TA+3 5D 2 VI				.86	.72 E	ZN+2 3D10 IV				.74	.60 *
PD+2 4D 8 IVSQ				.78	.64	TA+4 5D 1 VI				.82	.68 E	V				.82	.68 *
IX				1.00	.86	TA+5 5P 6 VI				.78	.64	VI				.880	.740 R*
PD+3 4D 7 VI				.90	.76	VII				.83	.69	VIII				1.04	.90 C
PD+4 4D 6 VI				.755	.615 R	VIII				.88	.74	ZR+4 4P 6 IV				.73	.59 R
PN+3 4F 4 VI				1.11	.97 R	IX				1.063	.923 R	V				.80	.66 C
VIII				1.233	1.093 R	TI+3 4F 8 VI				1.12	.98 E	VI				.86	.72 R*
IX				1.284	1.144 R	VII				1.180	1.040 R	VII				.92	.78 *
PD+4 6S 2 VI				1.08	.94 R	VIII				1.235	1.095 R	VIII				.98	.84 *
VIII				1.22	1.08 R	IX				.90	.76 R	IX				1.03	.89
PD+6 5D10 VI				.81	.67 A	TI+4 4F 7 VIII				1.02	.88						

VIII V^{4+} , IV Pb^{4+} , and X Th^{4+} obtained from these plots were used to help determine the values in Table 1. The first estimate of VIII V^{4+} was made from distances in $\text{C}_{32}\text{H}_{28}\text{S}_8\text{V}$ (Bonamico, Dessy, Fares & Scaramuzza, 1974).

Another method used to estimate radii was based on the empirical relationship between interatomic distances and bond strengths. Brown & Shannon (1973) derived these relationships for the cations in the first three rows of the periodic table from a large number of experimental interatomic distances. These curves can be used to calculate hypothetical distances for cations in any coordination (Brown & Shannon, 1973; Shannon, 1975; Brown, 1975). Examples of cations whose radii were calculated in this way are: IV Mn^{2+} , VI Be^{2+} , VI B^{3+} , VI P^{5+} , VI S^{6+} , VIII Mg^{2+} , and VIII Fe^{2+} . These are marked with a C in Table 1. In certain cases, these values were combined with known structural data (see Table 2) to obtain the radii in Table 1. Although the

majority of radii were derived from oxides and fluorides,* some were taken from chlorides, bromides, iodides, and sulfides. For large electropositive cations with highly ionic bonds, very little covalent shortening is believed to occur and radii derived from these other compounds should differ only slightly from those derived from fluorides and oxides. Examples are divalent rare earths such as Yb^{2+} , Tm^{2+} , Dy^{2+} , Sm^{2+} , Nd^{2+} and the ions Am^{2+} , Ac^{3+} , Np^{3+} , and U^{4+} .

Another useful scheme for estimation of radii is the comparison of unit-cell volumes of compounds containing cations of similar size. McCarthy (1971) prepared a number of isotopic Sr^{2+} and Eu^{2+} ternary oxides and generally found the unit cells of the Sr^{2+}

* Because of covalency differences in M-O and M-F bonds, oxide distances were emphasized. Therefore the radii in Table 1 are more applicable to oxides than fluorides. This subject is treated further in the discussion *Effects of covalence*.

Table 2. References for Table 1

The references here and in Tables 4, 5, 6 and 8 are abbreviated according to *Codens for Periodic Titles* (1966).

AG+3 VI	68 JINCA	30	823 AC CL3
AG+1 II	71 INDOCA	10	719 AG FE 02
72 ZAACA	393	246	58 AG 04
73 ZENBA	280	263	BA AG 04
AG+1 IV	71 JSSCB	3	364 AG 02 CR 04
AG+1 IVS0	42 JACSA	64	354 AG 03 AS 04
69 ACSAA	23	2261	AG 2 S 03
AG+1 V	70 JSSCB	1	484 AG 06 MO10 033
AG+1 V	32 ZKKA	82	161 AG 02 S04
47 JACSA	69	222	AG 03 P04
71 JSSCB	3	364	AG 02 CR 04
69 ACACB	25	5116	AG 02 CR 07
70 JSSCB	1	484	AG 02 MO 04
AG+1 VII	70 JSSCB	1	484 AG 06 MO10 033
69 ACACB	25	5116	AG 02 CR 07
AG+1 VIII	65 ACCRA	19	180 AG 7 N 011
AG+2 IVS0	71 JPCSA	32	543 AG F2
AG+2 VI	71 JPCSA	32	543 AG F2
AG+3 IVS0	65 ACCRA	19	180 AG 7 N 011
AL+3 IV	67 ACCRA	23	754 NA T12 AL5 012
68 NJMHA	1968	80	CA AL B 04
70 AGACA	26	1230	CA AL B 04
70 NJMHA	1970	547	CA12 AL10 033
71 SPMDA	15	905	CA AL 010 (OH)6
71 SPMDA	15	905	CA AL 010 (OH)6
71 SPMDA	15	905	CA AL 010 (OH)6
72 JACSA	27	1826	BE14 AL2 03
72 JSSCB	4	60	AG AL11 017
AL+3 V	68 ACBCA	24	1518 (MG,FE) AL3 S1 B 09
68 AMNIA	53	1096	AL2 P04 (OH)3
AL+3 VI	71 AMNIA	56	18 NA3 AL2 L13 F12
72 JSSCB	4	11	ND AL 03
72 JSSCB	4	11	ND AL 03
58 ACBCA	5	684	MG AL2 04
72 ACBCA	28	1899	AL2 BE3 S10 D18
68 JACSA	80	22	AL1AC1A
73 ACBCA	29	2291	AL P 0412 H2 0
67 ZKKA	125	1423	CS BE4 B12-X1 AL4 O28 H2
74 ACBCA	30	1311	NA AL 1P 0412 IO H14
74 ACBCA	139	125	AL IO H13
AM+2 VII	72 JINCA	34	3427 AM 12
AM+2 VIII	73 JINCA	35	403 AM BR2
AM+2 IX	73 JINCA	35	403 AM CL2
AM+3 VIII	72 JINCA	11	2233 AM2 (S 04)3.0H2 0
AM+4 VI	67 ACBCA	71	228 NA AM 03
67 INUCA	3	327	R (BK+)
AS+5 IV	69 ZKKA	130	231 ZH2 CU AS2 08
68 CJCHA	46	917	CU3 AS2 08
63 BAPCA	11	361	MG AS2 07
69 ACBCA	25	1544	CA H AS 04.2 H2 0
69 ACBCA	25	2658	R H AS 04.2 H2 0
68 AMNIA	53	1841	MN2 0 H AS 04
63 CARIA	7	561	CA CU AS 04 0 H
70 ACBCA	24	1584	NA2 H AS 04.7 H2 0
69 ACBCA	26	1574	NA2 H AS 04.7 H2 0
70 CHDCA	268	1694	BA H12 AS2 08
70 AMNIA	55	2023	MN2 IO H19 (H2 012
70 ACBCA	26	1809	IN H12 H AS 04
70 ACBCA	24	1711	LI H2 02 AS 04
70 INDOCA	9	2259	CA2 AS 04 CL
69 ACBCA	18	777	CU3 AS 04 IO H13
70 CJCHA	48	801	CU3 AS2 08
71 CJCHA	49	1036	CA AS 04
70 AMNIA	55	1409	MN2 H AS 012
71 ACBCA	27	2124	NA3 AS 04.12 H2 0
73 ACBCA	29	2611	MG AS2 08
61 AMNIA	46	1077	CA2 B AS 04 (OH)4
73 CJCHA	51	2082	NA4 AS2 07
68 ZAACA	347	133	CR H AS 04 H2 0
66 ZAACA	347	140	SR H AS 04 H2 0
71 AMNIA	56	1167	ZNA AS2 08 (OH)2.2H2 0
70 ACBCA	26	403	CA H AS 04
70 ZKKA	132	332	CU3 AS2 08
73 ACBCA	29	141	LU AS 04
73 ACBCA	29	2121	MN4 H AS 04
AS+5 VI	71 CJCHA	49	2539 CL F2 AS F6
73 JSSCB	6	80	MGAS AS3 016
70 CJCHA	48	3124	CU8 AS3 016
73 ACACB	29	266	CALCULATED
74 INDOCA	13	780	XL AS F11.4E2 AS F9
74 ACBCA	30	250	K AS F6
AU+3 IVS0	69 JPCSA	1969	1936 R AU F4
70 ZAACA	375	43	L13 AU O3.4 AU O2.8B AU O2
70 JCSIA	1970	1092	R AU (OH)34
AU+5 VI	74 INUCA	13	775 RE2 AU F17
D+3 III	68 NJMHA	1968	80 CA AL B 04
70 AGACA	26	906	B2 03 1
71 SPMDA	15	902	R BE2 B 03 F2
71 ACBCA	27	672	ZN B4 07
70 ACBCA	26	1189	B 02
71 ACBCA	27	904	L13 B 03
70 ZKKA	132	241	CA B3 05 (OH)1
71 JACSA	4	284	LU B 04
74 JPCSA	60	1899	MN B4 07
74 MRBUA	9	1661	ND AL3 (B 03)4
B+3 IV	68 ACBCA	24	869 B2 J3 11
68 ACBCA	24	1703	NA B F4
69 CJCHA	47	2579	R B F4
71 ACBCA	27	677	CU B2 04
71 ACBCA	27	1102	R H4 F4
70 ZKKA	132	241	CA B3 05 0 H
63 ACBCA	16	1233	NA B IO H14.2 H2 0
74 JPCSA	60	1899	MN B4 07
71 AMNIA	56	1553	MG (NO 07 IO H16) .2 H2 0
73 ACBCA	27	672	ZN B4 07
B+3 V	73 ACACB	29	266 CALCULATED
BA+2 VI	70 ZKKA	131	161 BA3 V2 08
73 ZENBA	280	263	BA AG 04
BA+2 VII	71 ACBCA	27	1263 BA FE2 04
73 ACBCA	29	2009	BA2 TI 04
BA+2 VIII	58 ZKKA	110	231 CU BA2 IC 0 H16.4 H2 0
69 JPCSA	51	428	BA MN F4
70 JPCSA	53	3279	BA CU F4
71 JPCSA	55	1093	BA W 04
71 AMNIA	56	758	BA C 03
71 ZAACA	386	1	BA2 C 04
73 ACBCA	29	2009	BA2 TI 04
BA+2 IX	71 ZAACA	386	1 BA2 C 04
73 ACBCA	27	1653	BA TE (S2 03)2.2 H2 0
73 ACBCA	27	1653	BA TE (S2 03)2.2 H2 0
BA+2 X	70 ZKKA	131	161 BA3 IV 0412
70 ACBCA	26	105	BA3 S14 NB6 026
67 BUFGA	90	24	BA P2 06
BA+2 XI	71 ACBCA	27	1263 BA FE2 04
BA+2 XII	70 ACBCA	26	102 BA5 TA 015
72 CSCMC	1	1	BA T16 013
71 MRBUA	6	725	BA CA FE4 08
69 CHDCA	208C	1694	BA H12 AS2 08
75 ACBCA	31	596	K2 BA CU (IN 02)6
BE+2 III	69 ACBCA	25	1647 SR BE3 04
66 ACBCA	20	295	CA12 BE17 029
BE+2 IV	68 ACBCA	24	733 NA BE P 04
68 ACBCA	24	672	L2 BE2 05
68 ACBCA	24	607	CS BE F3
69 ACBCA	25	1647	SR BE3 04
71 SPMDA	15	909	FE3 BE S13 09 (F,OH)2
72 SPMDA	14	1021	BE2 S14 0 P
73 ACBCA	28	1899	AL2 BE3 S16 018
73 ACBCA	229	2976	NA3 BE TH10 F45
69 ACBCA	12	634	BE AR F4T
67 ZKKA	125	423	CU BE4 B12-X1 AL4 O28 H2
74 ACBCA	30	396	NA6 (S116 AL2)BE10H2 0391
74 ACBCA	30	2434	L12 BE S1 04
74 AMNIA	59	1267	CA BE2 P2 08
BI+3 V	69 JSCDA	7	1797 B12 M 06
70 ACBCA	24	384	B12 03 ALPHA
BI+3 VI	70 ACBCA	24	384 B12 03 ALPHA
71 JPCSA	32	1315	BI FE 03
BI+3 VIII	72 MRBUA	7	1025 BI TITANATES
BI+5 VI	R3 VS V (BA2 LA B1 06)		
BR+4 VI	67 INUCA	3	327 R (BK+)
BR+4 IV S0	71 JPCSA	1969	1936 K AR F4
BR+5 III	69 ACACB	25	421 SR (BR 03)3.9H2 0
67 ACBCA	21	2834	MG BR 03
BR+7 IV	71 JCSIA	1971	1857 BR(+7)0
C+4 III	65 ACCRA	18	689 CA C 03
71 JNBAR	754	27	CA C 03
73 AMNIA	58	1029	MG C 03
67 PLRAA	92	125	MN C 03
75 ACBCA	31	890	NA2 C 03.2H2 0
CA+2 VI	68 NJMHA	1968	80 CA AL B 04
69 ACBCA	25	1533	CA IN2 BE3 P 0213
57 JPCSA	26	563	CA IO H12
55 ACBCA	18	689	CA C 03
CA+2 VII	71 CJCHA	49	1036 CA3 AS2 08
71 ACBCA	27	2311	CA2 AL FE 05
73 MRBUA	8	593	CA CR F5
69 ACBCA	25	1534	CA10 (P 04)6 IO H12
CA+2 VIII	71 INDOCA	7	1345 CA2 P2 07
74 CJCHA	52	1155	CA18 MG2 H2 (P 04)14
CA+2 IX	71 JNBAR	75	27 CA C 03
69 ACBCA	25	1534	CA10 (P 04)6 IO H12
CA+2 X	69 ACBCA	25	955 CA B2 04 111
CA+2 XII	69 ACBCA	25	965 CA B2 04 1V
74 AMNIA	59	41	CA AL3 IO H16
74 JACSA	98	6606	K2 CA CU (IN 02)6
CD+2 IV	59 ACBCA	12	1049 CO IN2 04
71 ZAACA	382	27	K2 CO2 04
CD+2 V	69 CJCHA	47	3409 CO2 P2 07
70 ZKKA	132	332	CU3 AS2 08
69 CJCHA	47	3409	CO2 P2 07
70 ZKKA	132	332	CU3 AS2 08
66 SPMDA	11	11	CO W 04
67 HCACA	50	2023	CO2 MN3 08
74 JCSIA	1974	674	CO C4 H6 06
74 ACBCA	30	1880	CO2 C4 H12 012
CD+2 VII	74 ACBCA	28A	119 CO D1C H2 C 0 D12.3 1/2 H2 0
74 JCSIA	1974	1922	CO C3 H5 05
CD+2 VIII	55 PRVBA	98	903 CO2 N82 07
69 ACBCA	25	1804	CO IN 03)2.4 D2 0
74 JCSIA	1974	674	CO C4 H6 06
CE+3 VIII	74 ZAACA	403	1 R3 VS V (CE F3)
74 JCSIA	1974	1165	C41 H24 CE F12 N DB 54
CE+3 IX	67 SPMDA	12	214 CE B S1 05
74 ZAACA	403	1	R3 VS V (CE F3)
CE+3 X	60 AMNIA	45	1 CE4 ME NE2 T12 S14 022
CE+4 VI	72 ACBCA	28	956 BA CE 03
73 JSSCB	8	331	R (CE+4)
CE+4 VII	69 INUCA	8	33 IN H612 CE F6
74 JCSIA	1974	2021	NA6 CE D10 D36.2.30H2 0
74 JCSIA	15	397	CE15 OH12
74 ACBCA	28	1079	AC CE (ACAC)4
CE+4 XII	68 JACSA	90	3589 (HMH)2 H6 ICE MD12 0421.12 H2 0
CF+3 VI	71 JINCA	36	2023 R3 VS V (CF2 S 04)3
CL+5 III	73 MRBUA	8	791 RB CL 03
CL+7 IV	72 ACBCA	28	839 TMPO CL 04
62 ZKKA	84	65	K CL 04
60 ACBCA	13	855	N U2 CL 04.8 H CL 04
54 JPCSA	63	270	H CL 04.2 H2 0
59 JACSA	80	5075	CA H6 H6 CL 04
57 PISAA	50	134	N H6 CL 04
57 PISAA	50	143	R CL 04
62 ACBCA	15	1201	N H6 CL 04
71 JCSIA	1971	1371	CU (C10 H9 N312 ICL 04)2
70 ACBCA	26	1928	N2 H5 CL 04
71 ACBCA	27	898	H CL 04.2 1/2 H2 0
73 INCHAA	7	477	IC N12-TRILEN-CU CL 04
71 ACBCA	27	898	H CL 04.2 1/2 H2 0
72 MRBUA	7	1281	CL1(+7) -0
71 JCSIA	1971	1857	CL1(+7) -0
62 ACBCA	15	18	H3 0 CL 04 (1-80 C1
59 ACBCA	25	1875	H3 0 H CL 04
73 ACBCA	27	2309	(P84 IO H14)3 C 03 ICL 0410
73 ACBCA	27	3523	CU (C3 H4 N214 ICL 04)2
LM+4 VI	67 INUCA	3	327 R (CH+4)
CU+2 IV	69 ZAACA	369	306 CO V2 04
CU+2 V	72 SCBCA	28	2803 CO2 P2 07 ALPHA
CU+2 VI	68 ZAACA	358	125 CO SE 04
68 ZKKA	126	298	CO GE 03
70 CJCHA	48	881	CO3 AS2 08
70 JPCSA	53	3279	BA CO F4
70 PERIA	3	181	CO2 S1 04
73 ACBCA	29	2304	CO3 V2 08
71 HCACA	54	1621	CO3 IO H12 (S 04)2.2 H2 0
REF 1	CO2 S1 04		
72 ACBCA	28	2883	CO2 P2 07
70 INDOCA	9	151	CO (OHMA)3 ICL 0412
73 ACBCA	29	2741	CO S1 F4.6 H2 0
74 AMNIA	59	475	CO2 S1 04
74 JCLMB	4	55	C16 H18 CO 06
CO+2 VIII	66 INDOCA	5	1208 (AS)CE H51412(COIN 03)4
CO+3 VI	68 CJCHA	1968	871 CO (IN 03)3
68 CJCHA	46	3472	CO3 04
68 JACSA	88	2951	CO (C5 H7 02)3
74 ACBCA	30	822	CO (H2 02)3
69 JACSA	91	6881	IN H416 (H4 CO2 MO10 0381
74 ZAACA	408	97	K CO2 04
CO+4 IV	71 ZAACA	386	1 BA2 CO 04
73 ZAACA	398	54	L18 CO 06
74 ZAACA	408	75	CS2 CO 03
74 ZAACA	409	152	K6 CO2 07
CO+4 VI	67 STGBA	3	1 R3 VS V (FLUORIDES)
74 ACBCA	408	97	K CO2 04
CR+2 VI	71 ANCPA	6	41 TA2 CR 06
69 ACBCA	25	925	R VS D ELECTRONS
CR+3 VI	69 MRBUA	4	621 NA3 CR F6
70 INDOCA	9	2289	NA3 ICR MO 06 024 H61.8 H2 0
70 SPMDA	15	902	NA2 CR3 08 0 H
73 MRBUA	8	593	CA CR F5
65 ACBCA	19	131	CR (C5 H7 02)3
CR+4 IV	74 ZAACA	407	129 BA2 CR 04
CR+4 VI	72 MRBUA	7	157 CR 02
CR+5 VI	67 STGBA	3	1 R3 VS V (FLUORIDES)
CR+6 IV	68 CJCHA	46	935 K2 CR2 07
70 ACBCA	26	222	CR 03
69 JCSIA	1969	1857	(HMH)2 CR 04
69 ACBCA	25	1516	AG2 CR2 07
70 SPMDA	15	930	K2 CR 013
70 AMNIA			

Table 2 (cont.)

74 ZAACA 403 1 R3 VS V (DY F3)	73 ACBCA 29 869 HG MO D4	74 ACBCA 30 2491 MG2 V2 D7
ER+3 VI 74 ACBCA 26 484 ER2 S12 D7	HO+3 VIII 74 ACBCA 30 2049 K MO BE F6	71 AMNIA 56 1593 MG 186 D7 (O M)61.2H2 U
ER+3 VII 70 SPHCA 15 36 ER2 GE2 D7	70 SSCOA 8 1745 MO3 FES D12	73 AMNIA 56 1029 MG C D3
72 JCMLB 2 197 ER8 U (THD)10 (O M)12	72 BUCCA 95 437 MO P5 D14	74 CJCHA 52 1185 CA18 MG2 H2 (P D4)14
ER+3 VIII 68 CHPLB 2 47 ER P D4, ER V D4	74 ZAACA 403 1 R3 VS V (HO F3)	70 INOCA 9 151 MG (OMPA)3 (CL D4)2
70 INOCA 9 1100 ER (C2 D4) (M C2 D4).JH2 D	74 ACBCA 30 2613 MOIC2 H5 S D4)3.9H2 D	72 CJCHA 50 3619 MG V2 U6
70 SSCOA 6 1745 ER3 FES D12	HO+4 IX 74 ACBCA 13 2535 HO1H2 D14 (M C 03)13.2H2 D	73 ACBCA 29 2613 MG3 AS2 D8
71 ACSAA 25 372 ER (M U C H2 C D D)13.2H2 D	74 INOCA 53 831 (N D12)HO1N D15)1	MG+2 VIII 73 ACBCA 29 266 CALCULATED
74 ZAACA 403 1 R3 VS V (ER F3)	71 JCPSA 54 2556 N H4 I D3	HN+2 VI 70 AMNIA 55 1489 MN7 S8 AS D12
72 JCMLB 2 197 ER8 D (THD)10 (O M)12	68 ACCRA 20 758 L1 I D3	70 ACBCA 369 306 MN V2 D4
ER+3 IX 59 ZKKKA 112 362 ER (C2 H5 S D4)3.9H2 D	66 ACCRA 20 841 L1 I D3	71 ACBCA 27 1044 MN CO CR D4
74 ZAACA 403 1 R3 VS V (ER F3)	58 ACCRA 9 1015 CE (I D3)14	69 PHSSA 32 891 MN CR2 D4
EU+2 VI 70 ZAACA 374 201 L1 EU3 D4	58 ACCRA 11 794 CE (I D3)14.H2 D	73 ACBCA 29 266 CALCULATED
EU+2 VII 69 ACBCA 25 1104 EU F2 (ER F3)	43 RTCPB 62 759 N H4 I D3	HN+2 VI 68 AMNIA 53 1841 MN2 O H AS D4
70 ZAACA 374 201 L1 EU3 D4	I+5 VI 71 JCPSA 54 2556 N H4 I D3	74 MPMTA 21 246 MN2 AS D4 OM
69 ACBCA 25 1104 EU F2 (ER F3)	I+7 IV 70 ACBCA 26 1782 NA I D4	69 ACBCA 25 925 R VS D ELECTRONS
73 REF 3 112 EU5 D8	26 ZEPHA 29 386 K I E D3	HN+2 VI 69 SCIEA 165 586 MN2 GE U4
EU+2 VIII 73 RVCHA 10 77 EU CL2	71 JCPSA 1971 1857 (I+7)U	69 JCPSA 51 4928 BA MN F4
UNPUL EU F2, EU D2	I+7 VI 71 ACBCA 20 765 H5 I U4	70 ZKKKA 132 1 NM5 (O M)12 S12 D8
EU+2 X 71 NATMA 58 218 EU2 S1 U4	65 ACCRA 19 629 K4 H2 I2 D10.8H2 D	69 AMNIA 54 1312 MN FE2 (P D4)12 (OH)2.8H2 D
EU+3 VI 68 REF 4 EU4 AL2 D9	37 JACSA 59 2036 (N H4)12 H3 I U6	70 NJMIA 113 1 MN7 NA12 (S D4)13.15H2 D
70 ZAACA 374 201 L1 EU2 D8	IN+3 IV 74 ZAACA 409 97 RB2 IN4 D7	65 ACCRA 19 854 MN S D4
73 REF 3 112 EU5 D8	74 ZAACA 395 280 SR2 IN2 D5	72 AMNIA 57 621 MN2 GE D4
EU+3 VII 68 REF 4 EU4 AL2 D9	IN+5 VI 74 ZAACA 409 97 RB2 IN4 D7	HN+2 VIII 72 AMNIA 57 621 MN2 GE D4
73 REF 3 112 EU5 D8	61 ACSAA 15 1437 (M O H S O4).1H2 D12	HN+2 VIII 69 ZKKKA 129 427 MN3 FE2 GE3 D12
EU+3 VIII 68 JCPSA 48 1094 EU3 FE2 GA3 D12	68 ACBCA 24 388 L12 IN2 D5	71 AMNIA 56 791 GARNETS
74 ZAACA 403 1 R3 VS V (EU F3)	70 ACSAA 24 1662 (M O D H)	73 SSCOA 12 109 MN3 AL2 GE3 D12
73 ACSAA 27 2827 EU2 (C3 H2 D4)3.8H2 D	69 INOCA 8 1985 IN2 D3	74 JCPSA 49 1899 MN H4 D7
EU+3 IX 74 ZAACA 403 1 R3 VS V (EU F3)	74 ACBCA 30 2613 MOIC2 H5 S D4)3.9H2 D	HN+3 VI 68 ACBCA 24 1233 MN O D H
73 ACSAA 27 2827 EU2 (C3 H2 D4)3.8H2 D	74 SPHDA 18 761 IN2 GE2 D7	67 ZKKKA 124 428 MN2 D3
71 ACSAA 25 3347 EU TRISOLYCOLATE	IR+4 VI 71 JSSCB 3 174 SR IR D3	68 ACBCA 24 1233 MN O D H
FE+2 IV SO HS 74 AMNIA 59 1166 BA FE S14 D10	IR+5 VI 74 MRBUA 9 1177 R3 VS V (CU2 IR2 D7)	69 JCPSA 50 1068 (N H4)12 MN F5
FE+2 IV HS 69 SCIEA 166 1399 (NA)K12 FE4 S112 D30.H2 D	K+1 IV 68 ZAACA 358 241 K AG D	65 PHSSA 3 8444 MN2 D3
69 ZAACA 369 306 FE V2 D4	REF 2 K2 D	68 BUCCA 91 339 TB MN D3, PR MN D3, NU MN D3
71 JUPSA 31 452 FE2 T1 D4	K+1 VI 51 ZAACA 264 144 K S8 F6	71 JSSCB 3 238 LA MN D3, MN3 D4
72 JUPSA 33 1296 FE2 MO D4	68 SPHDA 12 1095 K F MO2 D8	LA-55 CA-05 MN D3
FE+2 VI LS 69 ACBCA 25 925 R VS A (FE S2)	69 CCJDA 11 406 K2 F4 D5	73 JSSCB 6 16 NA MN7 D12
FE+2 VI HS 69 NMMA 1069 430 FE AL2 (P D4)12 (O M)12 (O H)12	69 ACBCA 25 1919 K UZ F9	74 AMNIA 59 985 MG2 MN B D5
70 BUCCA 93 190 FE S D4	K+1 VII 68 JCPSA 46 935 K2 CR2 D7	68 ACBCA 24 1114 NA4 MN4 T15 D18
71 SPHCA 15 999 FE3 BE S13 D9 (F4)12	69 JCPSA 1969 849 K2 MO D4	74 INOCA 13 1854 MN (C7 M5 D2)13/4 CO H5 CH3
67 ACCRA 22 775 FE (NH4)1215 D4)2.8H2 D	71 SSCOA 9 335 K FE F4	74 INOCA 13 1864 MN (ACAC)3
68 CMYTA 68 290 L1 FE D4	K+1 VIII 74 ZKKKA 74 306 K H2 P D4	HN+4 IV 73 JSSCB 13 275 R3 VS V (NA4 MN D4)
74 AMNIA 59 486 FE2 S1 D4	62 ZKKKA 117 411 K2 T16 D13	73 JSSCB 8 234 BA MN D3
FE+2 VIII 71 AMNIA 56 791 GARNETS	72 ZKKKA 98 286 K H2 (M5 D1) 85 D10	69 INOCA 8 335 NA12 MN NB12 D38.50H2 D
71 ZKKKA 134 333 FE3 AL2 S13 D12	71 INUCA 7 873 K H2 C D4	65 CZIPA 13 998 NA4 MN H1 D4)13.15H2 D
73 ACBCA 29 266 CALCULATED	68 JCPSA 46 935 K2 CR2 D7	70 HCACA 50 2023 MN5 D8, CD2 MN3 D8
FE+3 IV HS 70 ACBCA 26 1469 CA2 FE2 D5	70 JCPSA 1970 3092 K H2 (O M)12	HN+6 IV 28 2845 K2 MN D4
70 SSCOA 8 1745 H3 FES D12	70 ZKKKA 132 27 K1.4 NA5.5 CA0.3 AL7.5	HN+7 IV 68 ACBCA 24 1053 AG MN U4
71 ACBCA 27 1263 BA FE2 D4	K+1 IX 69 ACBCA 25 400 L10.5 D32	HN+5 VI 69 ACBCA 25 400 K3 MO CL6
71 MRBUA 6 725 BA CA FE4 D8	69 ACBCA 25 1919 K UZ F9	69 INOCA 8 2694 K3 MO F6
71 ACSAA 25 3616 CA2 FE2 D5	K+1 X 71 JCCHA 51 2613 K AL P2 D7	71 MRBUA 6 555 L12 MO F6
73 ACBCA 29 832 BA FE2 D4	K+1 XII 68 SPHCA 13 420 K Y W2 D8	HN+5 VI 71 INOCA 13 2715 R3 VS V (RE MO D4)
FE+3 V 71 JSSCB 4 1 FE V D4	71 INOCA 10 1264 K2 PB CU (N D2)16	HN+6 VI 71 INOCA 10 922 BA2 ND MO D6
FE+3 VI HS 70 ACBCA 26 1469 CA2 FE2 D5	67 INOCA 5 514 K2 BA CU (N D2)16	MO+6 IV 68 JCPSA 48 2619 CU MO D4
70 SSCOA 8 1745 H3 FES D12	74 JACSA 96 6606 K2 CA CU (N D2)16	68 SPHDA 12 1095 K Y MO2 D8
71 SSCOA 9 335 K FE F4	75 ACBCA 31 594 K2 BA CU (N D2)16	69 JCPSA 1969 849 K2 MO D4
71 JSSCB 4 1 FE V D4	57 PISAA 50 143 K CL D4	72 ACBCA 28 60 GU2 MO3 D12
71 JCPSA 32 1315 L1 FE D3	LA+3 VI 69 ZKKKA 129 259 CU LA D2	69 JCPSA 50 181 L13 FE MO3 D12
71 ACSAA 25 3616 CA2 FE2 D5	74 MRBUA 8 1269 R3 VS V (REZ H3 D12)	71 SPHCA 15 829 K AL MO2 D8, K FE MO2 D8
67 ACCRA 23 239 FE (C5 H7 D2)13	LA+3 VIII 59 1277 LA5 MG2 T13 S14 D22	71 JCPSA 55 1093 CA MO D4, MO MO D4
69 CCJDA 1969 440 FE (C7 H5 D2)13	73 ACBCA 29 2074 LA2 MO3 D12	73 ACBCA 29 2074 LA2 MO3 D12
FE+3 VIII 73 JSSCB 8 331 ESTIMATED	68 INOCA 7 2295 LA (C5 H7 D2)13	71 JCPSA 1971 1857 MO+6) -D
FE+4 VI 73 JSSCB 8 331 R3 VS V (PEROVSKITES)	74 ZAACA 403 1 R3 VS V (LA F3)	67 CCJDA 1967 374 K2 MO3 D10
73 JSSCB 8 331 R3 VS V (ISA FE D3)	74 SPHCA 18 675 LA2 SR3 (B D3)14	68 JCPSA 1968 1398 K2 MO3 D10
FE+6 IV 73 JSSCB 8 43 K2 FE D4	LA+3 IX 71 MRBUA 6 23 LA FE D3	70 JSSCB 1 486 AG6 MO3 D33
GA+3 IV 71 ACBCA 27 616 L15 GA D4	74 ZAACA 403 1 R3 VS V (LA F3)	70 INOCA 9 2228 NA3 (CR MO D6)24 H61.8H2 D
75 ACBCA 31 560 SR GA2 S12 D8	59 1277 LA5 MG2 T13 S14 D22	70 ACSAA 24 3711 L1 MO D2 AS D4
74 ACBCA 30 1364 C15 H21 D6 GA	L1+1 IV 39 ZKKKA 102 119 L1 O H2 D	66 ACBCA 20 2698 MO F6 (GA)5
GO+3 VII 70 ACBCA 26 484 GD2 S12 D7	70 ZAACA 39 1977 L1 C D2	70 CCJDA 1970 50 MO D3 H2 D12
72 ACBCA 28 60 GD2 MO3 D12	71 AMNIA 56 18 NA3 AL2 L13 F12	72 ACBCA 28 2222 MO D3.2H2 D
72 SPHCA 16 790 GD2 GE2 D7	71 ACBCA 27 616 L15 GA D4	64 INOCA 3 1803 K2 (MO D2 (C2 D4) H2 D12 D
69 IVNMA 5 1823 GD9.33 S16 D26	73 JSSCB 6 530 L13 V D4	73 ACBCA 29 869 MG MO D4
72 JSSCB 5 266 GD9.33 S16 D26	73 ACBCA 29 2625 L1 (N2 H5) BE F4	74 ACBCA 30 1795 MO D3H2 D
GO+3 VIII 71 SPHCA 15 926 NA GD S1 D4	64 ACBCA 17 703 L12 C2 D4	N+3 IV REF 6 MG3 N2.513 N4.8 N.TI N
72 SPHCA 16 790 GD2 GE2 D7	74 ACBCA 30 2434 L12 BE S1 D4	N+5 III REF 6 NM4 N O3.NA N O3.K N O3, BAIN D3)2.TIIN D3)14
74 ZAACA 403 1 R3 VS V (GD F3)	L1+1 VI 68 ACBCA 24 225 L13 AL F6	NA+1 IV 74 ZAACA 409 69 NA6 IN D4
GO+3 IX 72 SPHCA 16 790 GD2 GE2 D7	69 ZAACA 371 306 L12 ZR O D4	REF 2 NA2 O
69 IVNMA 5 1823 GD9.33 S16 D26	70 ZKKKA 132 118 L12 AL2 S13 D10	68 ACBCA 24 1077 NA2 S12 D5
74 ZAACA 403 1 R3 VS V (GD F3)	71 MRBUA 6 555 L12 MO F6	68 SPHDA 12 987 NA2 S12 D7
GE+4 IV 68 ZKKKA 126 299 CO GE D3	59 ACBCA 19 561 L1 CO UT H7	64 JACSA 329 110 NA2 MG D2
69 SCIEA 165 586 MN2 GE D4	74 ACTEA 86 819 L1 NB D2	NA+1 VI 70 ACSAA 24 1287 NA4 S2 GE4 D12 (O M)14
69 ZKKKA 129 427 MN3 FE2 GE3 D12	68 CMYTA 68 290 L1 FE P D4	65 ACCRA 19 501 NA CO D7 H7
70 JSSCB 2 612 MG28 GE10 D48	71 ACSAA 25 3337 L1 MO3 D8	63 ACCRA 15 1233 NA B (OH)4.2H2 D
71 SPHCA 15 926 NA S8 GE D4	73 JCCHA 51 265 L1 V D3	60 ZKKKA 113 430 NA2 AL2 S13 D10.2H2 D
70 ACSAA 24 1287 NA4 S2 GE4 D12 (O M)14	73 ACBCA 29 2294 L12 ZR F6	58 ZKKKA 111 241 NA CL D3
67 ACSAA 21 1281 NA8 S4 GE4 D10 D30 (O M)14	70 ZAACA 377 70 CA LUG D4	56 ACCRA 9 811 (NA AS D3)1X
70 MOCBM 102 966 NA2 GE D3	71 JACCA 4 284 LU B D3	53 ARKEA 8 77 NA S8 F4
71 MOCBM 102 1245 K2 GE4 D9	LU+3 VIII 74 ZAACA 403 1 R3 VS V (LU F3)	59 ACCRA 12 526 NA U ACETATE
72 SPHCA 17 244 CO GE D13	LU+3 IX 74 ZAACA 403 1 R3 VS V (LU F3)	74 ACBCA 30 1872 NA2 N D4
72 MOCBM 103 1560 GE5 D (P D4)16	MG+2 IV 72 ACBCA 28 267 K2 MG5 S112 D30	75 ACBCA 31 890 NA2 C O3.H2 D
GE+5 VI 70 SSCOA 1 557 CA2 GE D4	22 ACCRA 5 684 MG AL2 O4	NA+1 VII 71 SPHCA 15 926 NA GD S1 D4
70 JSSCB 2 612 MG28 GE10 D48	72 ACBCA 28 2583 K2 MG5 S116 D15	70 NJMIA 113 1 MN7 NA12 (S D4)13.15H2 D
71 MOCBM 102 1245 K2 GE4 D9	74 ACBCA 30 2667 K6 MG U4	73 ACBCA 29 890 NA2 CR2 OT ALPHA
71 ACBCA 27 2133 GE D2	MG+2 V 68 ACSAA 22 1966 MG3 P2 D8	68 ACBCA 24 1703 NA B F4
72 AMNIA 57 62 MN2 GE D4 DELTA	66 NMMA 1966 142 MG B4 D7	68 SPHDA 12 987 NA2 S12 D7
72 ZKKKA 136 387 GE (O M)1 P D4	UNPUL MG2 P2 D8	71 AMNIA 56 18 NA3 AL2 L13 F12
72 MOCBM 103 1560 GE5 D (P D4)16	UNPUL MG2 P2 D7	NA+1 XII 71 JSSCB 3 89 NA13 NB35 D94
HN+1 I 57 JUMSA 1 43 T F	MG+2 VI 65 JCCHA 43 1139 MG2 P2 D7	72 ZKKKA 81 135 NA AL S1 D4
56 JCPSA 45 275 H F	63 BARCA 11 361 MG2 AS2 D7	NB+3 VI 74 ACBCA 30 1872 NA2 N D4
HN+2 IV 73 JSSCB 13 275 R3 VS V (NA4 MN D4)	70 ACBCA 26 1429 MO N H4 P D4	HN+5 VI 68 JCPSA 48 2619 CU MO D4
70 JACCA 53 126 HF D2	71 JCCHA 49 1610 MG2 P2 D7	70 JSSCB 1 439 M-NB2 D5
69 ACSAA 27 3347 HF4 (OH)18 (CR D4)14.H2 D	69 INOCA 8 1065 C54 MG3 F10	54 ACBCA 45 NA2 MN D11
HN+3 VIII 73 ACSAA 27 2455 HF (O M)12 S O4	69 ZKKKA 129 427 MN3 FE2 GE3 D12	70 AMNIA 55 90 CA NB2 D6
HO+1 VI 71 CCJDA 1971 468 MG2 F2	65 MMLD 1965 196 MG AL B U4	55 PRVAA 98 903 CU2 NB2 D7
MG+2 II 71 JCPSA 1971 1857 MO+6) -D	70 BSCCA 1970 4243 MG S D4.H2 D	71 JSSCB 3 89 NA13 NB35 D94
	71 ACBCA 27 815 M4 TE D6	74 JINCA 380 119 MN NB2 D6
	68 ACSAA 22 1466 CA MG S1 D4	71 JCPSA 1971 1857 MO3 D12

Table 2 (cont.)

70 ACSEA	26	105 BA3 S1A N86 D26	70 ACACB	26	501 PB2 O3	58B+ IV	70 ACSSA	24	320 SB P 04
71 ACSAA	25	3347 LI N83 O8	PB+2 VII			58B+ V			
71 ACSEA	4	786 U1 V81 N8 04	69 ZKKKA	128	213 PB CAZ S13 O9		71 ACSAA	55	1489 MNT SB AS O12
73 JSSCB	8	1501 NB D4	64 ACORCA	17	1539 PB P2 O6		71 JCSIA	1971	942 AS SB F8
69 ACSSA	20	72 NB P 05	PB+2 VIII				71 JCSIA	1971	2318 WR2 SB8 F16
74 BUCFA	97	3 NA3 NB D4	71 SPHCA	15	928 PB W 04		74 JCS59	9	345 NA SB O3
NB+5 VII			64 ACORCA	17	1539 PB P2 O6		68 CJCHA	46	1446 SC2 S12 O7
70 JSSCB	1	454 NA NB O11	73 CJCHA	51	10 P2B V2 O6		68 ARREA	29	342 O3
71 JSSCB	3	89 NA13 N895 U94	72 HBUA	7	1025 B1 TITANATES		UNPU4		SC2 S12 O7
27 IJNCA	27	1410 IMAH NB O IC2 O413.H2 O	PB+2 IX				73 SPHCA	17	749 SC2 S12 O7
75 ACSEA	31	673 N82 O5	67 ACSEA	24	74 PA B F2		73 INDOA	1	27 SC2 S12 O7
NB+2 IX			73 CJCHA	51	10 P2B V2 O7		73 ACBGA	29	2613 NA SC S12 O6
UNPU1		NO I2	74 INDOA	52	2701 PB V2 O6		74 INDOA	13	158 SC IC7 HS O213
NB+3 VI		NO CL2, NO BR2	PB+2 X				73 ACBGA	27	2842 NA IC7 HS O213
71 INDOA	10	922 BA2 NO MO D6	70 ZKKKA	132	228 PB3 P2 O8		69 SPHDA	14	9 NA3 SC S12 O7
74 HBUA	9	1601 NO AL3 BA O12	57 ACORCA	10	103 PB IN O312		SC+3 VIII		
NB+3 VII			70 ZKKKA	132	228 PB3 P2 O8		74 INDOA	10	137 SC H IC7 HS O214
69 JCPSA	50	86 ND2 MO3 O12	70 ZKKKA	132	228 PB3 P2 O8		72 ACSAA	26	1337 SC2 IC2 O413.BM2 O
71 JSSCB	4	458 ND V 04	71 INDOA	10	1264 K2 PB CU IN O216		74 INDOA	13	1886 H SC IC7 HS O214
68 ACSEA	14	318 K NCA MO D8	PB+4 IV				73 INDOA	13	1886 H SC IC7 HS O214
70 ACSEA	26	484 ND2 T12 O7	72 JCSIA	1972	2448 NA3 RS VS INAA PB O31		SC+6 IV		
70 ACSEA	24	3406 ND4 NE T11 O6	PB+4 V				68 ZAKCA	358	125 MN SE O4, CO SE O4, M
71 SPHDA	15	630 ND2 W 04	70 ZAKCA	375	255 R82 PB O3		51 JCSIA	217	928 H2
71 SPHCA	15	991 NA3 VS O15	70 ACBGA	26	501 PB2 O3		70 ACBGA	26	430 NA2 SE O4
74 HBUA	9	129 ND P5 O13	70 ACBGA	26	1591 PB3 O4		70 ACBGA	26	1451 K2 SE O4
24 ZAKCA	403	1 R3 VS V (ND F3)	74 CJCHA	52	2175 R3 VS V		70 ACBGA	20	NA2 SC O4
74 ACSEA	30	468 ND P3 O9	69 HBUA	3	153 PB O6		72 ACBGA	28	2845 K2 SE O4
70 ACSEA	24	2969 ND2 IC2 O413.10.5H2 O	PB+4 VIII				69 ACBGA	25	1510 IN O4.NA M S12 O6
71 SPHCA	15	991 NA3 VS O15	PB+2 IV				71 JCSIA	1971	1957 SE11H+O
71 SPHCA	15	2441 ND2 IC2 H2 O413.BM2 O	PB+2 V				51+4 IV		
74 ZAKCA	403	1 R3 VS V (ND F3)	67 INDOA	6	730 PD IC6 HS GWS CHIC O1212		72 ZKKKA	137	86 MO2 SI O4
74 ACSEA	27	2813 ND2 IC2 H2 O413.BM2 O	68 JSTCA	9	166 PD IC6 HS12 CH GZ O212		71 ZKKKA	14	835 MO3 AL2 S13 O12
73 JSTCA	1973	2070 ND O413 O	PB+4 VI				70 ZKKKA	132	1010 H2 S12 O8
74 AMHIA	59	1277 ND4 MG2 T13 S14 O22	68 HBUA	3	699 R3 VS V (H2 PZ O7)		68 ACORCA	17	1437 CAZ CA2 S13 O10.2H2 O
NB+3 X			73 INDOA	12	1726 KE PD F11		71 AMHIA	56	193 CAZ CA2 S13 O10.2H2 O
71 JSSCB	4	11 ND AL O4	PM+3 VII				71 SPHCA	5	928 NA2 SE O4
N1+2 IV			PM+3 VIII				71 SPHCA	15	808 Y2 S1 O5
61 JAPFA	32	685 NI CR2 O4	74 ZAKCA	403	1 R3 VS V (PM F3)		71 WATMA	59	218 UZ S1 O4
68 ACSEA	19	1085 SPINELS	PM+3 IX				70 PEPIA	8	161 NA2 SE O4
N1+2 IV S0			74 ZAKCA	403	1 R3 VS V (PM F3)		70 ACBGA	26	105 BA3 S1A N86 O26
68 INDOA	5	1200 NI IDPM12	PM+4 VI				71 ACBGA	27	747 CAZ SI O4.CA CL2
N1+2 V			74 CJCHA	52	2175 R3 VS V		71 ACSEA	27	846 NA2 SE O4
67 BAPCA	15	47 NI2 P2 O7	PB+4 VIII				71 AMHIA	56	1222 NA16 K84 CA IS18 O20
N1+2 VI			PR+3 VI				71 AMHIA	56	1155 MG5-6 FE4 S13 O12.MG F
74 AMHIA	59	486 NI2 S1 O4	PR+3 VII				69 NSAPA	2	31 NI O4.NA M S12 O6
74 ACSEA	30	1086 NI (PY N D10 (B F+12	71 HBUA	6	545 R3 VS V (PR2 MO3 O12)		CA NG S12 O6		
68 ACSEA	15	47 NI2 P2 O7	PR+3 VIII				69 NSAPA	2	95 FE6-11 MG-8 CA-1 S11
67 BAPCA	15	47 NI2 P2 O7	70 SPHCA	15	28 PR2 M2 O9		69 NSAPA	2	101 LI2.2 NA1 MG12-9 S11S1-
70 ACBGA	26	1464 RB NI F3	74 ZAKCA	403	1 R3 VS V (PM F3)		CA1 O43-4 F+3 OH13-		
70 ACSEA	24	378 ND2 RB NI T11 O6	PR+3 IX				70 ZKKKA	132	288 NA2 S12 O7 IC O312
70 JSSCB	2	416 RB NI F3	70 SPHCA	15	28 PR2 M2 O9		71 ACBGA	27	2609 NA2 S1 U3-6H2 O
71 PHSSA	38	125 NI O1 H12	59 ZKKKA	112	362 PR IC2 HS S O413-2H2 O		72 SPHCA	16	1021 BE2 SI O4
70 JSSCB	2	416 RB NI F3	74 ZAKCA	403	1 R3 VS V (PM F3)		72 ACSEA	23	1889 NA2 SE S15 O18
64 ACSEA	17	1481 NI IC5 H7 O212-2H2 O	PR+4 VI				74 ACBGA	30	2434 LI2 BE S1 O4
73 ACSEA	29	2741 NI S1 F6.OH2 O	72 ACBGA	28	956 BA PR U3		51+4 VI		
63 ZAKCA	118	63 NI IC5 H7 O212-2H2 O	71 ACSEA	31	971 PR7 O12		69 CJCHA	47	3859 CU S1 F6-4H2 O
74 JCPSA	61	852 NI C4 O4.2H2 O	73 JSSCB	8	331 R (PU+4)		70 ACBGA	26	233 S1 P2 O7
73 JCLRL	183	NI IC5 H7 O212-IC2 HS O H12	74 CJCHA	52	2175 R3 VS V		71 ACSEA	27	2133 S1 O7
74 AMHIA	29	2304 NI V2 O8	PT+2 REF 5				71 ACSEA	27	594 CA3 S1 O1 H16.12H2 O.504
N1+3 VI	LS		PT+4 VI				73 ACSEA	29	2741 NI S1 F6.OH2 O
74 ZAKCA	403	167 M2 NI M1 F6	69 JINCA	31	3803 PT O2		74 CJCHA	52	2175 R3 VS V
71 CHODCA	472	2163 HO NI O3	75 ACSEA	52	2175 R3 VS V		SM+2 VII	UNPU1	SM I2
54 JACSEA	76	1499 NA NI O2	PT+5 VI				SM+2 VIII	UNPU1	SM BR2, SM F2
67 STGBA	3	1 R3 VS V (FLUORIDES)	67 STGBA	3	1 R3 VS V (FLUORIDES)		SM+2 IX	UNPU1	SM CL2, SM BR2
74 INDOA	36	1561 K2 NI F6	67 JCSIA	1967	478 KE PT F11		SM+3 VI	UNPU1	SM GE O4
NB+2 VI			PM+3 VI				SM+3 VII	UNPU1	SM GE O4
74 INDOA	13	2233 ESTIMATED	67 INUCA	3	327 R (PU+3)		74 SPHCA	18	575 K2 S12 O7
68 JINCA	30	823 NP CL3	75 JINCA	37	743 R (PU+3)		SM+3 VIII	UNPU1	SM GE O4
NB+4 VI			PM+4 VI				SM+3 IX	UNPU1	SM GE O4
67 INUCA	3	327 ESTIMATED	67 INUCA	3	327 R (PU+4)		SM+4 I	UNPU1	SM GE O4
74 CJCHA	52	2175 R3 VS V	73 JSSCB	8	331 R (PU+4)		SM+4 II	UNPU1	SM GE O4
NB+6 VI			74 CJCHA	52	2175 R3 VS V		SM+4 III	UNPU1	SM GE O4
OM+1 II			PM+6 VI				SM+4 IV	UNPU1	SM GE O4
71 AMHIA	56	1155 MG6-6 FE4 S13 O12 F O H,	RB+1 VI				SM+4 V	UNPU1	SM GE O4
OM+1 III			70 ZAKCA	375	255 R82 PB O3		SM+4 VI	UNPU1	SM GE O4
71 AMHIA	56	1155 MG6-6 FE4 S13 O12 F O H,	74 ACSEA	30	1640 RB2 S O4		SM+4 VII	UNPU1	SM GE O4
OM+1 IV			RB+1 VII				SM+4 VIII	UNPU1	SM GE O4
71 AMHIA	56	1155 MG6-6 FE4 S13 O12 F O H,	74 ACSEA	30	1640 RB2 S O4		SM+4 IX	UNPU1	SM GE O4
OM+1 V			RB+1 VIII				SM+4 X	UNPU1	SM GE O4
OS+4 VI			70 ACSEA	26	1464 RB NI F3		SM+4 XI	UNPU1	SM GE O4
69 JCPSA	17	459 O5 O5	70 JSSCB	2	416 RB NI F3		SM+4 XII	UNPU1	SM GE O4
70 ACSSA	24	123 O5 O5	70 JSSCB	2	582 RB NI F3		SM+4 XIII	UNPU1	SM GE O4
71 JCSIA	1971	2789 O5 O5	RB+1 XIV				SM+4 XIV	UNPU1	SM GE O4
74 SSCDA	14	357 R3 RS V (CD2 O52 O7)	65 ACSEA	19	205 RB U2 IN O312		SM+4 XV	UNPU1	SM GE O4
56 JINCA	2	79 K D5 F6	RE+4 VI				SM+4 XVI	UNPU1	SM GE O4
OS+6 VI			74 CJCHA	52	2175 R3 VS V		SM+4 XVII	UNPU1	SM GE O4
OS+7 VI			RE+5 VI				SM+4 XVIII	UNPU1	SM GE O4
OS+8 VI			70 ACSSA	24	3406 ND2 RE2 O11		SM+4 XIX	UNPU1	SM GE O4
68 ACSEA	14	309 K D5 F6	UNPU2				SM+4 XX	UNPU1	SM GE O4
OS+9 VI			RE+6 VI				SM+4 XXI	UNPU1	SM GE O4
69 JCPSA	50	86 ND2 RE2 O11	75 JSSCB	13	77 BA2 MN RE O6		SM+4 XXII	UNPU1	SM GE O4
71 JSSCB	3	89 NA13 N895 U94	RE+7 VI				SM+4 XXIII	UNPU1	SM GE O4
27 IJNCA	27	1410 IMAH NB O IC2 O413.H2 O	68 ACSEA	17	295 RE2 O7 IC O212		SM+4 XXIV	UNPU1	SM GE O4
75 ACSEA	31	673 N82 O5	71 JCSIA	1971	1957 RE1+7 O		SM+4 XXV	UNPU1	SM GE O4
NB+2 IX			68 JSTCA	9	166 PD IC6 HS12 CH GZ O212		SM+4 XXVI	UNPU1	SM GE O4
UNPU1		NO I2	74 ZAKCA	403	1 R3 VS V (PM F3)		SM+4 XXVII	UNPU1	SM GE O4
NB+3 VI		NO CL2, NO BR2	PM+3 VII				SM+4 XXVIII	UNPU1	SM GE O4
71 INDOA	10	922 BA2 NO MO D6	PM+3 VIII				SM+4 XXIX	UNPU1	SM GE O4
74 HBUA	9	1601 NO AL3 BA O12	PM+3 IX				SM+4 XXX	UNPU1	SM GE O4
NB+3 VII			74 ZAKCA	403	1 R3 VS V (PM F3)		SM+4 XXXI	UNPU1	SM GE O4
69 JCPSA	50	86 ND2 MO3 O12	PM+4 VI				SM+4 XXXII	UNPU1	SM GE O4
71 JSSCB	4	458 ND V 04	PT+2 REF 5				SM+4 XXXIII	UNPU1	SM GE O4
68 ACSEA	14	318 K NCA MO D8	PT+4 VI				SM+4 XXXIV	UNPU1	SM GE O4
70 ACSEA	26	484 ND2 T12 O7	67 INUCA	3	327 R (PU+3)		SM+4 XXXV	UNPU1	SM GE O4
70 ACSEA	24	3406 ND4 NE T11 O6	75 JINCA	37	743 R (PU+3)		SM+4 XXXVI	UNPU1	SM GE O4
71 SPHDA	15	630 ND2 W 04	PM+3 VI				SM+4 XXXVII	UNPU1	SM GE O4
71 SPHCA	15	991 NA3 VS O15	PM+3 VII				SM+4 XXXVIII	UNPU1	SM GE O4
74 HBUA	9	129 ND P5 O13	PM+3 VIII				SM+4 XXXIX	UNPU1	SM GE O4
24 ZAKCA	403	1 R3 VS V (ND F3)	PM+3 IX				SM+4 XL	UNPU1	SM GE O4
74 ACSEA	30	468 ND P3 O9	74 ZAKCA	403	1 R3 VS V (PM F3)		SM+4 XLI	UNPU1	SM GE O4
70 ACSEA	24	2969 ND2 IC2 O413.10.5H2 O	PM+4 VI				SM+4 XLII	UNPU1	SM GE O4
71 SPHCA	15	991 NA3 VS O15	PT+2 REF 5				SM+4 XLIII	UNPU1	SM GE O4
71 SPHCA	15	2441 ND2 IC2 H2 O413.BM2 O	PT+4 VI				SM+4 XLIV	UNPU1	SM GE O4
74 ZAKCA	403	1 R3 VS V (ND F3)	67 INUCA	3	327 R (PU+3)		SM+4 XLV	UNPU1	SM GE O4
74 ACSEA	27	2813 ND2 IC2 H2 O413.BM2 O	75 JINCA	37	743 R (PU+3)		SM+4 XLVI	UNPU1	SM GE O4
73 JSTCA	1973	2070 ND O413 O	PM+3 VI				SM+4 XLVII	UNPU1	SM GE O4
74 AMHIA	59	1277 ND4 MG2 T13 S14 O22	PM+3 VII				SM+4 XLVIII	UNPU1	SM GE O4
NB+3 X			PM+3 VIII				SM+4 XLIX	UNPU1	SM GE O4
71 JSSCB	4	11 ND AL O4	PM+3 IX				SM+4 L	UNPU1	SM GE O4
N1+2 IV			74 ZAKCA	403	1 R3 VS V (PM F3)		SM+4 LI	UNPU1	SM GE O4
61 JAPFA	32	685 NI CR2 O4	PM+4 VI				SM+4 LII	UNPU1	SM GE O4
68 ACSEA	19	1085 SPINELS	PT+2 REF 5				SM+4 LIII	UNPU1	SM GE O4
N1+2 IV S0			PT+4 VI				SM+4 LIV	UNPU1	SM GE O4
68 INDOA	5	1200 NI IDPM12	67 INUCA	3	327 R (PU+3)		SM+4 LV	UNPU1	SM GE O4
N1+2 V			75 JINCA	37	743 R (PU+3)		SM+4 LVI	UNPU1	SM GE O4
67 BAPCA	15	47 NI2 P2 O7	PM+3 VI				SM+4 LVII	UNPU1	SM GE O4
N1+2 VI			PM+3 VII				SM+4 LVIII	UNPU1	SM GE O4
74 AMHIA	59	486 NI2 S1 O4	PM+3 VIII				SM+4 LVIX	UNPU1	SM GE O4
74 ACSEA	30	1086 NI (PY N D10 (B F+12	PM+3 IX				SM+4 LX	UNPU1	SM GE O4
68 ACSEA	15	47 NI2 P2 O7	74 ZAKCA	403	1 R3 VS V (PM F3)		SM+4 LXI	UNPU1	SM GE O4
67 BAPCA	15	47 NI2 P2 O7	PM+4 VI				SM+4 LXII	UNPU1	SM GE O4
70 ACBGA	26	1464 RB NI F3	PT+2 REF 5				SM+4 LXIII	UNPU1	SM GE O4
70 ACSEA	24	378 ND2 RB NI T11 O6	PT+4 VI				SM+4 LXIV	UNPU1	SM GE O4
70 JSSCB	2	416 RB NI F3	67 INUCA	3	327 R (PU+3)		SM+4 LXV	UNPU1	SM GE O4
71 PHSSA	38	125 NI O1 H12	75 JINCA	37	743 R (PU+3)		SM+4 LXVI	UNPU1	SM GE O4
70 JSSCB	2	416 RB NI F3	PM+3 VI				SM+4 LXVII	UNPU1	SM GE O4
64 ACSEA	17	1481 NI IC5 H7 O212-2H2 O	PM+3 VII				SM+4 LXVIII	UNPU1	SM GE O4
73 ACSEA	29	2							

Table 2 (cont.)

72 ACBCA	28	956 BA TB 03	71 JINCA	33	2867 CR2 U 06	69 PHSSA	32	K91 ZN FE2 O4
TC+5 VI			72 ACBCA	28	3609 U 02 0 H12	73 ACSCA	27	1541 ZN S O3.2 1/2H2 O
67 STBGA	3	1 R3 VS V (FLUORIDES)	73 ACBCA	29	T U F6	64 INDOCA	3	245 ZN (OPNH2)
TC+7 IV			U6+ VII			ZN+2 V		
69 ACIEA	8	381 TG2 07	72 ACBCA	28	3609 U 03	70 JSSCB	1	120 ZN2 P2 07
71 ZAACA	380	146 TG2 07	U6+ VIII			73 CJCMA	51	1004 ZN2 V2 07
TE+4 IV			69 ACBCA	25	787 CA U 04	71 ANMIA	56	1147 ZN4 AS2 O8 0 H12.2H2 O
69 ACBCA	25	1551 H3 FE2 TE4 O12 CL	69 ACBCA	19	205 RB U 02 (IN O313)	ZN+2 VI		
71 ACBCA	27	602 TI TE3 O8, 3N TE3 O8, TE O2, HF TE3 O8, ZR TE3 O8	V+2 VI			65 CJCMA	43	1147 ZN2 P2 07
71 ACBCA	27	608 U TE3 O9	UNPUS		V F2	70 JSSCB	1	120 ZN2 P2 07
TE+6 VI			V+3 VI			71 CJCMA	49	3056 ZN3 V2 07
61 ZKKA	116	345 TE 02	70 PRVBA	2	3771 V2 03	71 ANMIA	56	1147 ZN4 AS2 O8 0 H12.2H2 O
71 ACBCA	27	602 M TE3 O8	73 JSSCB	6	419 V4 07	73 ACBCA	29	2741 ZN S1 F6.4H2 O
71 ACBCA	27	608 U TE3 O9	69 ACBCA	25	787 CA U 04	73 ACSCA	27	1541 ZN S O3.2 1/2H2 O
TE+6 IV			74 MRBBA	9	1091 UVO.99 CR0.0112 O3	ZR+4 IV		
71 JCSCA	1971	1857 TE(+6)+O	70 JPCSA	31	2569 V2 03	75 JSSCB	13	275 R3 VS V (M4 ZR F6)
TE+6 VI			V4+ V			ZR+4 V		
69 ZENBA	24	647 L16 TE 06	65 ACBCA	19	432 L1 V2 05	69 CCJDA	1969	727 K2 ZR O3
70 MRBBA	5	109 M3 TE 06	61 JPCSA	35	55 V O IC5 H7 O212	70 JSSCB	2	410 K2 ZR O3
69 ACSCA	23	3062 NA2 KA TE2 O8 0 H12 IH2 O114	73 ACBCA	29	269 CA V3 07	ZR+4 VI		
64 INDOCA	3	634 K TE 0 10 H15.H2 O	73 ACBCA	29	1335 CA V4 09	69 ACBCA	25	2658 ZR IH AS O412.H2 O
64 NATMA	51	552 K TE 0 O.H	V4+ VI			69 ZAACA	371	306 L12 ZR O3
66 ACSCA	20	2138 K4 TE2 O6 0 H14.H2 O	72 JSSCB	5	446 CU V 03	70 JSSCB	1	478 K2 ZR2 O5
70 NATMA	57	393 M3 TE 06	73 JSSCB	6	419 V4 07	73 ACBCA	29	2294 L12 ZR F6
70 ZAACA	378	129 SR2 NI TE 06	72 PRVBA	5	2541 V O2 CR	71 ACBCA	27	1944 RB5 ZR F21
70 ACSCA	24	3178 TE 10 H16	74 ACBCA	30	2644 V3 07	74 CJCMA	52	2175 R3 VS V
66 ACSCA	20	1535 TE F6	71 ACSCA	25	2675 V6 O13	ZR+4 VII		
71 ACBCA	27	615 M3 TE 06	70 ACSCA	24	420 VO2	69 ACBCA	25	2164 NA2 ZR F6
65 ZAACA	334	225 K TE 02 0 H13	74 PRVBA	10	490 VO2	70 ACBCA	26	417 IH M413 ZR F7
68 CHODA	267	1435 CU2 TE 06	V4+ IV			70 JACTA	53	126 ZR O2
69 MOCBM	100	1809 AG2 TE 02 0 H14	68 ACBCA	24	292 Y V O4	73 ACSCA	27	177 ZR4 0 H16 (CR O415.H2 O
71 BUFGA	94	172 TE 10 H16	68 CHPLB	2	47 ER V O4	73 ACSCA	27	2614 ZR 0 H12 S O4.H2 O
73 ACBCA	29	643 TE 06	67 ACSCA	25	250 H7 H2 07	71 ACBCA	27	1944 RB5 ZR F21
73 ACBCA	29	643 TE 06	70 ZKKA	131	161 BA3 (V O412	ZR+4 VIII		
73 ACSCA	29	956 H2 TE2 O5	71 JSSCB	3	458 ND V O4	69 ACBCA	25	1558 ZR2 S O414 IH2 O18.H2 O
73 ACSCA	27	85 TE 10 H16	71 CJCMA	49	1629 MG3 V2 08	69 ACBCA	25	1566 ZR2 S O414 IH2 O18.H2 O
74 ACBCA	30	1813 H2 TE 04	70 INDOCA	9	2259 CA2 O4 CL	69 ACBCA	25	1572 ZR2 S O414.H2 O
74 ACBCA	30	2095 IN H416 (TE M06 O24) TE (H016	71 CJCMA	49	1629 MG3 V2 08	71 ANMIA	56	782 ZR S1 O4
			72 JSSCB	4	29 FE V O4	63 INDOCA	2	243 ZR (KAC414)
			73 CJCMA	51	1004 ZN2 V2 07	63 INDOCA	2	250 NA4 ZR IC2 O414.3H2 O
			71 CJCMA	49	1629 MG3 V2 08			
			73 JSSCB	6	518 L13 V O4			
			72 CJCMA	50	3944 CUS V2 08			
			71 CJCMA	49	1629 MG3 V2 08			
			73 ACBCA	29	141 Y V O4			
			73 ACBCA	29	1338 CUS V2 O10			
			73 CJCMA	51	265 L1 V O3			
			74 ACBCA	30	1678 NA V O3			
			74 ACBCA	30	1678 NA V O3			
			74 NJMMA	5	2110 CS IV O413 O H			
			V4+ V					
			50 ACSCA	4	1119 V2 05			
			71 RVCBA	2	509 V2 05			
			74 ACBCA	30	2644 V3 07			
			74 ACBCA	30	2491 MG2 V2 07			
			73 ACBCA	29	587 ZR V2 07			
			70 CHODA	270	952 CA V2 06			
			V4+ VI					
			73 JSSCB	5	432 V P O5			
			71 ACSCA	25	2675 V6 O13			
			72 CJCMA	50	3619 MG V2 06			
			73 CJCMA	51	2621 V P O5 ALPHA			
			74 CJCMA	52	2184 K3 V O2 C2 O4.3H2 O			
			73 ACBCA	29	1743 CU V2 06			
			V4+ VII					
			67 STBGA	3	1 R3 VS V (FLUORIDES)			
			M4+ IV					
			69 ACBCA	25	1704 K2 M O4			
			71 SPHDA	15	626 ND2 M O6			
			71 SPHDA	15	928 B W M O4			
			72 ACBCA	28	3174 SN O4			
			71 JPCSA	55	1093 SR M O4.BA M O4			
			71 JCSCA	1971	1857			
			74 ACBCA	30	1872 NA2 M O4			
			74 ACBCA	30	1878 AL2 IN O413			
			M4+ V					
			74 ACBCA	30	2587 CA3 M O5 CL2			
			M4+ VI					
			69 SPHCA	13	933 MG M O4			
			69 SSCDA	7	1797 B12 M O6			
			70 SPHCA	14	518 K ND (M O412			
			70 SPHCA	14	515 L12 FE M2 O8			
			70 SPHCA	15	28 PR2 M2 O9			
			70 ACBCA	26	1020 CU M O4			
			70 JSSCB	2	278 L1 FE (M O412			
			66 ACSCA	20	2698 M F6 (GAS)			
			72 ZENBA	27	203 SN M O4			
			71 SPHCA	15	991 ND4 M3 O15			
			74 JSSCB	10	5 FE2 M O6			
			74 ACBCA	30	2069 BA M O4			
			X4+0 IV					
			71 JPCSA	52	812 XE O4			
			71 JCSCA	1971	1857 XE(+8)+O			
			X4+0 VI					
			64 INDOCA	3	1412 NA4 XE O6.0H2 O			
			64 INDOCA	3	1417 NA4 XE O6.0H2 O			
			V4+ V					
			67 ACBCA	22	354 V2 BE O4			
			68 ZAACA	358	138 SR Y2 O4			
			67 SPHCA	11	583 NA Y S1 O4			
			69 ACBCA	25	2140 Y2 O3			
			71 SPHCA	15	806 Y2 S1 O5			
			74 JCSCA	1974	229 C66 H72 13 N12 O6 Y			
			V4+ VII					
			68 INDOCA	7	1777 YIC65CCHCCH313.H2O			
			V4+ VIII					
			68 ACBCA	24	292 Y V O4			
			57 ACBCA	10	239 Y3 FE5 O12			
			68 SPHDA	12	1095 K Y ND2 O8			
			69 SPHCA	13	420 K Y W2 U8			
			70 ZKKA	131	278 V2 T12 07			
			67 ACBCA	23	939 Y TA O4			
			74 ZAACA	403	1 R3 VS V (Y F3)			
			V4+ IX					
			59 ZKKA	112	362 Y (CZ H5 S O413.0H2 O			
			74 ZAACA	403	1 R3 VS V (Y F3)			
			YB+2 VI					
			74 ACBCA	386	221 YB BR2, YB 12			
			YB+2 VII					
			74 ZAACA	403	45 YB CL2			
			71 ZAACA	386	221 YB BR2			
			YB+2 VIII					
			71 ZAACA	386	221 YB F2			
			YB+3 VI					
			70 SPHCA	14	854 YB2 S1 O5			
			70 ACBCA	26	1020 CU M O4			
			70 ZAACA	377	70 CA YB2 O4, SR YB2 O4			
			74 ACBCA	30	1857 YB P3 O9			
			YB+3 VII					
			70 SPHCA	14	854 YB2 S1 O5			
			69 INDOCA	8	22 YB (CZ H5 S O413.0H2 O			
			69 INDOCA	8	29 YB (CZ H5 S O413.0H2 O) 1/2 C6 H6			
			YB+3 VIII					
			9 INDOCA	9	1096 YB L1 F4			
			70 SSCDA	8	1745 YB3 FE5 O12			
			74 MRBBA	9	179 YB P5 O14			
			74 ZAACA	403	1 R3 VS V (YB F3)			
			YB+3 IX					
			74 ZAACA	403	1 R3 VS V (YB F3)			
			ZN+4					
			68 SPHDA	12	987 NA2 ZN2 S12 O7			
			69 ACBCA	25	1233 ZN O3			

compounds to be slightly larger than those of the Eu^{2+} compounds. This difference was assumed to exist for all Sr^{2+} and Eu^{2+} coordinations. Because compounds of Am^{2+} and Sr^{2+} have similar cell volumes, the radius of Am^{2+} was made equal to that of Sr^{2+} .

Wolfe & Newnham (1969) studied $\text{Bi}_{4-x}\text{RE}_x\text{Ti}_3\text{O}_{12}$ and concluded that Bi^{3+} and La^{3+} have nearly equal radii. From a study of BiTaO_4 Sleight & Jones (1975) have concluded that although Bi^{3+} and La^{3+} have essentially equal radii, the size of Bi^{3+} depends on the degree of the $6s^2$ lone-pair character. When BiTaO_4 transforms from a structure where the lone-pair character is dominant to the LaTaO_4 structure, it undergoes a volume reduction. Table 3 shows a comparison of isotypic Bi^{3+} and La^{3+} compounds where the lone-pair character of Bi^{3+} is (1) constrained and (2) dominant. Bi pyrochlores such as $\text{Bi}_2\text{Ru}_2\text{O}_7$, $\text{Bi}_2\text{Ir}_2\text{O}_7$ and $\text{Bi}_2\text{Pt}_2\text{O}_7$ were omitted from the table because no corresponding La pyrochlore exists, but they have unit-cell volumes close to those of the Sm or Nd pyrochlores and thus have smaller volumes than those of La. When Bi^{3+} is forced into high symmetry, a Bi^{3+} compound has a smaller volume than that of La^{3+} , but when the lone-pair character is dominant, the Bi^{3+} compound is distorted and Bi^{3+} and La^{3+} compounds have approximately equal volumes. This behavior was also noted in the highly symmetric garnet structure where the hypothetical $\text{Bi}_3\text{Fe}_5\text{O}_{12}$ was estimated to have cell dimensions between those of the hypothetical $\text{Nd}_3\text{Fe}_5\text{O}_{12}$ and $\text{Pr}_3\text{Fe}_5\text{O}_{12}$ (Geller, Williams, Espinosa, Sherwood & Gilleo, 1963). For practical purposes, Bi^{3+} is listed as slightly smaller than La^{3+} but this dependence on lone-pair character must be kept in mind when comparing the volumes of Bi^{3+} and La^{3+} compounds. Similar behavior may also exist for Pb^{2+} and Sr^{2+} , but this relationship was not investigated.

Table 3. Cell volumes of isotypic Bi^{3+} and La^{3+} compounds

(a) Lone pair character of Bi^{3+} constrained

Compound	Cell volume	Ratio
$\text{BiLi}(\text{MoO}_4)_2$	314.7	0.96
$\text{LaLi}(\text{MoO}_4)_2$	328.7	
$\text{BiNa}(\text{MoO}_4)_2$	320.5	0.97
$\text{LaNa}(\text{MoO}_4)_2$	332.1	
BiOF	87.6	0.90
LaOF	97.7	
BiOCl	110.7	0.95
LaOCl	116.8	
BiOBr	123.8	0.98
LaOBr	126.4	
BiPO_4	293.0	0.96
LaPO_4	304.7	

(b) Lone pair character of Bi^{3+} dominant

Bi_2MoO_6	268.5 ($\times 8$)	1.00
La_2MoO_6	267.3	
BiFeO_3	62.49 ($\times 6$)	1.03
LaFeO_3	60.77 ($\times 4$)	
$\text{Bi}_2\text{Sn}_2\text{O}_7$	1219.9 ($\times 8$)	1.00
$\text{La}_2\text{Sn}_2\text{O}_7$	1225.3	

A similar study of relative cell volumes of isotypic compounds involving the pairs Cu^+-Li^+ , Ag^+-Na^+ , Tl^+-Rb^+ , and $\text{Pb}^{2+}-\text{Sr}^{2+}$ was used to obtain more reliable estimates of the radii of Cu^+ , Ag^+ , Tl^+ , and Pb^{2+} (Shannon & Gummerman, 1975).

The nature of Sn^{2+} , NH_4^+ , and H^- made it impossible to define their ionic radii. The coordination of Sn^{2+} by oxygen or fluorine is always extremely irregular,* leading to average distances which depend on the degree of distortion. Since this distortion varies widely from one compound to another, it is not meaningful to define an ionic radius.

Khan & Baur (1972) derived an apparent radius of the NH_4^+ ion by analyzing the N-O distances in a large number of ammonium salts. They concluded that NH_4^+ has an octahedral radius of 1.61 Å, between that of Rb^+ (1.52 Å) and Cs^+ (1.67 Å). Alternatively, cell volumes of NH_4^+ and Rb^+ fluorides, chlorides, bromides, iodides and oxides may be compared. This leads to the conclusion that NH_4^+ is not significantly different in size from Rb^+ . No explanation is offered for this inconsistency and therefore the radius of NH_4^+ is not included.

The radius of the hydride ion, H^- , has been the subject of some controversy. A number of different radii have been proposed: 2.08 (Pauling, 1960); 1.40 (Gibb, 1962); and 1.53 Å (Morris & Reed, 1965). Gibb studied interatomic distances in many hydrides and concluded that good agreement between observed and calculated distances could be obtained using $r(\text{VIH}^-) = 1.40$ Å if corrected for cation and anion coordination. The value of $r(\text{IVH}^-)$ was taken to be 1.22 Å.

Morris & Reed (1965) concluded that differences in observed distances in hydrides were caused by the large H^- polarizability. Because of such wide variations in the apparent H^- radius, it was omitted. However, an explanation for the variations based on covalence differences will be discussed later.

* Although cell dimensions of $\text{Sn}_2\text{M}_2\text{O}_7$ pyrochlores were used in SP 69 to derive $r(\text{VIIISn}^{2+})$, Stewart, Knop, Meads & Parker (1973) and Birchall & Sleight (1975) recently found that the pyrochlore A site in $\text{Sn}_2\text{Ta}_2\text{O}_7$ is not fully occupied. Thus, even this example of apparently regular Sn^{2+} polyhedra is not valid.

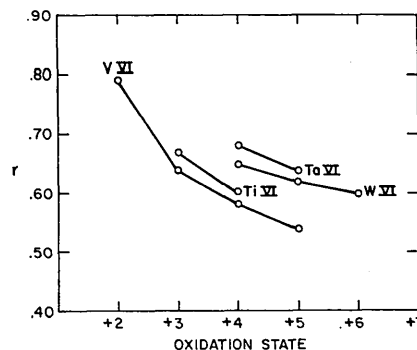
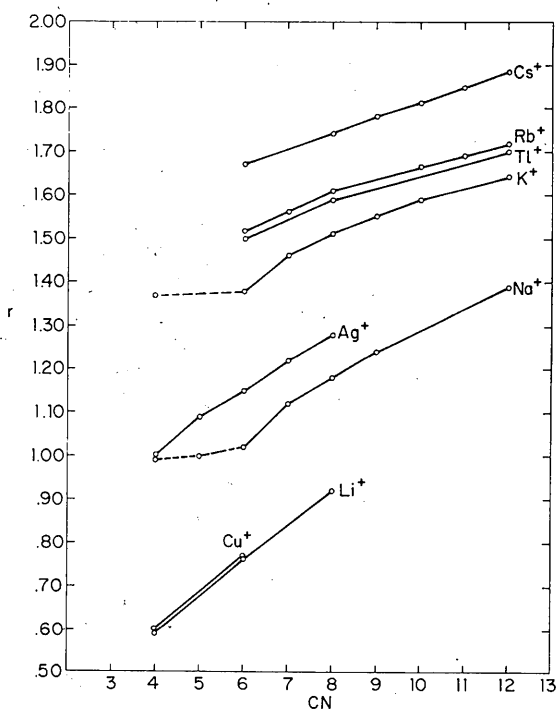


Fig. 1. Effective ionic radius (Å) vs oxidation state.

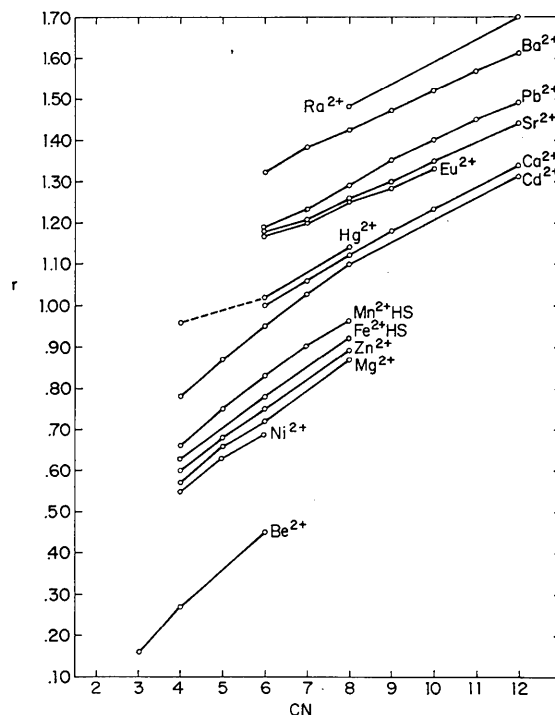
Results and discussion

In Table 1 two sets of radii are included. The first is a set of traditional radii based on $r(\text{VI}\text{O}^{2-}) = 1.40 \text{ \AA}$. The

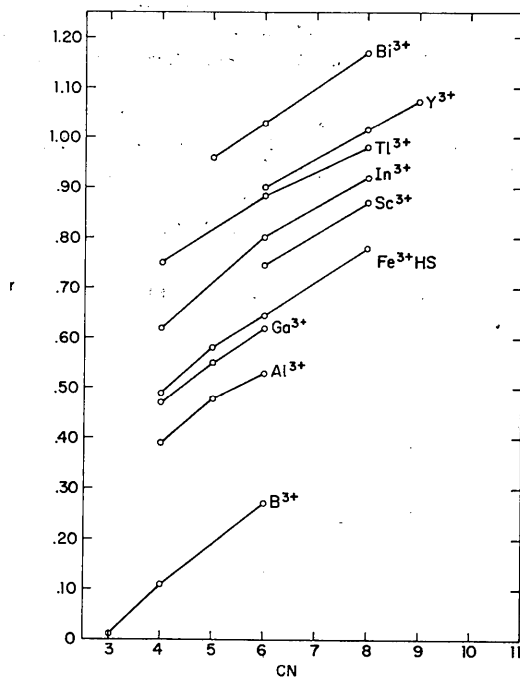
other set is based on $r(\text{VI}\text{O}^{2-}) = 1.26$ and $r(\text{VI}\text{F}^-) = 1.19 \text{ \AA}$, and corresponds to crystal radii as defined by Fumi & Tosi (1964). As pointed out in SP 69, crystal radii differ from traditional radii only by a constant factor



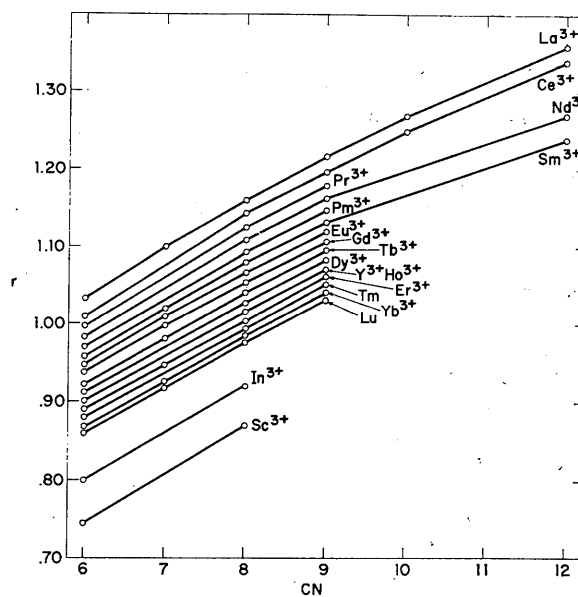
(a)



(b)

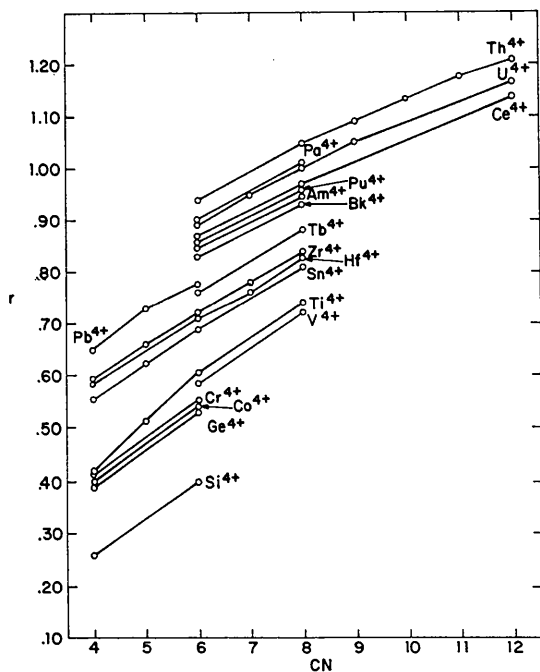


(c)



(d)

Fig. 2. (a)–(e) Effective ionic radius (\AA) vs CN for some common cations.



(e)

Fig. 2. (cont.)

of 0.14 Å. Although their inclusion in Table 1 may seem superfluous, it is felt that crystal radii correspond more closely to the physical size of ions in a solid. They should be used, for example, in discussions of closest packing of spheres, structure field maps (Muller & Roy, 1974), and diffusion in solids (Flygare & Huggins, 1973). Traditional radii have been retained because of their familiarity to crystal chemists and physicists. They will probably continue to be used for comparison of unit-cell volumes and interatomic distances. In the table, the ion is followed by electron configuration (EC), coordination number (CN), spin state (SP), crystal radius (CR), and effective ionic radius (IR), and in the last column, a symbol indicating the derivation of the radii and their reliability. Those with a question mark are doubtful because of: uncertainty in CN, or deviation from radii *vs* CN, or radii *vs* valence plots. Where at least five structural determinations resulted in radii differing by no more than ± 0.01 Å, the values are marked with an asterisk.

When the choice of a radius was influenced by any of the various correlations described earlier, it is indicated by the following: *R* – from r^3 *vs* unit cell volume plots; *C* – calculated from bond length–bond strength equations; *E* – estimated from one or more plots of r *vs* valence, r *vs* CN, and r *vs* cell volume. *E* implies poor or nonexistent structural data. Radii in this category include $^{VI}\text{Fe}^{2+}\text{LS}$, $^{VI}\text{Mn}^{2+}\text{LS}$, $^{VI}\text{Cr}^{2+}\text{LS}$, $^{VI}\text{V}^{2+}$, $^{VI}\text{Ni}^{3+}\text{HS}$, $^{VI}\text{Ir}^{3+}$, $^{VI}\text{Mo}^{3+}$, $^{VI}\text{Ta}^{3+}$, $^{VI}\text{Pa}^{3+}$, $^{VI}\text{Ta}^{4+}$, $^{IV}\text{Pb}^{4+}$, $^{VI}\text{Ir}^{5+}$, $^{VI}\text{Os}^{5+}$, $^{VI}\text{Re}^{5+}$, $^{VI}\text{Pu}^{5+}$, $^{VI}\text{Bi}^{5+}$,

$^{VI}\text{Os}^{6+}$, $^{VI}\text{Re}^{6+}$, and $^{VI}\text{Os}^{7+}$. The symbol *A* means that Ahrens (1952) ionic radius was used whereas *P* means Pauling's (1960) crystal radius was used. The symbol *M* means that the radius was derived from a compound having metallic conductivity. Distances calculated from these radii may be too small for use in compounds having localized electrons. (See discussion *Effects of electron delocalization*.)

In addition, the sources of the radii are indicated in Table 2.

Fig. 2(a)–(e) shows that r –CN plots are reasonably regular. Notable exceptions are $^{IV}\text{Na}^+$, $^{V}\text{Na}^+$, and $^{IV}\text{K}^+$. It is apparent that Na–O and K–O distances do not decrease as much as anticipated from the r –CN curve* when the CN falls below six. Typical distances and corresponding radii in Table 4 show that Na–O distances in four-coordination are only slightly less than in six-coordination. The reduction in interatomic distances is caused primarily by the decreased repulsive forces due to fewer ligands according to the expression of Pauling (1960):

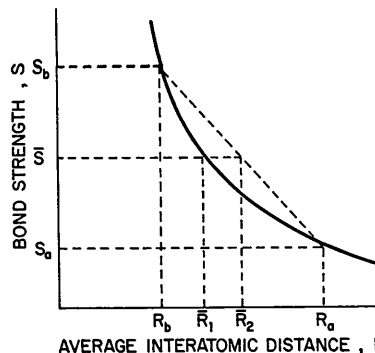
$$\frac{R_{\text{CsCl}}}{R_{\text{NaCl}}} = \left[\frac{A_{\text{NaCl}}}{A_{\text{CsCl}}} \frac{B_{\text{CsCl}}}{B_{\text{NaCl}}} \right]^{1/(n-1)}$$

where R = interatomic distance, A = Madelung constant, B = the cation CN and n = Born repulsion coefficient. It appears that this equation is not valid for four-coordinated Na^+ or K^+ .

There are a few small irregularities in r –CN plots probably caused by poor or insufficient data, *e.g.* curves for Ti^{3+} *vs* Y^{3+} . The differences in slopes of Ti^{4+} *vs* Cr^{4+} and V^{5+} *vs* As^{5+} are probably caused by Ti^{4+} –O and V^{5+} –O octahedra being generally more distorted, which leads to greater average interatomic distances.

It is also interesting to compare distances in square planar coordination *versus* tetrahedral coordination. Radii of square planar Cu^{2+} and Ag^+ are equal to or slightly greater than corresponding tetrahedral radii, consistent with the trend anticipated from anion

* Extrapolation of the Na curve gives $r(^{IV}\text{Na}^+) = 0.90$ Å.

Fig. 3. Typical bond length *vs* bond strength plot.

repulsion effects. A similar comparison with Fe^{2+} and Ni^{2+} cannot be made because of electron distribution changes from tetrahedral to square planar coordination.

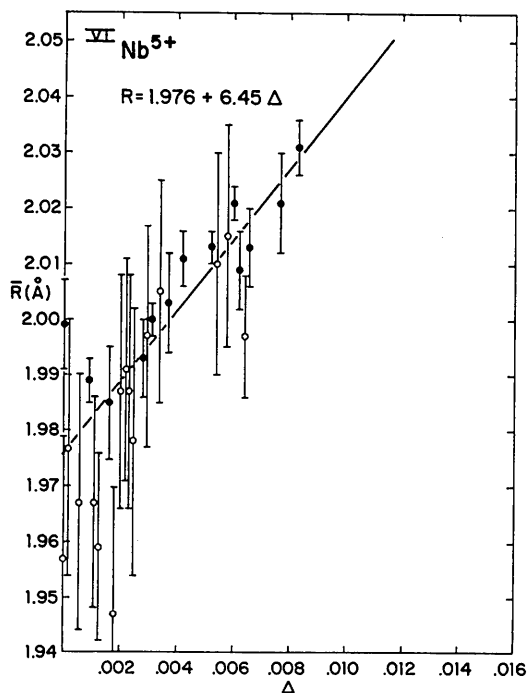


Fig. 4. Mean Nb^{5+} -O bond length *vs* distortion. Vertical bars represent average e.s.d.'s quoted by the authors. Solid circles represent more accurate data.

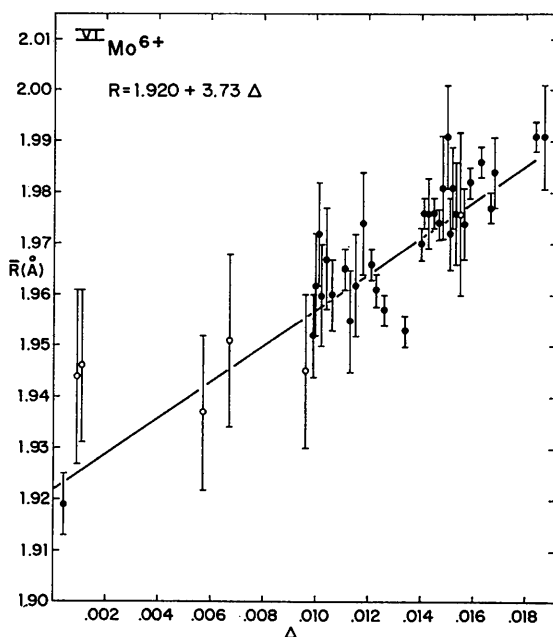


Fig. 5. Mean Mo^{6+} -O bond length *vs* distortion.

Table 4. *Interatomic distances in some compounds containing tetrahedral and octahedral Na^+*

Compound	\bar{R} (Å)	r (Å)	Reference
(a) IVNa^+			
Na_2O	2.40	1.02	
$\text{Na}_5\text{P}_3\text{O}_{10}$	2.37	0.99	60 ACCRA 13 263
$\text{NaOH} \cdot \text{H}_2\text{O}$	2.36	1.00	57 ACCRA 10 462
Na_6ZnO_4	2.39	0.99	69 ZAACA409 69
Mean	2.38	1.00	
(b) VI Na^+			
Na_2WO_4	2.38	1.00	74 ACBCA 30 1872
$\text{NaC}_6\text{O}_7\text{H}_7$	2.37	1.01	65 ACCRA 19 561
$\text{Na}_4\text{Sn}_2\text{Ge}_4\text{O}_{12}(\text{OH})_4$	2.39	1.02	70 ACSAA 24 1287
$\text{Na}_2\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$	2.48	1.10	64 ACCRA 17 672
NaHCO_3	2.44	1.06	65 ACCRA 18 818
$\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2 \cdot 3\text{H}_2\text{O}$	2.41	1.04	67 SCIEA 154 1453
$\text{Na}_4\text{P}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$	2.415	1.05	61 ACCRA 14 555
$\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	2.45	1.10	67 ACCRA 22 182
$\text{NaB}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$	2.460	1.09	63 ACCRA 16 1233
NaU acetate	2.375	1.025	59 ACCRA 12 526
$\text{C}_{10}\text{H}_{13}\text{N}_5\text{NaO}_6\text{P} \cdot 6\text{H}_2\text{O}$	2.406	1.046	75 ACBCA 31 19
Mean	2.42	1.05	

Factors affecting mean interatomic distances

Additivity of radii to give mean interatomic distances is not so important to the synthetic chemist who is primarily interested in ionic radii for predicting substitution in crystal structures. Crystallographers and physicists, however, are concerned with comparing calculated and experimental interatomic distances and predicting distances, *e.g.* for distance least-squares (DLS) structure refinements (Baur, 1972; Tillmanns, Gebert & Baur, 1973; Dempsey & Strens, 1975). The effective ionic radii in Table 1 can be used to reproduce moderately well most average interatomic distances in oxides and fluorides. However, certain deviations do occur. Some of these are unexplained but others can be attributed to (1) polyhedral distortion, (2) covalence, (3) partial occupancy of cation sites, or (4) electron delocalization.

1. Polyhedral distortion

To see the effects of polyhedral distortion consider the relationship between bond length (R) and Pauling bond strength (s) (Brown & Shannon, 1973). The analytical expression $s = s_0(R/R_0)^{-N}$, where s_0 is an ideal bond strength associated with R_0 , and R_0 and N are fitted parameters, was evaluated for cation-oxygen pairs for the first three rows of the periodic table. Using these relationships, the sums of bond strengths about cations and anions were found to equal the valences with a mean deviation of about 5%. Accepting the approximate validity of Pauling's second rule, $p = \sum s$ where p = valence, it is possible to derive the effects of distortion of various polyhedra on their mean bond distances. Fig. 3 shows a typical R - s curve. An undistorted octahedron results in an average bond strength \bar{s} and a mean distance \bar{R}_1 . A distorted octahedron with three bonds of length R_a and three of length R_b results in the same average bond strength, \bar{s} , but a mean distance $\bar{R}_2 > \bar{R}_1$.

The effects of distortion on mean bond lengths in numerous polyhedra have been determined. Although distortions in tetrahedra are not as important as in octahedra, they can contribute to variations in mean tetrahedral distances (Baur, 1974; Hawthorne, 1973). Strongly distorted octahedra like those containing V^{5+} , Cu^{2+} , and Mn^{3+} show a significant variation in mean distance with distortion, Δ^* (Brown & Shannon, 1973; Shannon & Calvo, 1973a; Shannon, Gurnerman & Chenavas, 1975). Octahedra containing Mg^{2+} , Zn^{2+} , Co^{2+} , and Li^+ are generally less distorted than those of V^{5+} , Cu^{2+} , and Mn^{3+} and show a less pronounced dependence on mean bond length (Brown & Shannon, 1973).

The effects of distortion on mean bond lengths in Nb^{5+} -O and Mo^{6+} -O octahedra are illustrated in Figs. 4 and 5. Tables 5 and 6 list the data used to derive the figures.

Table 7 lists the results of linear regression analyses of mean bond length on distortion for all octahedra studied. It is clear from Fig. 4 that undistorted Nb^{5+} octahedra in pyrochlores have a distinctly smaller mean value than in compounds like $NbOPO_4$, $CaNb_2O_6$, and Na_3NbO_4 . Most of the accurately refined molybdates have relatively distorted octahedra. However, certain ordered perovskites with no octahedral distortion such as Ba_2CaMoO_6 would be expected to have much smaller mean Mo^{6+} -O distances than a typical molyb-

date. In fact, the Mo^{6+} -O octahedra in $Mo_2(O_2C_6Cl_4)_6$ with a very small distortion have the short mean distance of 1.919 Å.

Table 7 also lists the results of regression analyses for Ta^{5+} -O and W^{6+} -O octahedra but they are only approximate because of the scarcity of accurate structural data. Analysis of Ti^{4+} -O octahedra was unsuccessful because of scatter in the data. Distances in $Ba_6Ti_{17}O_{40}$ (Tillmanns & Baur, 1970) and $BaTiO_3$ (Evans, 1951) deviated significantly from a linear relation.

Relations between mean distance and distortion should be particularly useful to help determine oxidation states in mixed valence compounds with such combinations as Mo^{5+} - Mo^{6+} , W^{5+} - W^{6+} , V^{4+} - V^{5+} , Nb^{4+} - Nb^{5+} and Mn^{3+} - Mn^{4+} . Such considerations helped rationalize Mn-O distances in $NaMn_7O_{12}$ and the mineral pinakolite (Shannon, Gurnerman & Chenavas, 1975).

The radii in Table 1 are generally derived for an average degree of distortion. Thus, interatomic distances calculated from these radii may be inaccurate if the distortion in a particular compound is much less or greater than usual. This applies particularly to cations whose polyhedra frequently show a large distortion, e.g. Mo^{6+} , Nb^{5+} , V^{5+} , Ba^{2+} , and the alkali ions.

2. Effects of partial occupancy of cation sites on mean cation-anion distances

In compounds with partially occupied sites, abnormally large cation-anion distances are usually found, as expected if the anions surrounding unoc-

* Octahedral distortion is defined by $\Delta = \frac{1}{6} \sum (R_i - \bar{R})^2$ where \bar{R} = average bond length and R_i = an individual bond length.

Table 5. Comparison of mean octahedral Nb^{5+} -O distances with distortion

Only structures with e.s.d.'s for Nb-O distances of <0.025 Å were used.

Compound	\bar{R} (Å)	Distortion $\Delta = \langle (\Delta R/R)^2 \rangle \times 10^4$	Reference	
$Hg_2Nb_2O_7$	1.999	0	68 INOCA	7 1704
$Cd_2Nb_2O_7$	1.957	0	72 CJCHA	50 3648
$Na_2Nb_4O_{11}$	1.977	1	70 JSSCB	1 454
$Ba_{0.27}Sr_{0.73}Nb_2O_{5.78}$	1.967	6	61 JCPSA	48 5048
$Na_{13}Nb_{35}O_{94}$	1.965	7	71 JSSCB	3 89
$Ba_3Si_4Nb_6O_{26}$	1.989	9	70 ACBCA	26 102
$Na_{13}Nb_{35}O_{94}$	1.967	11	71 JSSCB	3 89
$Na_{13}Nb_{35}O_{94}$	1.959	12	71 JSSCB	3 89
$Na_{13}Nb_{35}O_{94}$	1.964	12	71 JSSCB	3 89
$NaNbO_3$	1.985	16	69 ACBCA	25 851
$Na_{13}Nb_{35}O_{94}$	1.947	18	71 JSSCB	3 89
$Na_{13}Nb_{35}O_{94}$	1.991	22	71 JSSCB	3 89
$Na_{13}Nb_{35}O_{94}$	1.987	22	71 JSSCB	3 89
$Na_{13}Nb_{35}O_{94}$	1.978	24	71 JSSCB	3 89
$LiNb_3O_8$	1.993	28	71 ACSAA	25 3337
$LiNbO_3$	2.000	31	66 JPCSA	27 997
$Ca_2Nb_2O_7$	1.997	31	74 JINCA	36 1965
$Ca_2Nb_2O_7$	2.005	34	74 JINCA	36 1965
$SbNbO_4$	2.003	37	65 CCJDA	1965 611
$KNbO_3$	2.011	42	67 ACACA	22 639
Na_3NbO_4	2.013	52	74 BUFCA	97 3
$Ca_2Nb_2O_7$	2.010	53	74 JINCA	36 1965
$Ca_2Nb_2O_7$	2.015	58	74 JINCA	36 1965
Na_3NbO_4	2.021	60	74 BUFCA	97 3
$CaNb_2O_6$	2.021	76	70 AMMIA	55 90
$GaNbO_4$	2.031	83	65 ACACA	18 874

Table 6. Comparison of mean octahedral Mo^{6+} -O distances with distortionOnly structures with e.s.d.'s for Mo-O distances of <0.025 Å were used.

Compound	\bar{R} (Å)	Distortion		Reference	
		$\Delta = \langle (\Delta R/R)^2 \rangle \times 10^4$			
$\text{Mo}_2(\text{O}_2\text{C}_6\text{Cl}_4)_6$	1.919	5	75 JACSA	97	2123
Mo_4O_{11} orthorhombic	1.944	9	63 ARKEA	21	365
Mo_4O_{11} monoclinic	1.946	10	63 ARKEA	21	365
Mo_4O_{11} monoclinic	1.937	56	63 ARKEA	21	365
Mo_4O_{11} orthorhombic	1.951	67	63 ARKEA	21	365
Mo_4O_{11} orthorhombic	1.911	96	63 ARKEA	21	365
Mo_4O_{11} monoclinic	1.945	96	63 ARKEA	21	365
$(\text{C}_{15}\text{H}_{11}\text{O}_2)_2\text{MoO}_2$	1.952	99	74 ACBCA	30	300
$(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$	1.962	99	75 JCSIA	1975	505
$(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$	1.972	101	75 JCSIA	1975	505
$(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$	1.960	104	75 JCSIA	1975	505
$\text{LiMoO}_2\text{AsO}_4$	1.967	104	70 ACSAA	24	3711
$(\text{NH}_4)_6\text{Mo}_8\text{O}_{27} \cdot 4\text{H}_2\text{O}$	1.960	106	74 ACBCA	30	48
HgMoO_4	1.965	111	73 ACBCA	29	869
$(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$	1.955	113	75 JCSIA	1975	505
$(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$	1.962	115	75 JCSIA	1975	505
$(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$	1.974	118	68 JACSA	90	3275
$\text{MoO}_3 \cdot 2\text{H}_2\text{O}$	1.966	121	72 ACBCA	28	2222
$\text{MoO}_3 \cdot 2\text{H}_2\text{O}$	1.961	123	72 ACBCA	28	2222
$\text{MoO}_3 \cdot 2\text{H}_2\text{O}$	1.957	126	72 ACBCA	28	2222
$\text{MoO}_3 \cdot 2\text{H}_2\text{O}$	1.953	134	72 ACBCA	28	2222
$(\text{NH}_4)_5[\text{MoO}_3]_5(\text{PO}_4)(\text{HPO}_4) \cdot 3\text{H}_2\text{O}$	1.970	140	74 JCSIA	1974	941
$\text{Na}_3(\text{CrMo}_6\text{O}_{24}\text{H}_6) \cdot 8\text{H}_2\text{O}$	1.976	141	70 INOCA	9	2228
$(\text{NH}_4)_6\text{Mo}_8\text{O}_{27} \cdot 4\text{H}_2\text{O}$	1.976	141	74 ACBCA	30	48
$\text{Na}_3\text{CrMo}_6\text{O}_{24}\text{H}_6 \cdot 8\text{H}_2\text{O}$	1.976	143	70 INOCA	9	2228
$(\text{NH}_4)_5[(\text{MoO}_3)_5(\text{PO}_4)(\text{HPO}_4)] \cdot 3\text{H}_2\text{O}$	1.974	145	74 JCSIA	1974	941
$(\text{NH}_4)_6[\text{TeMo}_6\text{O}_{24}] \cdot \text{Te}(\text{OH})_6 \cdot 7\text{H}_2\text{O}$	1.981	147	74 ACBCA	30	2095
CoMoO_4	1.991	150	65 ACACA	19	269
$(\text{NH}_4)_6\text{Mo}_8\text{O}_{27} \cdot 4\text{H}_2\text{O}$	1.972	151	74 ACBCA	30	48
MoO_3	1.981	151	63 ARKEA	21	357
$(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$	1.976	152	68 JACSA	90	3275
$\text{K}_2\{[\text{MoO}_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]_2\text{O}\}$	1.976	152	64 INOCA	3	1603
$(\text{NH}_4)_6\text{Mo}_8\text{O}_{27} \cdot 4\text{H}_2\text{O}$	1.974	152	74 ACBCA	30	48
$(\text{NH}_4)_5[(\text{MoO}_3)_5(\text{PO}_4)(\text{HPO}_4)] \cdot 3\text{H}_2\text{O}$	1.982	159	74 JCSIA	1974	941
$\text{Na}_3\text{CrMo}_6\text{O}_{24}\text{H}_6 \cdot 8\text{H}_2\text{O}$	1.986	163	70 INOCA	9	2228
$(\text{NH}_4)_5[(\text{MoO}_3)_5(\text{PO}_4)(\text{HPO}_4)] \cdot 3\text{H}_2\text{O}$	1.977	167	74 JCSIA	1974	941
$\text{MoO}_3 \cdot \text{H}_2\text{O}$	1.984	167	74 ACBCA	30	1795
$(\text{NH}_4)_5[(\text{MoO}_3)_5(\text{PO}_4)(\text{HPO}_4)] \cdot 3\text{H}_2\text{O}$	1.991	186	74 JCSIA	1974	941
$(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$	1.991	189	75 JCSIA	1975	505
$(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$	2.008	197	75 JCSIA	1975	505

Table 7. Variation of mean M-O distance and effective ionic radius in octahedral environments as a function of distortion

Ion	Maximum $\Delta \times 10^4$	N^*	R_0^\dagger	r_0^\ddagger	m	Correlation coefficient	Goodness of fit ($\times 10^3$)
Mo^{6+}	212	38	1.920		3.73	0.74	67
				0.572	3.01	0.63	70
W^{6+}	122	7	1.925		3.30	0.75	19
				0.565	3.28	0.66	24
V^{5+}	576	16	1.887		2.62	0.98	8
Nb^{5+}	83	29	1.976		6.45	0.69	71
				0.599	6.83	0.44	99
Ta^{5+}	79	6	1.984		6.70	0.81	18
				0.617	3.79	0.15	46
Mn^{3+}	71	15	1.994		7.08	0.82	30
				0.624	6.15	0.54	50
Cu^{2+}	316	26	2.085		3.99	0.82	77
Mg^{2+}	156	28	2.094		8.31	0.72	21
				0.728	8.86	0.77	18
Co^{2+}	46	15	2.106		7.38	0.42	19
				0.734	11.70	0.70	16
Zn^{2+}	71	16	2.099		7.70	0.64	21
				0.736	8.20	0.74	16
Li^+	148	11	2.159		8.42	0.81	30
				0.784	9.02	0.79	35

* N = number of independent octahedra $^\dagger R = R_0 + m\Delta$. $^\ddagger r = r_0 + m\Delta$.

cupied sites relax toward their bonded cation neighbors. Therefore average distances should increase as the occupancy factor decreases. In general, partial occupancy seems to be more prevalent for cations which are weakly bonded to oxygen like Cu^+ , Ag^+ , alkali ions, and large alkaline earths. The most prominent examples are Li and Na compounds. Table 8 summarizes the existent data on some structures with partial cation occupancy. Fig. 6 shows the dependence of mean Li–O bond length on the degree of occupancy. Although the data are not extensive, it is apparent that mean distance increases as occupancy factor decreases. Extrapolation of the Li curve in Fig. 6 to zero occupancy, *i.e.* a tetrahedral Li vacancy, gives 2.10–2.15 Å, which is close to the 2.11 Å found for $\alpha\text{-Li}_5\text{GaO}_4$ by Stewner & Hoppe (1971) and for β eucryptite by Tscherry, Schulz & Laves (1972).

Another example of the effects of partial occupancy can be found in the non-stoichiometric feldspar $\text{Sr}_{0.84}\text{Na}_{0.03}\text{Al}_{1.69}\text{Si}_{2.29}\text{O}_8$ reported by Grundy & Ito (1974). The mean Sr–O distance in this compound is 0.03 Å greater than in the stoichiometric $\text{SrAl}_2\text{Si}_2\text{O}_8$ (Chiari, Calleri, Bruno & Ribbe, 1975).

The relation between mean distance and occupancy probably cannot be quantified precisely because the relaxation of oxygen ions will depend on the nature and number of other cation neighbors.

3. Effects of covalence

Changes in interatomic distances due to covalence effects are anticipated in compounds with (1) anions less electronegative than fluorine or oxygen, *i.e.* chlor-

ides, bromides, sulfides, selenides, *etc.* and (2) tetrahedral oxyanions such as the VO_4^{3-} and AsO_4^{3-} groups. The effects of covalence show up as a lack of additivity of the radii and are generally referred to as 'covalent shortening'.

(a) *Halides and chalcogenides.* Covalence effects can be observed by comparing the relative contraction of cation–anion distances in two different isotypic compounds as the anion becomes less electronegative, *e.g.* Fe^{2+} in Fe_2GeO_4 and Fe_2GeS_4 vs Mg^{2+} in Mg_2GeO_4 and Mg_2GeS_4 . Covalence shortens both Fe–S and Mg–S bonds relative to Fe–O and Mg–O bonds, but because of the greater electronegativity of Fe^{2+} (1.8) compared to Mg^{2+} (1.2), the Fe–S bonds are shortened to a greater extent. Thus a 'covalency contraction' parameter (Shannon & Vincent, 1974) can be defined:

$$R_d = \frac{d(\text{Fe-X})^3}{d(\text{Mg-X})^3}$$

where $d(\text{Fe-X})$ = mean Fe–X distance.

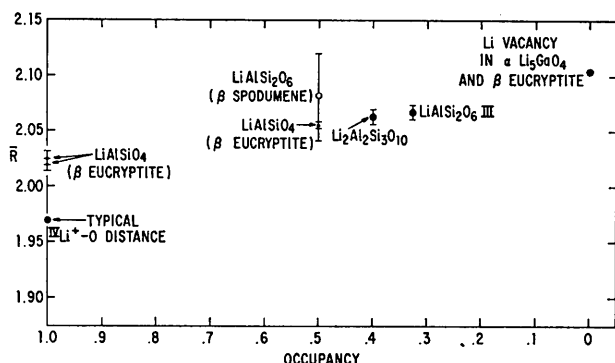
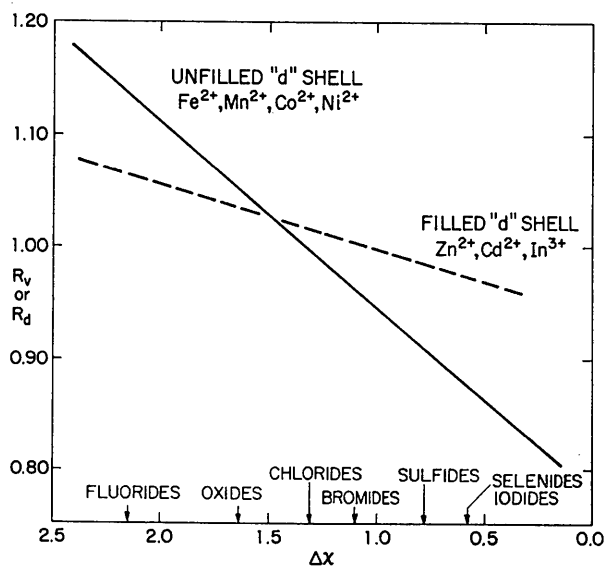
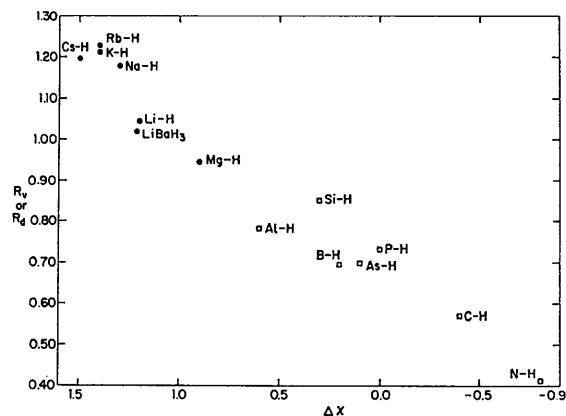
A similar parameter

$$R_v = \frac{V(\text{Fe}_m\text{X}_n)}{V(\text{Mg}_m\text{X}_n)}$$

compares the volume of an Fe^{2+} compound with that of an isotypic Mg^{2+} compound. To see the effects of covalence on the Fe–X distance relative to the Mg–X distance, the ratio R_v or R_d may be plotted against the difference in electronegativity of the Fe–X bond, $\Delta\chi_{\text{Fe-X}}$. Such schematic R_v – $\Delta\chi$ plots are shown in Fig. 7. The reference ions for Cd^{2+} and In^{3+} are Ca^{2+} and Sc^{3+} respectively. Such plots usually show a strong

Table 8. Mean distances in structures with partially occupied cation sites

Compound	Occupancy factor	\bar{R}	Reference		
(a) $^{\text{IV}}\text{Li}^+$					
Typical	1.00	1.97	Table 1		
LiAlSiO_4 (β eucryptite)	1.00	2.020 (4)	73 AMMIA	58	681
		2.025 (7)	72 ZKKKA	135	175
$\text{LiAlSi}_2\text{O}_6$ II (β spodumene)	0.50	2.08 (4)	68 ZKKKA	126	46
		2.085 (9)	69 ZKKKA	130	420
LiAlSiO_4 (β eucryptite)	0.50	2.056 (2)	72 ZKKKA	135	161
$\text{Li}_2\text{Al}_2\text{Si}_3\text{O}_{10}$	0.40	2.064 (4)	70 ZKKKA	132	118
$\text{LiAlSi}_2\text{O}_6$ III	0.33	2.068 (5)	68 ZKKKA	127	327
$\alpha\text{-Li}_5\text{GaO}_4$	0.00	2.11	71 ACBCA	27	616
LiAlSiO_4	0.00	2.11	72 ZKKKA	135	175
(b) $^{\text{VI}}\text{Na}^+$					
Typical	1.00	2.42	Table 1		
$\text{Na}_2\text{Fe}_2\text{Al}(\text{PO}_4)_3$ (wyllieite)	0.91	2.533 (6)	74 AMMIA	59	280
NaSbO_3	0.82	2.74	74 JSSCB	9	345
$\text{Na}_2\text{Fe}_2\text{Al}(\text{PO}_4)_3$ (wyllieite)	0.70	2.723 (6)	74 AMMIA	59	280
$\text{NaAlSi}_3\text{O}_8$ (high albite)	0.50	2.600 (9)	69 ACBCA	25	1503
$\text{NaAl}_{11}\text{O}_{17}$ ($\beta\text{-Al}_2\text{O}_3$)	0.35	2.839 (1)	68 ZKKKA	127	94
NaSbO_3	0.29	2.65	74 JSSCB	9	345
$\text{Na}_{2.58}\text{Al}_{21.81}\text{O}_{34}$ ($\beta\text{-Al}_2\text{O}_3$)	0.25	2.88	71 ACBCA	27	1826
(c) $^{\text{VI}}\text{Ag}^+$					
Typical	1.00	2.50	Table 1		
AgSbO_3	0.44	2.64	74 JSSCB	9	345
AgSbO_3	0.33	2.75	74 JSSCB	9	345
$\text{Ag}_{2.4}\text{Al}_{22}\text{O}_{34.2}$	0.22	2.83	72 JSSCB	4	60

Fig. 6. Mean $\text{Li}^+\text{-O}$ bond length vs partial occupancy.Fig. 7. Covalency contraction parameter, R_v or R_d , vs $\Delta\chi$ for filled and unfilled d shell cations.Fig. 8. Covalency contraction parameter, R_v or R_d , vs $\Delta\chi$ for hydrides. Solid circles represent ratios of cell volumes of isotopic compounds. Squares represent ratios of the cubed M-H distances to the cubed M-F distances.

dependence of R_v on $\Delta\chi$. For $\text{Fe}^{2+}\text{-Mg}^{2+}$ the Fe^{2+} fluoride volumes are $\sim 110\%$ of the corresponding Mg^{2+} fluoride volumes whereas the Fe^{2+} sulfide volumes are $\sim 96\%$ of the corresponding Mg^{2+} sulfide volumes. Plots for the cations with filled ' d ' shells show a markedly smaller dependence on $\Delta\chi$. This appears to be due to the difference in covalence of hybrid orbitals formed from metal ' d ' orbitals vs metal ' s - p ' orbitals.

These relations show that effective ionic radii derived primarily from oxides are not strictly applicable to fluorides – note the change in R_v for Fe^{2+} , Co^{2+} , Ni^{2+} , and Mn^{2+} from fluorides to oxides. This effect is particularly noticeable in $R_v\text{-}\Delta\chi$ plots for the pairs $\text{Cu}^+\text{-Li}^+$ and $\text{Ag}^+\text{-Na}^+$ (Shannon & Gummerman, 1975). The $\text{Cu}^+\text{-Li}^+$ and $\text{Ag}^+\text{-Na}^+$ plots are very steep, e.g. the volume of AgF is 120% of the volume of NaF , whereas the volume of Ag_2Se is only 72% of the volume of Na_2Se . Although most of this change arises from covalency, double repulsion effects present in the Li and Na halides described by Pauling (1960) may also play a role.

Covalence effects are useful in explaining certain differences between the effective ionic radii of Table 1 and the ionic radii of Pauling (1927) and Ahrens (1952). Pauling's radii for Cu^+ (0.96 Å) and Ag^+ (1.26 Å) are considerably larger than those in Table 1 (0.77 and 1.15 Å respectively). Since these radii were derived from comparison of alkali halide distances, using an equation relating effective nuclear charge and screening constants (Pauling, 1927), they are valid in primarily ionic crystals. The smaller radii in Table 1 are applicable in the more covalent oxides. Extrapolation of R vs $\Delta\chi$ curves such as in Fig. 7 leads to values of 0.91 Å and 1.23 Å for fluorides, which are close to Pauling's ionic values.

A final example of covalence effects concerns $\text{M}^+\text{-H}^-$ distances. According to Gibb (1962), the radius of the hydride ion is slightly larger than the radius of the fluoride ion. To rationalize the behavior of the hydride ion, the M-H bond has been treated as covalent. Therefore, it is useful to make R_v vs $\Delta\chi$ plots similar to those just discussed for Fe^{2+} , Cu^+ , etc. In this case, the reference ion is F^- and volumes of certain hydrides are compared to those of isotopic fluorides. The results of this analysis are shown in Fig. 8. The solid circles represent volume ratios, $R_v = V(\text{M}_m\text{H}_n)/V(\text{M}_m\text{F}_n)$; open squares represent ratios of typical distances $R_d = d(\text{M-H})^3/d(\text{M-F})^3$. In the more ionic hydrides of Cs, Rb, K, and Na, hydride volumes are considerably larger than those of the fluorides. For the Li and Mg compounds, hydride and fluoride volumes are approximately equal, whereas the more covalent hydrides have increasingly smaller relative volumes than the corresponding fluorides. Fig. 8 partly explains the differences in reported radii. The Morris & Reed (1965) value of 1.53 Å was derived essentially from the large alkali halides, while Gibb's value of 1.40 Å was derived primarily from hydrides of the more electronegative

metals such as: Sc, Ti, Y, Zr, Hf, Nb, Ta, and Th. Because of this strong dependence of M–H distances on cation electronegativity, it does not seem very useful to quote a unique radius for H^- .

(b) *Tetrahedral oxyanions.* Lack of additivity also appears in most small tetrahedral groups and is particularly noticeable for the ions $^{IV}B^{3+}$, $^{IV}Fe^{3+}$, $^{IV}Ge^{4+}$, $^{IV}As^{5+}$, $^{IV}V^{5+}$, $^{IV}S^{6+}$, $^{IV}Se^{6+}$, and $^{IV}Cl^{7+}$. The deviations in vanadates have been studied in detail (Shannon & Calvo, 1973b). Assuming that the V–O bond is strongly covalent, and that relatively electronegative cations such as Cu^{2+} , Ni^{2+} , and Co^{2+} tend to remove electron density from the V–O bond, a V–O bond length increase in Cu, Ni, and Co vanadates is anticipated. Plots of mean radii (\bar{r}) *vs* mean cation electronegativity ($\bar{\chi}$) show a marked slope with a gradual increase in $\bar{r}(^{IV}V^{5+})$ from vanadates of the alkali and alkaline earth ions to those of Cu, Ni, and Co. Similar plots for other ions, P^{5+} , As^{5+} (Shannon & Calvo, 1973b), B^{3+} , Si^{4+} , Se^{6+} (Shannon, 1975), showed the same behavior. The statistical data on the tetrahedra of B^{3+} , Si^{4+} , Ge^{4+} , P^{5+} , As^{5+} , S^{6+} , Se^{6+} , Cr^{6+} , Mo^{6+} , W^{6+} , and Cl^{7+} have been summarized by Shannon (1975). The slopes of the \bar{r} *vs* $\bar{\chi}$ plots were greatest for V^{5+} , Se^{6+} , and Cl^{7+} , and least for Si^{4+} . Although the evidence for covalence as the origin of these effects in the above systems is only indirect, this behavior is consistent with accepted ideas of ‘covalent shortening’ of bonds.

The evidence for covalent shortening of $^{IV}Fe^{3+}$ –O bonds is more direct. Jeitschko, Sleight, McClellan & Weiher (1976) have found a good correlation between (1) the Fe Mössbauer isomer shift and mean Fe–O distance and (2) $\bar{\chi}$ and mean Fe–O distance (\bar{R}). Thus, in β - $NaFeO_2$ $\bar{R}=1.86$ Å and $\delta=0.18$ mm s $^{-1}$ relative to α Fe whereas in $Bi_3(FeO_4)(MoO_4)_2$ $\bar{R}=1.909$ Å and $\delta=0.282$ mm s $^{-1}$.

4. Effects of electron delocalization

At a pressure of 6.5 kbar SmS (NaCl structure) undergoes a semiconductor to metal transition and a reduction in cell edge from 5.97 to 5.70 Å (Jayaraman, Narayanamurti, Bucher & Maines, 1970). The reduction in cell volume was attributed to a partial conversion of Sm^{2+} to Sm^{3+} ; some of the electrons presumably go into a conduction band.

Electron delocalization effects can also be seen by comparing the volumes of the conducting V sulfides VS, V_7S_8 , V_3S_4 and V_5S_8 with the corresponding Cr sulfides which have localized ‘*d*’ electrons (de Vries & Jellinek, 1974). The V compounds have volumes ~5% smaller than the corresponding chromium compounds. This does not agree with the relative sizes of V and Cr in oxides and fluorides, *e.g.* $r(^{IV}V^{3+})=0.64$ and $r(^{VI}Cr^{3+})=0.615$ Å. For the sulfides, this unit-cell volume anomaly is not simply attributable to metallic *vs* semiconducting behavior. While Cr_3S_4 , Cr_5S_6 , and Cr_7S_8 show a positive temperature dependence of resistivity typical of a metal, magnetic susceptibility

measurements indicate Curie–Weiss behavior and therefore nearly localized electrons (van Bruggen, 1969). This is in contrast to the Pauli paramagnetic behavior of the corresponding V sulfides (de Vries & Haas, 1973) characteristic of delocalized electrons. Thus, in SmS and the sulfides of V metallic character accompanied by electron delocalization appears to be associated with reduced bond distances.

A further example of delocalization effects occurs in the compound $NaVS_2$ (Weigers, van der Meer, van Heinigen, Kloosterboer & Alberink, 1974). The molecular volume of Pauli paramagnetic $NaVS_2$ I (67.9 Å 3) is significantly less than that of $NaVS_2$ II (72.7 Å 3). $NaVS_2$ II is characterized by localized electrons (Jellinek, 1975) and its molecular volume is consistent with that of isotypic $NaCrS_2$ (71.1 Å 3).

If electron delocalization in oxides results in reduced metal–oxygen distances and thereby an effective increase in valence, radii derived for the ions Mo^{4+} , Tc^{4+} , Ru^{4+} , Rh^{4+} , W^{4+} , Re^{4+} , Os^{4+} , and Ir^{5+} from metallic oxides may not be reliable when applied to insulating oxides. Thus, radii obtained from distances in the metallic phases, *e.g.* RhO_2 , ReO_2 , and $Cd_2Ir_2O_7$, will be smaller than radii obtained from semiconducting or insulating compounds.* When both types of compounds have been studied, a significant difference in distances is generally found. The mean octahedral Re^{4+} –O distance in insulating $K_4[Re_2O_2(C_2O_4)_4] \cdot 3H_2O$ (Lis, 1975) of 2.021 (10) Å ($r=0.671$ Å) is greater than the estimated mean distance in metallic ReO_2 of 1.99 Å ($r=0.63$ Å). Knop & Carlow’s (1974) value of $r=0.662$ Å derived from cell volumes of the insulating Cs_2ReF_6 phases is consistent with the radius of Re^{4+} from $K_4[Re_2O_2(C_2O_4)_4] \cdot 3H_2O$. The Re^{5+} –O distance in $Nd_4Re_2O_{11}$ (Wilhelmi, Lagervall & Muller, 1970) of 1.987 (12) Å ($r=0.607$ Å) is significantly greater than the distance in metallic $Cd_2Re_2O_7$ (Sleight, 1975) of 1.93 (2) Å ($r=0.55$ Å). The radii of 0.58 Å derived from XeF_2RuF_6 and 0.60 Å from $XeFRuF_6$ (Bartlett, Gennis, Gibler, Morrell & Zalkin, 1973) are greater than the radius of 0.565 Å derived from the r^3 – V plot for metallic $Cd_2Ru_2O_7$. In contrast, however, the Mo^{4+} radius of 0.64 Å derived from insulating Li_2MoF_6 (Brunton, 1971) is not greatly different from the radius of 0.65 Å derived from metallic MoO_2 (Brandt & Skapski, 1967).

Although there appears to be ample evidence to show that M–O bond distances in compounds with localized electrons are greater than M–O distances in compounds with delocalized electrons, the data are not yet sufficient to derive a reliable set of radii for semiconducting compounds containing Mo^{4+} , Tc^{4+} , Ru^{4+} , Rh^{4+} , W^{4+} , Re^{4+} , Os^{4+} , and Ir^{5+} . This will become possible as additional accurate structure refinements of fluorides, molecular inorganic compounds, and semiconducting oxides containing these ions become available.

* This assumes that metallic character can be equated with delocalized electron behavior in these compounds.

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