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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 Nb^{5+}–O and Mo^{6+}–O octahedral distances are linearly dependent on distortion. A decrease in cation occupancy increases mean Li^+–O, Na^+–O, and Ag^+–O distances in a predictable manner. Covalence strongly shortens Fe^{2+}–X, Co^{2+}–X, Ni^{2+}–X, Mn^{2+}–X, Cu^+–X, Ag^+–X, and M–H^- bonds as the electronegativity of X or M decreases. Smaller effects are seen for Zn^{2+}–X, Cd^{2+}–X, In^{3+}–X, Pb^{2+}–X, and Tl^+–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): Bi^{3+}-La^{3+}; McCarthy (1971): Eu^{2+}-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 Å to $^{IX}La^{3+}$, $^{IX}Ce^{3+}$, $^{IX}Pr^{3+}$, and $^{IX}Nd^{3+}$; +0·025 Å to all other Greis & Petzel $^{IX}RE^{3+}$ radii, and 0·015 Å to all $^{VIII}RE^{3+}$ 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: $^{VI}Os^{5+}$, $^{VI}Os^{6+}$, $^{VI}Os^{7+}$, $^{VI}Re^{4+}$, $^{VI}Re^{5+}$, $^{VI}Re^{6+}$, $^{VI}Re^{7+}$, $^{VI}Rh^{4+}$, $^{VII}U^{4+}$, $^{VII}U^{5+}$, and $^{VII}U^{6+}$.

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 $^{IV}Cu^+$, $^{VI}Cu^+$, $^{IX}Rb^+$, $^{V}Ni^{2+}$, $^{VII}Er^{3+}$, $^{VII}Yb^{3+}$, $^{VII}Tb^{3+}$, $^{XII}Nd^{3+}$, $^{IV}Cr^{4+}$,

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'	
AG+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				VIII		1.193	1.053	R
		IV		1.14	1.00	C	CL+7	2P 6	IV		.22	.08	*			IX		1.247	1.107	RC
		IVSQ		1.16	1.02				VI		.41	.27	A	GE+2	4S 2	VI		.87	.73	A
		V		1.23	1.09	C	CM+3	5F 7	VI		1.11	.97	R	GE+4	3D10	IV		.530	.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			VIII		1.04	.90				VIII		.97	.83	
AL+3	2P 6	IV		.53	.39	*	CO+3	3D 6	VI	LS	.685	.545	R*	HG+1	6S 1	III		1.11	.97	
		V		.62	.48					HS	.75	.61				VI		1.33	1.19	
		VI		.675	.535	R*	CO+4	3D 5	IV		.54	.40		HG+2	5D10	II		.83	.69	
AM+2	5F 7	VII		1.35	1.21				VI	HS	.67	.53	R			IV		1.10	.96	
		VIII		1.40	1.26		CR+2	3D 4	VI	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	ER	I	-1 5P 6	VI		2.06	2.20	A
AS+5	3D10	IV		.475	.335	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	VI		1.81	1.67				VI		.67	.53	
AU+3	5D 8	IVSQ		.82	.68				VIII		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
B	+3 1S 2	III		.15	.01	*			XI		1.99	1.85		IR+3	5D 6	VI		.82	.68	E
		IV		.25	.11	*			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	C			VI		.91	.77	E			VI		1.52	1.38	
		VIII		1.56	1.42		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				XII		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			VII		1.27	1.13				VIII		1.300	1.160	R
BI+3	6S 2	V		1.10	.96	C			VIII		1.33	1.19				IX		1.356	1.216	R
		VI		1.17	1.03	R*	DY+3	4F 9	VI		1.052	.912	R			X		1.41	1.27	
		VIII		1.31	1.17	R			VII		1.11	.97				XII		1.50	1.36	C
BI+5	5D10	VI		.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	1.96	P			VIII		1.144	1.004	R			VIII		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		MG+2	2P 6	IV		.71	.57	
BR+7	3D10	IV		.39	.25				VII		1.34	1.20				V		.80	.66	
		VI		.53	.39	A			VIII		1.39	1.25				VI		.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		MN+2	3D 5	IV	HS	.80	.66	
		VI		.30	.16	A	EU+3	4F 6	VI		1.087	.947	R			V	HS	.89	.75	C
CA+2	3P 6	VI		1.14	1.00				VII		1.15	1.01				VI	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			VII	HS	1.04	.90	C
		IX		1.32	1.18		F	-1 2P 6	II		1.145	1.285				VIII		1.10	.96	R
		X		1.37	1.23	C			III		1.16	1.30		MN+3	3D 4	V		.72	.58	
		XII		1.48	1.34	C			IV		1.17	1.31				VI	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	MN+4	3D 3	IV		.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	HS	.78	.64		MN+5	3D 2	IV		.47	.33	R
		VIII		1.24	1.10	C			VI	LS	.75	.61	E	MN+6	3D 1	IV		.395	.255	
		XII		1.45	1.31					HS	.920	.780	R*	MN+7	3P 6	IV		.39	.25	
CE+3	6S 1	VI		1.15	1.01	R			VIII	HS	1.06	.92	C			VI		.60	.46	A
		VII		1.21	1.07	E	FE+3	3D 5	IV	HS	.63	.49	*	MO+3	4D 3	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					HS	.785	.645	R*			VI		.75	.61	R
		XII		1.48	1.34	C			VIII	HS	.92	.78		MO+6	4P 6	IV		.55	.41	R*
CE+4	5P 6	VI		1.01	.87	R	FE+4	3D 4	VI		.725	.585	R			V		.64	.50	
		VIII		1.11	.97	R	FE+6	3D 2	IV		.39	.25	R			VI		.73	.59	R*
		X		1.21	1.07		FR+1	6P 6	VI		1.94	1.80	A			VII		.87	.73	
		XII		1.28	1.14		GA+3	3D10	IV		.61	.47	*	N	-3 2P 6	IV		1.32	1.46	
CF+3	6D 1	VI		1.09	.95	R			V		.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	
		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'	
NA+1	2P 6	IV		1.13	.99	
		V		1.14	1.00	
		VI		1.16	1.02	
		VII		1.26	1.12	
		VIII		1.32	1.18	
		IX		1.38	1.24	C
		XII		1.53	1.39	
NB+3	4D 2	VI		.86	.72	
NB+4	4D 1	VI		.82	.68	RE
		VIII		.93	.79	
NB+5	4P 6	IV		.62	.48	C
		VI		.78	.64	
		VII		.83	.69	C
		VIII		.88	.74	
ND+2	4F 4	VIII		1.43	1.29	
		IX		1.49	1.35	
ND+3	4F 3	VI		1.123	.983	R
		VIII		1.249	1.109	R*
		IX		1.303	1.163	R
		XII		1.41	1.27	E
NI+2	3D 8	IV		.69	.55	
		IVSQ		.63	.49	
		V		.77	.63	E
		VI		.830	.690	R*
NI+3	3D 7	VI	LS	.70	.56	R*
			MS	.74	.60	E
NI+4	3D 6	VI	LS	.62	.48	R
NO+2	5F14	VI		1.24	1.1	E
NP+2	5F 5	VI		1.24	1.10	
NP+3	5F 4	VI		1.15	1.01	R
NP+4	5F 3	VI		1.01	.87	R
		VIII		1.12	.98	R
NP+5	5F 2	VI		.89	.75	
NP+6	5F 1	VI		.86	.72	R
NP+7	6P 6	VI		.85	.71	A
O -2	2P 6	II		1.21	1.35	
		III		1.22	1.36	
		IV		1.24	1.38	
		VI		1.26	1.40	
		VIII		1.28	1.42	
OH-1		II		1.18	1.32	
		III		1.20	1.34	
		IV		1.21	1.35	E
		VI		1.23	1.37	E
OS+4	5D 4	VI		.770	.630	RM
OS+5	5D 3	VI		.715	.575	E
OS+6	5D 2	V		.63	.49	
		VI		.685	.545	E
OS+7	5D 1	VI		.665	.525	E
OS+8	5P 6	IV		.53	.39	
P +3	3S 2	VI		.58	.44	A
P +5	2P 6	IV		.31	.17	*
		V		.43	.29	
		VI		.52	.38	C
PA+3	5F 2	VI		1.18	1.04	E
PA+4	6D 1	VI		1.04	.90	R
		VIII		1.15	1.01	
PA+5	6P 6	VI		.92	.78	
		VIII		1.05	.91	
		IX		1.09	.95	
PB+2	6S 2	IVPY		1.12	.98	C
		VI		1.33	1.19	
		VII		1.37	1.23	C
		VIII		1.43	1.29	C
		IX		1.49	1.35	C
		X		1.54	1.40	C
		XI		1.59	1.45	C
		XII		1.63	1.49	
PB+4	5D10	IV		.79	.65	E
		V		.87	.73	E
		VI		.915	.775	R
		VIII		1.08	.94	R
PD+1	4D 9	II		.73	.59	
PD+2	4D 8	IVSQ		.78	.64	
		VI		1.00	.86	
PD+3	4D 7	VI		.90	.76	
PD+4	4D 6	VI		.755	.615	R
PM+3	4F 4	VI		1.11	.97	R
		VIII		1.233	1.093	R
		IX		1.284	1.144	R
PO+4	6S 2	VI		1.08	.94	R
		VIII		1.22	1.08	R
PO+6	5D10	VI		.81	.67	A
PR+3	4F 2	VI		1.13	.99	R
		VIII		1.266	1.126	R
		IX		1.319	1.179	R
PR+4	4F 1	VI		.99	.85	R
		VIII		1.10	.96	R
PT+2	5D 8	IVSQ		.74	.60	
		VI		.94	.80	A
PT+4	5D 6	VI		.765	.625	R
PT+5	5D 5	VI		.71	.57	ER
PU+3	5F 5	VI		1.14	1.00	R
PU+4	5F 4	VI		1.00	.86	R
		VIII		1.10	.96	
PU+5	5F 3	VI		.88	.74	E
PU+6	5F 2	VI		.85	.71	R
RA+2	6P 6	VIII		1.62	1.48	R
		XII		1.84	1.70	R
RB+1	4P 6	VI		1.66	1.52	
		VII		1.70	1.56	
		VIII		1.75	1.61	
		IX		1.77	1.63	E
		X		1.80	1.66	
		XI		1.83	1.69	
		XII		1.86	1.72	
		XIV		1.97	1.83	
RE+4	5D 3	VI		.77	.63	RM
RE+5	5D 2	VI		.72	.58	E
RE+6	5D 1	VI		.69	.55	E
RE+7	5P 6	IV		.52	.38	
		VI		.67	.53	
RH+3	4D 6	VI		.805	.665	R
RH+4	4D 5	VI		.74	.60	RM
RH+5	4D 4	VI		.69	.55	
RU+3	4D 5	VI		.82	.68	
RU+4	4D 4	VI		.760	.620	RM
RU+5	4D 3	VI		.705	.565	ER
RU+7	4D 1	IV		.52	.38	
RU+8	4P 6	IV		.50	.36	
S -2	3P 6	VI		1.70	1.84	P
S +4	3S 2	VI		.51	.37	A
S +6	2P 6	IV		.26	.12	*
		VI		.43	.29	C
SB+3	5S 2	IVPY		.90	.76	
		V		.94	.80	
		VI		.90	.76	A
SB+5	4D10	VI		.74	.60	*
SC+3	3P 6	VI		.885	.745	R*
		VIII		1.010	.870	R*
SE-2	4P 6	VI		1.84	1.98	P
SE+4	4S 2	VI		.64	.50	A
SE+6	3D10	IV		.42	.28	*
		VI		.56	.42	C
SI+4	2P 6	IV		.40	.26	*
		VI		.540	.400	R*
SM+2	4F 6	VII		1.36	1.22	
		VIII		1.41	1.27	
		IX		1.46	1.32	
SM+3	4F 5	VI		1.098	.958	R
		VII		1.16	1.02	E
		VIII		1.219	1.079	R
		IX		1.272	1.132	R
		XII		1.38	1.24	C
SN+4	4D10	IV		.69	.55	R
		V		.76	.62	C
		VI		.830	.690	R*
		VII		.89	.75	
		VIII		.95	.81	C
SR+2	4P 6	VI		1.32	1.18	
		VII		1.35	1.21	
		VIII		1.40	1.26	
		IX		1.45	1.31	
		X		1.50	1.36	C
		XII		1.58	1.44	C
TA+3	5D 2	VI		.86	.72	E
TA+4	5D 1	VI		.82	.68	E
TA+5	5P 6	VI		.78	.64	
		VII		.83	.69	
		VIII		.88	.74	
TB+3	4F 8	VI		1.063	.923	R
		VII		1.12	.98	E
		VIII		1.180	1.040	R
		IX		1.235	1.095	R
TB+4	4F 7	VI		.90	.76	R
		VIII		1.02	.88	
TC+4	4D 3	VI		.785	.645	RM
TC+5	4D 2	VI		.74	.60	ER
TC+7	4P 6	IV		.51	.37	
		VI		.70	.56	A
TE-2	5P 6	VI		2.07	2.21	P
TE+4	5S 2	III		.66	.52	
		IV		.80	.66	
		VI		1.11	.97	
TE+6	4D10	IV		.57	.43	C
		VI		.70	.56	*
TH+4	6P 6	VI		1.08	.94	C
		VIII		1.19	1.05	RC
		IX		1.23	1.09	*
		X		1.27	1.13	E
		XI		1.32	1.18	C
		XII		1.35	1.21	C
TI+2	3D 2	VI		1.00	.86	E
TI+3	3D 1	VI		.810	.670	R*
TI+4	3P 6	IV		.56	.42	C
		V		.65	.51	C
		VI		.745	.605	R*
		VIII		.88	.74	C
TL+1	6S 2	VI		1.64	1.50	R
		VIII		1.73	1.59	R
		XII		1.84	1.70	RE
TL+3	5D10	IV		.89	.75	
		VI		1.025	.885	R
		VIII		1.12	.98	C
TM+2	4F13	VI		1.17	1.03	
		VII		1.23	1.09	
TM+3	4F12	VI		1.020	.880	R
		VIII		1.134	.994	R
		IX		1.192	1.052	R
U +3	5F 3	VI		1.165	1.025	R
U +4	5F 2	VI		1.03	.89	
		VII		1.09	.95	E
		VIII		1.14	1.00	R*
		IX		1.19	1.05	
		XII		1.31	1.17	E
U +5	5F 1	VI		.90	.76	
		VII		.98	.84	E
U +6	6P 6	II		.59	.45	
		IV		.66	.52	
		VI		.87	.73	*
		VII		.95	.81	E
		VIII		1.00	.86	
V +2	3D 3	VI		.93	.79	
V +3	3D 2	VI		.780	.640	R*
V +4	3D 1	V		.67	.53	
		VI		.72	.58	R*
		VIII		.86	.72	E
V +5	3P 6	IV		.495	.355	R*
		V		.60	.46	*
		VI		.68	.54	
W +4	5D 2	VI		.80	.66	RM
W +5	5D 1	VI		.76	.62	R
W +6	5P 6	IV		.56	.42	*
		V		.65	.51	
		VI		.74	.60	*
XE+8	4D10	IV		.54	.40	
		VI		.62	.48	
Y +3	4P 6	VI		1.040	.900	R*
		VII		1.10	.96	
		VIII		1.159	1.019	R*
		IX		1.215	1.075	R
YB+2	4F14	VI		1.16	1.02	
		VII		1.22	1.08	E
		VIII		1.28	1.14	
YB+3	4F13	VI		1.008	.868	R*
		VII		1.065	.925	E
		VIII		1.125	.985	R
		IX		1.182	1.042	R
ZN+2	3D10	IV		.74	.60	*
		V		.82	.68	*
		VI		.880	.740	R*
		VIII		1.04	.90	C
ZR+4	4P 6	IV		.73	.59	R
		V		.80	.66	C
		VI		.86	.72	R*
		VII		.92	.78	*
		VIII		.98	.84	*
		IX		1.03	.89	

$^{VIII}V^{4+}$, $^{IV}Pb^{4+}$, 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 $C_{32}H_{28}S_8V$ (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 isotypic 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).

AC+3 VI
68 JINCA 30 823 AC CL3
AG+1 II
71 INOCA 10 719 AG FE O2
72 ZAACA 393 266 SR AG6 O4
73 ZENBA 288 263 BA AG6 O4
AG+1 IV
71 JSSCB 3 364 AG2 CR O4
AG+1 IVSQ
42 JACSA 64 354 AG3 AS O4
69 ACSAA 23 2261 AG2 S O3
AG+1 V
70 JSSCB 1 484 AG6 MO10 O33
AG+1 VI
32 ZKKKA 82 161 AG2 SO4
47 JACSA 69 222 AG3 PO4
71 JSSCB 3 364 AG2 CR O4
69 ACACB 25 S116 AG2 CR2 O7
70 JSSCB 1 484 AG2 MO O4
AG+1 VII
70 JSSCB 1 484 AG6 MO10 O33
69 ACACB 25 S116 AG2 CR2 O7
AG+1 VIII
65 ACCRA 19 180 AG7 N O11
AG+2 IVSQ
71 JPCSA 32 543 AG F2
AG+2 VI
71 JPCSA 32 543 AG F2
AG+3 IVSQ
65 ACCRA 19 180 AG7 N O11
AL+3 IV
67 ACCRA 23 756 NA TI2 AL5 O12
68 NJMMA 1968 80 CA AL BO4
70 ACBCA 26 1230 CA AL4 O7
70 NJMMA 1970 547 CA12 AL14 O33
71 SPHDA 15 905 CA4 AL6 O10 (OH)6
71 SPHDA 15 995 CA AL4 O7
71 ACBCA 27 1826 BETA-AL2 O3
72 JSSCB 4 60 AG AL11 O17
AL+3 V
68 ACBCA 24 1518 (MG,FE) AL3 SI B O9
68 AMMIA 53 1096 AL2 PO4 (OH)3
AL+3 VI
71 AMMIA 56 18 NA3 AL2 LI3 F12
72 JSSCB 4 11 ND AL O3
72 JSSCB 4 60 AG AL11 O17
58 ACCRA 5 684 MG AL2 O4
72 ACBCA 28 1899 AL2 BE3 SI6 O18
66 JACSA 88 2951 AL(ACAC)3
73 ACBCA 29 2292 AL P O4.2 H2 O
67 ZKKKA 125 423 CS BE4 B(12-X) AL4 O28 H2
74 ACBCA 30 1311 NA AL3 (P O4)2 (O H)4
74 ZKKKA 139 129 AL (O H)3
AM+2 VII
72 JINCA 34 3427 AM I2
AM+2 VIII
73 JINCA 35 483 AM BR2
AM+2 IX
73 JINCA 35 483 AM CL2
AM+3 VIII
72 INOCA 11 2233 AM2 (S O4)3.8H2 O
AM+4 VI
67 ADCSA 71 228 BA AM O3
67 INUCA 3 327 R (BK+4)
AS+5 IV
69 ZKKKA 130 231 ZN2 CU AS2 O8
68 CJCHA 46 917 CU3 AS2 O8
63 BAPCA 11 361 MG2 AS2 O7
69 ACBCA 25 1546 CA H AS O4.2 H2 O
69 ACBCA 25 2658 ZR (H AS O4)2 H2 O
68 AMMIA 53 1841 MN2 O H AS O4
63 CAMIA 7 561 CA CU AS O4 O H
70 ACBCA 26 1584 NA2 H AS O4.7 H2 O
70 ACBCA 26 1574 NA2 H AS O4.7 H2 O
69 CHDCA 268 1694 BA NI2 AS2 O8
70 AMMIA 55 2023 MN9 (O H)9 (H2 O)2 (AS O3) (AS O4)2
70 ACBCA 26 1889 (M NA)2 H AS O4
70 ACSAA 24 3711 LI MO O2 AS O4
70 INOCA 9 2259 CA2 AS O4 CL
65 ACCRA 18 777 CU3 AS O4 (O H)3
70 CJCHA 48 890 MG2 AS2 O7
70 CJCHA 48 881 CO3 AS2 O8
71 CJCHA 49 1036 CA3 AS2 O8
70 AMMIA 55 1489 MN7 SB AS O12
71 ACBCA 27 2124 NA3 AS O4.12 H2 O
73 ACBCA 29 2611 MG3 AS2 O8
61 AMMIA 46 1077 CA2 B AS O4 (OH)4
73 CJCHA 51 2082 NA4 AS2 O7
66 ZAACA 347 133 CA H AS O4 H2 O
66 ZAACA 347 140 SR H AS O4 H2 O
71 AMMIA 56 1147 ZN4 AS2 O8 (OH)2.2H2 O
70 ACBCA 26 403 CA H AS O4
70 ZKKKA 132 332 CO3 AS2 O8
73 ACBCA 29 141 LU AS O4
73 ACBCA 29 2721 NH4 H2 AS O4
AS+5 VI
71 CJCHA 49 2539 CL F2 AS F6
73 JSSCB 6 80 MGB.5 AS3 O16
70 CJCHA 48 3124 CO8 AS3 O16
73 ACACO 29 266 CALCULATED
74 INOCA 13 780 XE AS F11.XE2 AS F9
74 ACBCA 30 250 K AS F6
AU+3 IVSQ
69 JCSIA 1969 1936 K AU F4
70 ZAACA 375 43 LI3 AU O3.K AU O2.RB AU O2
70 JCSIA 1970 3092 K AU (NO)F4
AU+5 VI
74 INUCA 13 775 XE2 AU F17
B +3 III
68 NJMMA 1968 80 CA AL B O4
70 ACBCA 26 906 B2 O3 I
71 SPHCA 15 802 K BE2 B O3 F2
71 ACBCA 27 672 ZN B4 O7
70 ACBCA 26 1189 K B O2
71 ACBCA 27 904 LI3 B O3
70 ZKKKA 132 241 CA B3 O5 O H
63 ACCRA 16 1233 NA B (U H)4.2 H2 O
74 JCPSA 60 1899 MN B4 O7
71 AMMIA 56 1553 MG (B6 O7 (O H)6) .2 H2 O
73 AMMIA 58 909 CA B SI U4 O H
71 ACBCA 27 672 ZN B4 O7
B +3 VI
73 ACACB 29 266 CALCULATED
BA+2 VI
70 ZKKKA 131 161 BA3 V2 O8
73 ZENBA 288 263 BA AG6 O4
BA+2 VII
71 ACBCA 27 1263 BA FE2 O4
73 ACBCA 29 2009 BA2 TI O4
BA+2 VIII
58 ZKKKA 110 231 CU BA2 (C U O H)6.4 H2 O
69 JCPSA 51 4928 BA MN F4
70 JCPSA 53 3279 BA CU F4
71 JCPSA 55 1093 BA W O4
71 AMMIA 56 758 BA C O3
71 ZAACA 386 1 BA2 CO O4
73 ACBCA 29 2009 BA2 TI O4
BA+2 IX
71 ZAACA 386 1 BA2 CO O4
73 ACSAA 27 1695 BA TE (S2 O3)2.2 H2 O
73 ACSAA 27 1653 BA TE (S2 O3)2.3 H2 O
BA+2 X
70 ZKKKA 131 161 BA3 (V O4)2
70 ACBCA 26 105 BA3 SI4 N8 O26
67 BUFCA 90 24 BA P2 O6
BA+2 XI
71 ACBCA 27 1263 BA FE2 O4
BA+2 XII
70 ACBCA 26 102 BA5 TA4 O15
72 CSCMC 1 1 BA TI6 O13
71 MRBUA 6 725 BA CA FE4 O8
69 CHDCA 268C 1694 BA NI2 AS2 O8
75 ACBCA 31 596 K2 BA CU (N O2)6
BE+2 III
69 ACBCA 25 1647 SR BE3 O4
66 ACBCA 20 295 CA12 BE17 O29
BE+2 IV
62 SPHCA 6 733 NA BE P O4
68 ACBCA 24 672 LA2 BE2 O5
68 ACBCA 24 807 CS BE F3
69 ACBCA 25 1647 SR BE3 O4
71 SPHCA 15 999 FE3 BE SI3 O9 (F,OH)2
72 SPHCA 16 1021 BE2 SI O4
72 ACBCA 28 1899 AL2 BE3 S16 O18
73 ACBCA 229 2976 NA3 BE TH10 F45
59 ACCRA 12 634 BE ACETATE
67 ZKKKA 125 423 CS BE4 B(12-X) AL4 O28 H2
74 ACBCA 30 396 NA6 (S116 AL2(BE(OH)2 O39) .1.5 H2 O
74 ACBCA 30 2434 LI2 BE SI O4
74 AMMIA 59 1267 CA BE2 P2 O8
BI+3 V
69 SSCOA 7 1797 BI2 W O6
70 ACSAA 24 384 BI2 O3 ALPHA
BI+3 VI
70 ACSAA 24 384 BI2 O3 ALPHA
71 JPCSA 32 1315 BI FE O3
BI+3 VIII
72 MRBUA 7 1025 BI TITANATES
BI+5 VI
R3 VS V (BA2 LA BI O6)
BK+4 VI
67 INUCA 3 327 R (BK+4)
BR+3 IV SQ
69 JCSIA 1969 1936 K BR F4
BR+5 III
69 ACACB 25 621 SM (BR O3)3.9H2 O
67 ACSAA 21 2834 HG BR O3
BR+7 IV
71 JCSIA 1971 1857 BR(+7)-O
C+4 III
65 ACCRA 18 689 CA C O3
71 JNBAA 75A 27 CA C O3
73 AMMIA 58 1029 MG C O3
67 PRLAA 92 125 MN C O3
75 ACBCA 31 890 NA2 C O3.H2 O
CA+2 VI
68 NJMAA 1968 80 CA AL B O4
69 ACBCA 25 1933 CA NA (M2 P O2)3
57 JCPSA 26 563 CA (O H)2
65 ACCRA 18 689 CA C O3
CA+2 VII
71 CJCHA 49 1036 CA3 AS2 O8
71 ACBCA 27 2311 CA2 AL FE O5
73 MRBUA 8 593 CA GA F5
69 ACBCA 25 1534 CA10 (P O4)6 (O H)2
CA+2 VIII
68 INOCA 7 1345 CA2 P2 O7
74 CJCHA 52 1155 CA18 MG2 H2 (P O4)14
CA+2 IX
71 JNBAA 75 27 CA C O3
69 ACBCA 25 1534 CA10 (P O4)6 (O H)2
CA+2 X
69 ACBCA 25 955 CA B2 O4 III
CA+2 XII
69 ACBCA 25 965 CA B2 O4 IV
74 AMMIA 59 41 CA AL3 (O H)6 (P O4)3 (O)1/2 (O H)1/2)12
74 JACSA 96 6606 K2 CA CU (N O2)6
CD+2 IV
59 ACCRA 12 1049 CD IN2 O4
71 ZAACA 382 270 K2 CD2 O3
CD+2 V
69 CJCHA 47 3409 CD2 P2 O7
70 ZKKKA 132 332 CD3 AS2 O8
CD+2 VI
69 CJCHA 47 3409 CD2 P2 O7
70 ZKKKA 132 332 CD3 AS2 O8
66 SPHDA 11 11 CD W O4
67 HCACA 50 2023 CD2 MN3 O8
74 JCSIA 1974 674 CD C4 H6 O6
74 ACBCA 30 1880 CD2 C4 H12 O12
CD+2 VII
74 ACSAA 28A 119 CD O(C H2 C O O)2.3 1/2 H2 O
CD O(C H2 C O O)2.3 H2 O
74 JCSIA 1974 1922 CD C3 H5 O5
CD+2 VIII
55 PRVBA 98 903 CD2 N82 O7
69 ACBCA 25 1804 CD (N O3)2.4 D2 O
74 JCSIA 1974 674 CD C4 H6 O6
CE+3 VIII
74 ZAACA 403 1 R3 VS V (CE F3)
74 JCSIA 1974 1165 C41 H24 CE F12 N O8 S4
CE+3 IX
67 SPHCA 12 214 CE B SI O5
74 ZAACA 403 1 R3 VS V (CE F3)
CE+3 X
60 AMMIA 45 1 CE4 ME ME2 TI2 SI4 O22
CE+4 VI
72 ACBCA 28 956 BA CE O3
73 JSSCB 8 331 R (CE4+)
CE+4 VIII
69 INUCA 8 33 (N H4)2 CE F6
74 JCSIA 1974 2021 NA6 CE W10 O36 H2.3OH2 O
74 JSTCA 15 397 CE(S O4)2
74 ACSAA 28 1079 A- CE (ACAC)4
CE+4 XII
68 JACSA 90 3589 (NH4)2 H6 (CE MO12 O42)1.12 H2 O
CF+3 VI
74 JINCA 36 2023 R3 VS V (CF2 (S O4)3)
CL+5 III
73 MRBUA 8 791 R8 CL O3
CL+7 IV
72 ACBCA 28 839 TMPD CL O4
32 ZKKKA 84 65 K CL O4
60 ACCRA 13 855 N U2 CL O4,M CL O4, M CL O4.H2 O,LI CL O4.3 H2 O
54 JPCHA 63 279 M CL O4.H2 O
58 JACSA 80 5075 C6 H6.AG CL O4
57 PISAA 56 134 N H4 CL O4
57 PISAA 56 143 K CL O4
62 ACGRA 15 1201 N H4 CL O4
71 JCSIA 1971 1371 CU (C10 H9 N3)2 (CL O4)2
70 ACGCA 26 1928 N2 H5 CL O4
71 ACBCA 27 898 M CL O4.2 1/2 H2 O
73 ICHAA 7 477 (C N12-TRIEN-CU CL O4
71 ACBCA 27 898 M CL O4.2 1/2 H2 O
72 MRBUA 7 1281 CL(+7) -O
71 JCSIA 1971 1857 CL(+7) -O
62 ACCRA 15 18 H3 O CL O4 (-80 C)
69 ACBCA 25 1875 N H3 O H CL O4
73 ACSAA 27 2309 (PB4 (O H)4)3 C O3 (CL O4)10 .6 H2 O
73 ACSAA 27 3523 CU (C3 H4 N2)4 (CL O4)2
CM+4 VI
67 INUCA 3 327 R (CM+4)
CO+2 IV
69 ZAACA 369 306 CO V2 O6
CO+2 V
72 ACBCA 28 2883 CO2 P2 O7 ALPHA
CO+2 VI
68 ZAACA 358 125 CO SE O4
68 ZKKKA 126 299 CO GE O3
70 CJCHA 48 881 CO3 AS2 O8
70 JCPSA 53 3279 BA CO F4
70 PEPIA 3 161 CO2 SI O4
73 ACBCA 29 2304 CO3 V2 O8
71 HCACA 54 1621 CO3 (O H)2 (S O4)2.2 H2 O
REF 1 CO2 SI O4
72 ACBCA 28 2883 CO2 P2 O7
70 INOCA 9 151 CO (OMPA)3 (CL O4)2
73 ACBCA 29 2741 CO SI F6.6 H2 O
74 AMMIA 59 475 CO2 SI O4
74 JCMLB 4 55 C16 H18 CO O6
CO+2 VIII
66 INOCA 5 1208 (AS(C6 H5)4)2(CO(N O3)4)
CO+3 VI LS
68 CGJDA 1968 871 CO (N O3)3
68 CJCHA 46 3672 CO3 O4
66 JACSA 88 2951 CO (C5 H7 O2)3
74 ACBCA 30 822 CO (C5 H7 O2)3
69 JACSA 91 6881 (N H4)6 (H4 CO2 MO10 O38) .7 H2 O
74 ZAACA 408 97 K CO2 O4
CO+4 IV
71 ZAACA 386 1 BA2 CO O4
73 ZAACA 398 54 LI8 CO O6
74 ZAACA 408 75 CS2 CO O3
74 ZAACA 409 152 K6 CO2 O7
CO+4 VI HS
67 STGBA 3 1 R3 VS V (FLUORIDES)
74 ZAACA 408 97 K CO2 O4
CR+2 VI LS
71 ANCPA 6 41 TA2 CR O6
69 ACBCA 25 925 R VS O ELECTRONS
CR+3 VI
69 MRBUA 4 621 NA3 CR F6
70 INOCA 9 2228 NA3 (CR MO O6 O24 H6).8 H2 O
70 ACSAA 24 3627 NA2 CR3 O8 O H
73 MRBUA 8 593 CA CR F5
65 ACCRA 19 131 CR (C5 H7 O2)3
CR+4 IV
74 ZAACA 407 129 BA2 CR O4
CR+4 VI
72 MRBUA 7 157 CR O2
CR+5 VI
67 STGBA 3 1 R3 VS V (FLUORIDES)
CR+6 IV
68 CJCHA 46 935 K2 CR2 O7
70 ACBCA 26 222 CR O3
69 JCSIA 1969 1857 (NH4)2 CR O4
69 ACACB 25 S116 AG2 CR2 O7
70 SPHDA 15 530 K2 CR4 O13
70 AMMIA 55 784 PB2 CR2 O5
70 ACSAA 24 3627 M2 CR3 O8 O H
71 SPHCA 15 820 NA2 CR2 O7.2 H2 O
71 SPHCA 15 826 LI2 CR2 O7.2 H2 O
73 ACBCA 29 890 NA2 CR2 O7 ALPHA
71 ACSAA 25 44 RB2 CR2 O7
70 CJCHA 48 537 RB2 CR2 O7
71 ACSAA 25 35 RB2 CR2 O7
71 JSSCB 3 364 AG2 CR O4
72 ACBCA 28 2845 K2 CR O4
73 ACSAA 27 177 ZR4 (O H)6 (CR O4)5.H2 O
73 ACBCA 29 2141 RB2 CR4 O13
73 ACBCA 29 2963 NA2 CR O4.4 H2 O
71 JCSIA 1971 1857 (NH4)2 CR O4
73 MRBUA 8 271 K2 CR2 O7
CR+6 VI
74 AMMIA 59 1160 PB6 CR CL6 X6 Y2
CS+1 VIII
69 SPHCA 13 930 CS2 BE F4
CS+1 X
69 INOCA 8 1665 CS4 MG3 F10
69 SPHCA 13 930 CS2 BE F4
CS+1 XI
69 INOCA 8 1665 CS4 MG3 F10
CS+1 XII
67 ACGRA 23 865 CS U F6
68 ACSAA 22 2793 CS CO CL3
71 ACBCA 27 245 CS U6 F25
CU+1 II
69 ZKKKA 129 259 CU LA O2
70 ZAACA 379 113 SR CU2 O2
CU+1 IV
REF 2 CU F, CU CL, CU BR
49 ACCRA 2 158 K2 CU CL3
CU+1 VI
70 MRBUA 5 207 CU TA O3
CU+2 IV
57 ACGRA 10 554 CU CR2 O4
71 ACJEA 10 413 SR CU F4, CA CU F4
CU+2 IV SQ
67 ZKKKA 124 91 ZN2 CU AS2 O8
68 ACBCA 24 388 CU2 IN2 O5
71 ACBCA 27 677 CU B2 O4
65 JCPSA 43 3959 CU (C6 H5IC H3)2 C3 O2)2
66 INOCA 5 517 CU (C10 H9 O2)2
67 JCSIA 1967 309 CU (O4 C12 H18)
66 PRLAA 289 161 C14 H10 O4 CU
70 ACBCA 26 8 CU O
CU+2 V
69 ACSAA 23 221 CU3 W O6
68 CJCHA 46 917 CU3 AS2 O8
68 JCPSA 48 2619 CU MO O4
CU+2 VI
63 NATUA 197 70 CU3 S O4 O H
63 ACCRA 16 124 CU5 (P O4)2 (O H)4
68 JCPSA 48 2619 CU MO O4
70 ACBCA 26 1020 CU W O4
68 CJCHA 46 605 CU2 P2 O7
68 JACSA 90 5623 CU(I(C H3)2 N)2 - (P(O)2 O)3 (CL O4)2
70 INOCA 9 151 CU (OMPA)3 (CL O4)2
73 ACBCA 29 1743 CU V2 O6
CU+3 VI
72 MRBUA 7 913 LA CU O3
DY+2 VI
UNPUI DY I2
DY+2 VII
UNPUI DY CL2, DY BR2
DY+2 VIII
UNPUI DY CL2
DY+3 VI
63 PHSSA 3 R446 DY2 O3
DY+3 VII
71 JCMLB 1 83 DY(THD)3.H2 O
DY+3 VIII
74 ZAACA 403 1 R3 VS V (DY F3)
70 SSCOA 8 1745 DY3 FE5 O12
DY+3 IX

Table 2 (*cont.*)

74 ZAACA 403 1 R3 VS V (DY F3)	73 ACBCA 29 869 HG MO O4	74 ACBCA 30 2491 MG2 V2 O7
ER+3 VI	HO+3 VIII	71 AMMIA 56 1553 MG (B6 O7 (O H)61.2M2 O
7u ACBCA 26 484 ER2 SI2 O7	74 ACBCA 30 2049 K HO BE F6	73 AMMIA 58 1029 MG C O3
ER+3 VII	70 SSCOA 8 1745 HO3 FE5 O12	74 CJCMA 52 1155 CA18 MG2 H2 (P O4)14
70 SPHCA 15 36 ER2 GE2 O7	72 BUFCA 95 437 HO P5 O14	70 INOCA 9 151 MG (OMPA)3 (CL O4)2
72 JCMLB 2 197 ER8 U (THD)10 (O H)12	74 ZAACA 403 1 R3 VS V (HO F3)	72 CJCMA 50 3619 MG V2 U6
ER+3 VIII	HO+3 IX	73 ACBCA 29 2611 MG3 AS2 O8
68 CMPLB 2 47 ER P O4, ER V O4	74 ZAACA 403 1 R3 VS V (HO F3)	MG+2 VIII
70 INOCA 9 2100 ER (C2 O4) (H C2 O4).3H2 O	74 ACBCA 30 2613 HO(C2 H5 S O4)3.9H2 O	73 ACACB 29 266 CALCULATED
70 SSCOA 8 1745 ER3 FE5 O12	HO+3 X	MN+2 IV HS
71 ACSAA 25 372 ER (H U C H2 C O O)3.2H2 O	74 INOCA 13 2535 HO(H2 O)4 (H C O)3)3.2H2 O	70 AMMIA 55 1489 MN7 SB AS O12
74 ZAACA 403 1 R3 VS V (ER F3)	75 CJCHA 53 831 (N O)2(HO(N O)3)5	69 ZAACA 369 306 MN V2 O4
72 JCMLB 2 197 ER8 U (THD)10 (O H)12	I+5 III	71 ACBCA 27 1044 MN CO CR O4
ER+3 IX	71 JCPSA 54 2556 N H4 I O3	69 PHSSA 32 K91 MN CR2 O4
59 ZKKKA 112 362 ER (C2 H5 S O4)3.9H2 O	66 ACCRA 20 758 LI I O3	73 ACACB 29 266 CALCULATED
74 ZAACA 403 1 R3 VS V (ER F3)	66 ACCRA 21 841 LI I O3	MN+2 V MS
EU+2 VI	58 ACCRA 9 1015 CE (I O3)4	68 AMMIA 53 1841 MN2 O H AS O4
70 ZAACA 374 201 LI EU3 O4	58 ACCRA 11 794 CE (I O3)4.H2 O	74 MPMTA 21 246 MN2 AS O4 OH
EU+2 VII	43 RTCPB 62 729 N H4 I O3	MN+2 VI LS
70 ZAACA 374 201 LI EU3 O4	I+5 VI	69 ACBCA 25 925 R VS O ELECTRONS
69 ACBCA 25 1104 EU I2	71 JCPSA 54 2556 N H4 I O3	MN+2 VI HS
73 REF 3 LI2 EU5 O8	I+7 IV	69 SCIEA 165 586 MN2 GE O4
EU+2 VIII	70 ACBCA 26 1782 NA I O4	69 JCPSA 51 4928 BA MN F4
UNPU1 EU FZ, EU BR2	26 ZEPYA 39 308 K I O4	70 ZKKKA 132 1 MN5 (O H)2 SI2 O8
EU+2 IX	71 JCSIA 1971 1857 I(+7)-U	69 AMMIA 54 1312 MN FE2 (P O4)2 (OH)2.8H2 O
73 RVCMA 10 7? EU CL2	I+7 VI	70 NJMIA 113 1 MN7 NA12 (S O4)13.15H2 O
UNPU1 EU F2	66 ACCRA 20 765 HS I U6	65 ACCRA 19 854 MN S O4
EU+2 X	65 ACCRA 19 629 K4 H2 I2 O10.8H2 O	72 AMMIA 57 621 MN2 GE O4
71 NATWA 58 218 EU2 SI O4	37 JACSA 59 2036 (N H4)2 H3 I O6	67 PRLAA 92 125 MN C O3
EU+3 VI	IN+3 IV	67 HCACA 50-2023 MN5 O8
68 REF 4 EU4 AL2 O9	74 ZAACA 409 97 RB2 IN4 O7	MN+2 VII
70 ZAACA 374 201 LI EU3 O4	73 ZAACA 395 280 SR2 IN2 O5	72 AMMIA 57 621 MN2 GE O4
73 REF 3 LI2 EU5 O8	IN+3 VI	MN+2 VIII
EU+3 VII	74 ZAACA 409 97 RB2 IN4 O7	69 ZKKKA 129 427 MN3 FE2 GE3 O12
68 REF 4 EU4 AL2 O9	61 ACSAA 15 1437 IN O H S O4.(H2 O)2	71 AMMIA 56 791 GARNETS
73 REF 3 LI2 EU5 O8	68 ACBCA 24 388 CU2 IN2 O5	73 SSCOA 12 109 MN3 AL2 GE3 O12
EU+3 VIII	70 ACSAA 24 1662 IN O O H	74 JCPSA 60 1899 MN B4 O7
68 JCPSA 48 1094 EU3 FE2 GA3 O12	69 INOCA 8 1985 IN2 O3	MN+3 VI HS
74 ZAACA 403 1 R3 VS V (EU F3)	74 ACBCA 30 1882 NA (N S12 O6	67 ACSAA 21 2871 MN2 O3
73 ACSAA 27 2827 EU2 (C3 H2 O4)3.8H2 O	74 SPHDA 18 761 IN2 GE2 O7	67 ZKKKA 124 428 MN2 O3
EU+3 IX	IR+4 VI	68 ACBCA 24 1233 MN O O H
74 ZAACA 403 1 R3 VS V (EU F3)	71 JSSCB 3 174 SR IR O3	69 JCPSA 50 1066 (N H4)2 MN F5
73 ACSAA 27 2827 EU2 (C3 H2 O4)3.8H2 O	IR+5 VI	63 PHSSA 3 K446 MN2 O3
71 ACSAA 25 3347 EU TRISGLYCOLATE	74 MRBUA 9 1177 RB VS V (CO2 IR2 O7)	68 BUFCA 91 339 TB MN O3, PR MN O3, ND MN O3
FE+2 IV SQ MS	K+1 IV	71 JSSCB 3 238 LA MN O3, MN3 O4,
74 AMMIA 59 1166 BA FE SI4 O10	68 ZAACA 358 241 K AG O	LA.95 CA.05 MN O3
FE+2 IV HS	REF 2 K2 O	73 JSSCB 6 16 NA MN7 O12
69 SCIEA 166 1399 (NA,K)2 FE4 SI12 O30.H2 O	K+1 VI	74 AMMIA 59 985 MG2 MN B O5
69 ZAACA 369 306 FE V2 O4	51 ZAACA 264 144 K SB F6	68 ACBCA 24 1114 NA4 MN4 TI5 O18
71 JUPSA 31 452 FE2 TI O4	68 SPHDA 12 1095 K Y MO2 O8	74 INOCA 13 1854 MN IC7 H5 O213.1/4 C6 H5 CH3
72 JUPSA 33 1296 FE2 MO O4	69 CCJDA 11 606 K2 ZR2 O5	74 INOCA 13 1864 MN (ACAC)3
FE+2 VI LS	69 ACBCA 25 1919 K U2 F9	MN+4 IV
69 ACACA 25 925 R VS A (FE S2)	K+1 VII	75 JSSCB 13 275 R3 VS V (M4 MN O4)
FE+2 VI HS	68 CJCHA 46 935 K2 CR2 O7	MN+4 VI
69 NJMMA 1969 430 FE AL2 (P O4)2 (O H)2 (O H)2.6 .2H2 O	69 JCSIA 1969 849 K2 MO O4	73 JSSCB 8 234 BA MN O3
70 BUFCA 93 190 FE S O4	71 SSCOA 9 335 K FE F4	69 INOCA 8 335 NA12 MN NB12 O38.50H2 O
71 SPHCA 15 999 FE3 BE SI3 O9 (F,O H)2	K+1 VIII	63 CZYPA 13 398 NA7 M4 MN (I O6)3.17H2 O
67 ACCRA 22 775 FE (NH4)2(S O4)2.6H2 O	30 ZKKKA 74 306 K H2 P O4	67 HCACA 50 2023 MN5 O8, CO2 MN3 O8
68 CIWYA 68 290 LI FE P O4	62 ZKKKA 117 411 K2 TI6 O13	MN+6 IV
74 AMMIA 59 486 FE2 SI O4	37 ZKKKA 98 266 K H2 (H3 O) B5 O10	72 ACBCA 28 2845 K2 MN O4
FE+2 VIII	71 INOCA 7 873 K H C2 O4	MN+7 IV
71 AMMIA 56 791 GARNETS	68 CJCHA 46 935 K2 CR2 O7	68 ACBCA 24 1053 AG MN O4
71 ZKKKA 134 333 FE3 AL2 SI3 O12	70 JCSIA 1970 3092 K AU (N O3)4	MO+3 VI
73 ACACB 29 266 CALCULATED	65 ACCRA 19 629 K4 H2 I2 O10.8H2 O	69 ACBCA 25 400 KJ MO CL6
FE+3 IV HS	K+1 IX	69 INOCA 8 2694 K3 MO F6
70 ACBCA 26 1469 CA2 FE2 O5	70 ZKKKA 132 27 K1.4 NA5.5 CA0.3 AL7.5	MO+4 VI
70 SSCOA 8 1745 M3 FE5 O12	L18.5 O32	71 MRBUA 6 555 LI2 MO F6
71 ACBCA 27 1263 BA FE2 O4	69 ACBCA 25 600 K GE F4	MO+5 IV
71 MRBUA 6 725 BA CA FE4 O8	69 ACBCA 25 1919 K U2 F9	74 INOCA 13 2715 R3 VS V (RE MO O4)
71 ACSAA 25 3616 CA2 FE2 O5	K+1 X	MO+5 VI
73 ACBCA 29 832 BA FE2 O4	73 CJCHA 51 2613 K AL P2 O7	71 INOCA 10 922 BA2 ND MO O6
FE+3 V	K+1 XII	MO+6 IV
71 JSSCB 4 1 FE V O4	68 SPHCA 13 420 K Y W2 O8	68 JCPSA 48 2619 CU MO O4
FE+3 VI HS	71 INOCA 10 1264 K2 PB CU (N O2)6	68 SPHDA 12 1095 K Y MO2 O8
70 ACBCA 26 1469 CA2 FE2 O5	67 INOCA 5 514 K2 BA CO (N O2)6	69 JCSIA 1969 849 K2 MO O4
70 SSCOA 8 1745 M3 FE5 O12	74 JACSA 96 6606 K2 CA CU (N O2)6	72 ACBCA 28 60 GU2 MO3 O12
71 SSCOA 9 335 K FE F4	75 ACBCA 31 596 K2 BA CU (N O2)6	69 JCPSA 50 86 ND2 MO3 O12
71 JSSCB 4 1 FE V O4	57 PISAA 56 143 K CL O4	71 SPHCA 15 611 LI3 FE MO3 O12
71 JPCSA 32 1315 BI FE O3	LA+3 VI	71 SPHCA 15 829 K AL MO2 O8, K FE MO2 O8
71 ACSAA 25 3616 CA2 FE2 O5	69 ZKKKA 129 259 CU LA O2	71 JCPSA 55 1093 CA MO O4, SR MO O4
67 ACCRA 23 239 FE (C5 H7 O2)3	73 MRBUA 8 1269 R3 VS V (RE2 W3 O12)	73 ACBCA 29 2074 LA2 MO3 O12
69 CCJDA 1969 440 FE (C7 H5 O2)3	LA+3 VIII	71 JCSIA 1971 1857 MO(+6) -O
FE+3 VIII	74 AMMIA 59 1277 LA4 MG2 TI3 SI4 O22	MO+6 V
73 JSSCB 8 331 ESTIMATED	73 ACBCA 29 2074 LA2 MO3 O12	67 CCJDA 1967 374 K2 MO3 O10
FE+4 VI	68 INOCA 7 2295 LA (C5 H7 O2)3 (H2 O)2	68 JCSIA 1968 1398 K2 MO3 O10
73 JSSCB 8 331 R3 VS V (PEROVSKITES)	74 ZAACA 403 1 R3 VS V (LA F3)	MO+6 VI
R3 VS V (SR FE O3)	74 SPHCA 18 675 LA2 SR3 (B O3)4	68 JCSIA 1968 1398 K2 MO3 O10
FE+6 IV	LA+3 IX	70 JSSCB 1 484 AG6 MO10 O33
73 JSSCB 8 43 K2 FE O4	71 MRBUA 6 23 LA FE O3	70 INOCA 9 2228 NA3 (CR MO O6 O24 H6).8H2 O
R3 VS V (K2 FE O4)	74 ZAACA 403 1 R3 VS V (LA F3)	70 ACSAA 24 3711 LI MO O2 AS O4
GA+3 IV	74 AMMIA 59 1277 LA4 MG2 TI3 SI4 O22	66 ACSAA 20 2698 MO F6 (GA3)
71 ACBCA 27 616 LI5 GA O4	LI+1 IV	70 CCJDA 1970 50 MO O3 (H2 O)2
75 ACBCA 31 560 SR GA2 SI2 O8	39 ZKKKA 162 119 LI O H.H2 O	72 ACBCA 28 2222 MO O3.2H2 O
GA+3 VI	70 ZAACA 379 157 LI2 CU O2	64 INOCA 3 1603 K2 (MO O2 (C2 O4) H2 O)2 O
74 ACBCA 30 1364 CI5 H21 O6 GA	70 INOCA 9 1096 YB LI F4	73 ACBCA 29 869 HG MO O4
GD+3 VII	71 AMMIA 56 18 NA3 AL2 LI3 F12	74 ACBCA 30 1795 MO O3HH2 O
70 ACBCA 26 484 GD2 SI2 O7	71 ACBCA 27 616 LI5 GA O4	N-3 IV
72 ACBCA 28 60 GD2 MO3 O12	73 JSSCB 6 538 LI3 V O4	REF 6 MG3 N2,SI3 N4,B N,TI N
72 SPHCA 16 790 GD2 GE2 O7	73 ACBCA 29 2625 LI (N2 H5) BE F4	N+5 III
69 IVNMA 5 1823 GD9.33 SI6 O26	73 ACBCA 29 2628 LI N H3 O H S O4	REF 6 NH4 N O3,NA N O3,K N O3,
72 JSSCB 5 266 GD9.33 SI6 O26	64 ACCRA 17 783 LI2 C2 O4	BAIN O3)2,TI(N O3)4
GD+3 VIII	74 ACBCA 30 2434 LI2 BE SI O4	NA+1 IV
71 SPHCA 15 926 NA GD SI O4	LI+1 VI	74 ZAACA 409 69 NA6 ZN O4
72 SPHCA 16 790 GD2 GE2 O7	68 ACBCA 24 225 LI3 AL F6	REF 2 NA2 O
74 ZAACA 403 1 R3 VS V (GD F3)	69 ZAACA 371 306 LI2 ZR O3	NA+1 V
GD+3 IX	70 ZKKKA 132 118 LI2 AL2 SI3 O10	68 ACBCA 24 1077 NA2 SI2 O5
72 SPHCA 16 790 GD2 GE2 O7	71 MRBUA 6 555 LI2 MO F6	68 SPHDA 12 987 NA2 ZN2 SI2 O7
69 IVNMA 5 1823 GD9.33 SI6 O26	65 ACCRA 19 561 LI C6 O7 H7	64 ZAACA 329 110 NA2 HG O2
74 ZAACA 403 1 R3 VS V (GD F3)	74 ACIEA 86 819 LI NB O2	NA+1 VI
GE+4 IV	68 CIWYA 68 290 LI FE P O4	70 ACSAA 24 1287 NA4 SN2 GE4 O12 (O H)4
68 ZKKKA 126 299 CO GE O3	71 ACSAA 25 3337 LI NB3 O8	65 ACCRA 19 561 NA C6 O7 H7
69 SCIEA 165 586 MN2 GE O4	73 CJCHA 51 2615 LI V O3	63 ACCRA 14 1233 NA B (OH)4.2H2 O
69 ZKKKA 129 427 MN3 FE2 GE3 O12	73 ACBCA 29 2294 LI2 ZR F6	60 ZKKKA 113 430 NA2 AL2 SI3 O10.2H2 O
70 JSSCB 2 612 MG28 GE10 O48	LU+3 VI	58 ZKKKA 111 241 NA CL O3
71 SPHCA 15 924 NA SM GE O4	70 ZAACA 377 70 CA LU2 O4	56 ACCRA 9 811 (NA AS O3)X
70 ACSAA 24 1287 NA4 SN2 GE4 O12 (O H)4	71 JACSA 4 284 LU B O3	53 ARKEA 6 77 NA SO P4
67 ACSAA 21 1281 NAB SN4 GE10 O30 (O H)4	LU+3 VIII	59 ACCRA 12 526 NA U ACETATE
70 MOCMB 102 964 NA2 GE O3	74 ZAACA 403 1 R3 VS V (LU F3)	74 ACBCA 30 1872 NA2 W O4
71 MOCMB 102 1245 K2 GE4 O9	LU+3 IX	75 ACBCA 31 890 NA2 C O3.H2 O
72 SPHCA 17 244 CD GE O3	74 ZAACA 403 1 R3 VS V (LU F3)	NA+1 VII
72 MOCMB 103 1560 GE5 O (P O4)6	MG+2 IV	71 SPHCA 15 926 NA GD SI O4
GE+4 VI	72 ACBCA 28 267 K2 MG5 SI12 O30	70 NJMIA 113 1 MN7 NA12 (S O4)3.15H2 O
70 SSCOA 1 557 CA2 GE O4	72 ACCRA 5 684 MG AL2 O4	73 ACBCA 29 890 NA2 CR2 O7 ALPHA
70 JSSCB 2 612 MG28 GE10 O48	72 ACBCA 28 3583 MG2 NA2 SI6 O15	NA+1 VIII
71 MOCMB 102 1245 K2 GE4 O9	74 ACBCA 30 2667 K6 MG U4	68 ACBCA 24 1703 NA B F4
71 ACBCA 27 2133 GE O2	MG+2 V	68 SPHDA 12 987 NA2 ZN2 SI2 O7
72 AMMIA 57 62 MN2 GE O4 DELTA	68 BAACSAA 22 1966 MG3 P2 O8	71 AMMIA 56 18 NA3 AL2 LI3 F12
72 ZKKKA 136 387 GE (O H) P O4	66 NJMMA 1966 142 MG B4 O7	NA+1 XII
72 MOCMB 103 1560 GE5 O (P O4)6	UNPU3 MG3 P2 O8	71 JSSCB 3 89 NA13 NB35 O94
H+1 I	UNPU3 MG2 P2 O7	32 ZKKKA 81 135 NA AL SI O4
57 JMOSA 1 43 T F	MG+2 VI	NB+3 VI
56 JCPSA 25 275 H F	65 CJCHA 43 1139 MG2 P2 O7	74 ACIEA 86 819 LI NB O2
HF+4 IV	63 BAPCA 11 361 MG2 AS2 O7	NB+4 VIII
75 JSSCB 13 275 R3 VS V (M4 HF O4)	70 ACBCA 26 1429 MG N H4 P O4	75 JACSA 97 2713 NB(OPH)4
HF+4 VII	71 CJCHA 49 1630 MG3 V2 O8	NB+5 VI
70 JACTA 53 126 HF O2	69 INOCA 8 1665 CS4 MG3 F10	68 JCPSA 48 5048 BA27 SR7.5 NB2 O5.78
69 ACSAA 23 3541 HF (O H)2 S O4.H2 O	69 ZKKKA 129 65 MG SI O3	70 JSSCB 1 419 M -NB2 O5
74 ACSAA 27 3467 HF4 (OH)8 (CH O4)4.H2 O	69 SPHCA 13 933 MG W O4	70 JSSCB 1 454 NA2 NB4 O11
HF+4 VIII	70 JSSCB 2 612 MG28 GE10 O48	70 AMMIA 55 90 CA NB2 O6
73 ACSAA 27 2455 HF (O H)2 S O4	65 MNLMB 1965 196 MG AL B O4	55 PRVAA 98 903 CU2 NB2 O7
HG+1 VI	70 BSCFA 1970 4243 MG S O4.H2 O	71 JSSCB 3 89 NA13 NB35 O94
71 CCJDA 1971 466 HG2 F2	71 ACBCA 27 815 MG5 TE O6	71 ZAACA 380 119 MN NB2 O6
HG+2 II	68 ACSAA 22 1466 MG3 P2 O8	74 JINCA 36 1965 CA2 NB2 O7
	70 REF 1 CA MG SI O4	71 JCSIA 1971 1280 BI3 NB17 O47

Table 2 (*cont.*)

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   70 ACBCA   26  105 BA3 S14 N86 026
   71 ACSAA   25 3347 LI NB3 O8
   59 SPHCA    4  796 (Y, YB) NB O4
   73 JSSCB    8  159 BI NB O4
   66 ACSAA   20   72 NB P O5
   74 BUFCA   97    3 NA3 NB O4
NB+5 VII
   70 JSSCB    1  454 NA2 NB4 O11
   71 JSSCB    3   89 NA13 NB95 O94
   71 ACBCA   27 1610 (NH4)3 NB O (C2 O413.H2 O
   75 ACBCA   31  673 NB2 O5
ND+2 VIII
      UNPU1            ND I2
ND+2 IX
      UNPU1            ND CL2, ND BR2
ND+3 VI
   71 INOCA   10  922 BA2 ND MO O6
   74 MRBUA    9 1661 NO AL3 B4 O12
ND+3 VIII
   69 JCPSA   50   86 ND2 MO3 O12
   71 JSSCB    3  458 ND V O4
   70 SPHCA   14  518 K ND W2 O8
   70 ACBCA   26  484 ND2 TI2 O7
   70 ACSAA   24 3406 ND4 RE2 O11
   71 SPHDA   15  636 ND2 W O6
   71 SPHCA   15  991 ND4 W3 O15
   74 MRBUA    9  129 ND P5 O14
   74 ZAACA  403    1 R3 VS V (ND F3)
   74 ACBCA   30  468 ND P3 O9
ND+3 IX
   70 ACSAA   24 2969 ND2 (C2 O413.10.5H2 O
   71 SPHCA   15  991 ND4 W3 O15
   73 ACSAA   27 2441 ND2 (C3 H2 O413.8H2 O
   74 ZAACA  403    1 R3 VS V (ND F3)
   73 ACSAA   27 2813 ND2 (C3 H2 O413.6H2 O
   73 ACSAA   27 2973 ND OH C O3
   74 AMMIA   59 1277 ND4 MG2 TI3 S14 O22
ND+3 XII
   72 JSSCB    4   11 ND AL O3
NI+2 IV
   61 JAPIA   32  685 NI CR2 O4
   65 BSCFA 1965 1085 SPINELS
NI+2 IV SQ
   66 INOCA    5 1200 NI (DPM)2
NI+2 V
   67 BAPCA   15   47 NI2 P2 O7
NI+2 VI
   74 AMMIA   59  486 NI2 SI O4
   74 ACBCA   30 1686 NI (PY N O16 (B F4)2
   68 ZAACA  358  125 NI SE O4
   67 BAPCA   15   47 NI2 P2 O7
   70 ACBCA   26 1464 RB NI F3
   70 ZAACA  378  129 SR2 NI TE O6
   70 JSSCB    2  416 RB NI F3
   71 PMSSA  438  125 NI (O H)2
   70 REF 1             NI2 SI O4
   64 ACCRA   17 1481 NI (C5 H7 O2)2.2H2 O
   73 ACBCA   29 2741 NI SI F6.6H2 O
   63 ZKKKA  118  291 NI (H C O)2.2H2 O
   74 JCPSA   61  852 NI C4 O4.2H2 O
   73 JCMLB    3  181 NI (C5 H7 O2)2.(C2 H5 O H)2
   73 ACBCA   29 2304 NI3 V2 O8
NI+3 VI  LS
   74 ZAACA  405  167 M2 M' NI F6
   71 CHDCA  272 2163 HO NI O3
NI+3 VI  HS
   54 JACSA   76 1499 NA NI O2
NI+4 VI  LS
   67 STGBA    3    1 R3 VS V (FLUORIDES)
   74 JINCA   36 1561 K2 NI F6
NO+2 VI
   74 INOCA   13 2233 ESTIMATED
NP+3 VI
   68 JINCA   30  823 NP CL3
NP+4 VI
   67 INUCA    3  327 ESTIMATED
   74 CJCHA   52 2175 R3 VS V
NP+6 VI
                      R3 VS V (BA2 SR NP O6)
OH-1 II
   71 AMMIA   56 1155 MG6.6 FE.4 SI3 O12 F O H,
                      R(OH-1)=R(F-1)+.04
OH-1 III
   71 AMMIA   56 1155 MG6.6 FE.4 SI3 O12 F O H,
                      R(OH-1)=R(F-1)+.04
OH-1 IV
                      R(OH-1)=R(F-1)+.04
OH-1 VI
                      R(OH-1)=R(F-1)+.04
OS+4 VI
   69 JCOMA   17  459 OS O2
   70 ACSAA   24  123 OS O2
OS+5 VI
   71 JCSIA 1971 2789 OS F5
   74 SSCOA   14  357 R3 VS V (CO2 OS2 O7)
   56 JINCA    2   79 K OS F6
OS+6 VI
                      R3 VS V (PEROVSKITES)
OS+7 VI
                      R3 VS V (PEROVSKITES)
OS+8 IV
   66 ACSAA   20  395 OS O4
   73 ACBCA   29 1983 OS O4
   65 ACCRA   19  157 OS O4
   71 JCSIA 1971 1857 OS(8+) -O
P+5  IV
   72 ACBCA   28 2883 CO2 P2 O7
   68 CJCHA   46  605 CU2 P2 O7
   65 CJCHA   43 1139 MG2 P2 O7
   68 INOCA    7 1345 CA2 P2 O7
   71 BSCFA 1971  424 ZR P2 O7
   70 ACBCA   26 1826 H3 P O4.1/2 H2 O
   71 ACBCA   27  291 NA2 H2 P2 O7.6H2 O
   71 NJMMA 1971  241 SR AL3 (P O4)2 (O H)5.H2 O
   69 ZKKKA  130  148 K ZR2 (P O4)3
   71 ACBCA   27 2124 NA3 P O4.12H2 O
   68 ACSAA   22 1822 NA ZR2 P3 O12
   68 ZKKKA  127   21 AL3 P2 O8.5H2 O
   68 CIWYA   68  290 LI FE P O4
   70 ACBCA   26 1826 H3 P O4
   72 AMMIA   57   45 MN.65 FE.35 P O4
   72 ACBCA   28 2065 (N M4)2 M P O4
   73 ACBCA   29  141 LU P O4
   71 ACBCA   27 2247 CA (H2 P O4)2.H2 O
   73 ACBCA   29 2292 AL P O4.2H2 O
   71 ACSAA   25  512 K H5 (P O4)2
   70 JSSCB    1  120 ZN2 P2 O7
P+5  V
   67 JACSA   89 2268 C23 H29 O5 P
   67 JACSA   89 2270 C23 H29 O5 P
P+5  VI
   71 ZAACA  380   51 P CL5
   72 CGJDA 1972  676 ET3 M H (C6 H4 O2)3 P
   73 ACACB   29  266 CALCULATED
PA+4 VI
   67 INUCA    3  327 R (PA+4)
   74 CJCHA   52 2175 R3 VS V
PA+5 VI
   71 ACBCA   27  731 K PA O3
PA+5 IX
   67 JCSIA 1967 1429 K2 PA F7
PB+2 IV  PY
   68 ZKKKA  126   98 PB SI O3
PB+2 VI
   70 ACACB   26  501 PB2 O3
PB+2 VII
   69 ZKKKA  128  213 PB CA2 SI3 O9
   64 ACCRA   17 1539 PB P2 O6
PB+2 VIII
   71 SPHCA   15  928 PB W O4
   64 ACCRA   17 1539 PB P2 O6
   73 CJCMA   51   70 PB2 V2 O7
   72 MRBUA    7 1025 BI TITANATES
PB+2 IX
   67 ACCRA   22  744 PB F2
   73 CJCMA   51   70 PB2 V2 O7
   74 ZKKKA  139  215 PB C O3
   74 CJCHA   52 2701 PB V2 O6
PB+2 X
   70 ZKKKA  132  228 PB3 P2 O8
PB+2 XII
   57 ACCRA   10  103 PB (N O3)2
                      R3 VS V (BA S O4)
   70 ZKKKA  132  228 PB3 P2 O8
   71 INOCA   10 1264 K2 PB CU (N O2)6
PB+4 IV
   72 JCSIA 1972 2448 R3 VS V (NA4 PB O4)
PB+4 V
   70 ZAACA  375  255 RB2 PB O3
PB+4 VI
   70 ACACB   26  501 PB2 O3
   65 JINCA   27 1509 PB3 O4
   74 CJCHA   52 2175 R3 VS V
PD+4 VIII
   68 MRBUA    3  153 PB O2
PD+2 IV SQ
   67 INOCA    6  730 PD (C6 H5 CH3 CH(C O)2)2
   68 JSTCA    9  166 PD ((C6 H5)2 CH C2 O2)2
PD+4 VI
   68 MRBUA    3  699 R3 VS V (M2 PD2 O7)
   73 INOCA   12 1726 XE PD F11
   61 JCSIA 1961 3728 K2 PD F6
PM+3 VI
PM+3 VIII
   74 ZAACA  403    1 R3 VS V (PM F3)
PM+3 IX
   74 ZAACA  403    1 R3 VS V (PM F3)
PO+4 VI
   74 CJCHA   52 2175 R3 VS V
PO+4 VIII
                      R3 VS V (FLUORITE)
PR+3 VI
   71 MRBUA    6  545 R3 VS V (PR2 MO3 O12)
PR+3 VIII
   70 SPHCA   15   28 PR2 W2 O9
   74 ZAACA  403    1 R3 VS V (PR F3)
PR+3 IX
   70 SPHCA   15   28 PR2 W2 O9
   59 ZKKKA  112  362 PR (C2 H5 S O4)3.9H2 O
   74 ZAACA  403    1 R3 VS V (PR F3)
PR+4 VI
   72 ACBCA   28  956 BA PR O3
   75 ACBCA   31  971 PR7 O12
   73 JSSCB    8  331 R (PR+4)
   74 CJCHA   52 2175 R3 VS V
PT+2 IV SQ
   72 REF 5             PT3 CO O6
PT+4 VI
   69 JINCA   31 3803 PT O2
                      R3 VS V (M2 PT2 O7)
   74 CJCHA   52 2175 R3 VS V
PT+5 VI
   67 STBGA    3    1 R3 VS V (FLUORIDES)
   67 JCSIA 1967  478 XE PT F11
PU+3 VI
   67 INUCA    3  327 R (PU+3)
   75 JINCA   37  743 R (PU+3)
PU+4 VI
   67 INUCA    3  327 R (PU+4)
   73 JSSCB    8  331 R (PU+4)
   74 CJCHA   52 2175 R3 VS V
PU+6 VI
                      R3 VS V (BA2 SR PU O6)
RB+1 VI
   70 ZAACA  375  255 RB2 PB O3
RB+1 IX
   74 ACBCA   30 1640 RB2 S O4
RB+1 XI
   74 ACBCA   30 1640 RB2 S O4
RB+1 XII
   70 ACBCA   26 1464 RB NI F3
   70 JSSCB    2  416 RB NI F3
   70 JSSCB    2  582 RB NI F3
RB+1 XIV
   65 ACCRA   19  205 RB U O2 (N O3)2
RE+4 VI
   68 INOCA    7  108 LA4 RE6 O19
   74 CJCHA   52 2175 R3 VS V
RE+5 VI
   70 ACSAA   24 3406 NO4 RE2 O11
      UNPU2            CO2 RE2 O7
   68 ACBCA   24  874 AE CL5
RE+6 VI
   75 JSSCB   13   77 BA2 MN RE O6
                      R3 VS V (PEROVSKITES)
                      R VS VALENCE
RE+7 IV
   68 ACIEA    7  295 RE2 O7 (O H2)2
   71 JCSIA 1971 1857 RE(+7) -O
   70 CJCHA   48  219 (RE2 (N-C4 H7 O2)2) (RE O4)2
RE+7 VI
   68 ACIEA    7  295 RE2 O7 (H2 O)2
RH+3 VI
   70 ACBCA   26 1876 RH2 O3
RH+5 VI
   73 INOCA   12 2640 RH F5
RU+3 VI
                      R3 VS V (LA RU O3)
RU+4 VI
   70 ACSAA   24  116 RU O2
   74 ACBCA   30 1459 NA(3-X) RU4 O9
   74 CJCHA   52 2175 R3 VS V
RU+5 VI
   71 JCSIA 1971 2789 RU F5
      REF 7             N3 VS V (CO2 RU2 O7)
   73 INOCA   12 1717 XE RU F11
RU+7 IV
   54 JACSA   76 3317 K RU O4
RU+8 IV
   67 ACSAA   21  737 RU O4
S+6  IV
   68 ACBCA   24  508 CU S O4.3 H2 O
   70 ZKKKA  132   99 PB2 S O5
   70 BUFCA   93  190 FE S O4 ALPHA
   70 BUFCA   93  185 FE S O4 O H
   70 BSCFA 1970 4243 MG S O4 H2 O
   71 ACBCA   27  272 N HN N S O4
   70 NJMIA  113    1 MN7 NA12 (S O4)13.15H2 O
   65 ACCRA   19  854 MN S O4
   71 ACSAA   25 3213 NA H S O4 H2 O
   72 ACBCA   28  864 SN S O4
   72 NATUA  238   95 CA S O4.2H2 O
   72 ACBCA   28 2845 K2 S O4
   73 JSTCA   14  499 TL2 S O4
   74 ACUCA   30  921 CA S O4.2H2 O
   74 NJMIA  121  208 FE2 (S O4)3
S+6  VI
   73 ACACB   29  266 CALCULATED
S8+3 IV
   70 ACSAA   24  320 SB P O4
S8+5 VI
   70 AMMIA   55 1489 MN7 SB AS O12
   71 JCSIA 1971  942 AS SB F6
   71 JCSIA 1971 2318 BR2 SB3 F16
   74 JCSSR    9  345 NA SB O3
SC+3 VI
   68 CJCHA   46 1446 SC2 O3
   68 ARKEA   29  343 SC2 O3
      UNPU4            SC2 SI2 O7
   73 SPHCA   17  749 SC2 SI2 O7
   73 INOCA   12  927 SC (C9 H7 O2)3
   73 ACBCA   29 2615 NA SC SI2 O6
   74 INOCA   13  158 SC (C7 H5 O2)3
   73 ACSAA   27 2841 SC U M (C3 H2 O4)1.2H2 O
   69 SPHDA   14    9 NA3 SC SI2 O7
SC+3 VII
   74 INUCA   10  137 SC M (C7 H5 O2)4
   72 ACSAA   26 1337 SC2 (C2 O4)3.6H2 O
   74 INOCA   13 1886 M SC (C7 H5 O2)4
   74 INOCA   13 1880 M SC (C7 H5 O2)4
SE+6 IV
   68 ZAACA  358  125 MN SE O4; CO SE O4; NI SE O4
   51 JCSIA  217  968 M2 SE O4
   70 ACBCA   26  436 NA2 SE O4
   70 ACBCA   26 1451 K2 SE O4
   70 ZAACA  379  204 NI SE O4.6H2 O
   72 ACBCA   28 2845 K2 SE O4
   69 ACBCA   25   19 CU (N H3)4 SE O4
   71 JSCIA 1971 1857 SE(+6) -O
SI+4 IV
   63 NATWA   50   91 FE2 SI O4
   73 ZKKKA  137   86 MG2 SI O4
   61 ACCRA   14  835 MG3 AL2 SI3 O12
   70 ZKKKA  132    1 MN5 (O H)2 SI2 O8
   58 ACCRA   11  437 CA3 AL2 SI3 O12 (GROSSULARITE)
   71 AMMIA   56  193 CU2 CA2 SI3 O10.2H2 O
   71 SPHCA   15  926 NA GD SI O4
   71 SPHCA   15  806 Y2 SI O5
   71 NATWA   58  218 EU2 SI O4
   70 PEPIA    3  161 CO2 SI O4
   70 ACBCA   26  105 BA3 SI4 N86 O26
   71 ACBCA   27  747 CA2 SI O4.CA CL2
   71 ACBCA   27  848 CA2 SI O4
   71 AMMIA   56 1222 NA.16 K.84 CA4 (SI8 O20)F.8H2 O
   71 AMMIA   56 1155 MG5.6 FE.4 SI3 O12.MG F O H
   69 MSAPA    2   31 LI M SI2 O6.NA M SI2 O6
                      CA MG SI2 O6
   69 MSAPA    2   95 FE6.1 MN.1 MG.8 CA.1 SI8
                      O22.1 (OH)1.4 F.5
   69 MSAPA    2  101 LI2.4 NA.1 MG12.9 SI15.7
                      AL.1 O43.4 F4.3 (OH).3
   70 ZKKKA  132  288 CA5 SI2 O7 (C O3)2
   71 ACBCA   27 2269 NA2 SI O3.6H2 O
   72 SPHCA   16 1021 BE2 SI O4
   72 ACBCA   28 1899 AL2 BE3 SI6 O18
   74 ACBCA   30 2434 LI2 BE SI O4
SI+4 VI
   62 NATWA   49  345 SI O2
   69 CJCHA   47 3859 CU SI F6.4H2 O
   70 ACBCA   26  233 SI P2 O7
   71 ACBCA   27 2133 SI O2
   71 ACBCA   27  594 CA3 SI (O H)6.12H2 O.SO4.CO3
   73 ACBCA   29 2741 M SI F6.6H2 O
   73 ACBCA   29 2748 CU SI F6.6H2 O
   74 CJCHA   52 2175 R3 VS V
SM+2 VII
      UNPU1            SM I2
SM+2 VIII
      UNPU1            SM BR2, SM F2
SM+2 IX
      UNPU1            SM CL2, SM BR2
SM+3 VI
   71 SPHCA   15  924 NA SM GE O4
SM+3 VII
   70 SPHCA   15  214 SM2 SI2 O7
   74 SPHCA   18  575 K2 SM F5
SM+3 VIII
   74 ZAACA  403    1 R3 VS V (SM F3)
   74 ACBCA   30 1751 SM P5 O14
SM+3 IX
   69 ACACB   25  621 SM (BR O3)3.9H2 O
   70 SPHCA   15  214 SM2 SI2 O7
   74 INOCA   13  290 N H4 SM (S O4)2.4H2 O
   70 ZAACA  403    1 R3 VS V (SM F3)
SM+3 XII
   72 JSSCB    4   11 SM AL O3
SN+4 IV
   75 ACBCA   31  511 K4 SN O4
   72 JCSIA 1972 2448 R3 VS V (NA4 SN O4)
   73 ACACB   29  266 CALCULATED
SN+4 V
   70 AMMIA   55  367 SN TA2 O7
   70 JSSCB    2  410 K2 SN O3
SN+4 VI
   69 ZAACA  368  248 LI8 SN O6
   70 ACSAA   24 1287 NA4 SN2 GE4 O12 (O H)2
   74 CJCHA   52 2175 R3 VS V
SN+4 VIII
   67 JCSIA 1967 1949 SN (N O3)4
SR+2 VI
   70 ZAACA  379  113 SR CU2 O2
   72 ZAACA  393  266 SR AG6 O4
SR+2 VII
   72 ACBCA   28 3688 SR10 (P O4)6 (O H)2
SR+2 VIII
   68 ZAACA  358  138 SR V2 O6
   71 JCPSA   55 1093 SR MO O4, SR W O4
   71 AMMIA   56  758 SR C O3
   71 ACBCA   27 2429 SR (H C O O)2.2H2 O
   74 SPHCA   18  575 LA2 SR3 B4 O12
SR+2 IX
   69 ACBCA   25 1647 SR BE3 O4
   70 ZKKKA  131  455 SR C O3
   72 ACBCA   28  679 SR (I O3)2.H2 O
   72 ACBCA   28 3688 SR5 (P O4)3 O H
   74 SPHCA   18  675 LA2 SR3 B4 O12
SR+2 X
   70 AMMIA   55 1911 SR CA B14 O20 (O H)6.5H2 O
   74 SPHCA   18  675 LA2 SR3 B4 O12
SR+2 XII
   70 ZAACA  378  129 SR2 NI TE O6
   71 JSSCB    3  174 SR IN O3
   71 NJMMA 1971  241 SR AL3 (P O4)2 (O H)5.H2 O
TA+5 VI
   71 AMMIA   55  307 SN TA2 O7
   70 JSSCB    1  454 CA TA4 O11
   71 JSSCB    3  145 TA2 O5
   67 ACBCA   26  102 BA5 TA4 O15
   67 ACCRA   23  939 Y TA O4
TA+5 VII
   70 JSSCB    1  454 CA TA4 O11
   71 JSSCB    3  145 TA2 O5
TA+5 VIII
   53 DANKA   90  781 TA B O4
TB+3 VI
   68 ZAACA  363  145 TB2 O3
TB+3 VIII
   70 SSCOA    8 1745 TB3 FE5 O12
   74 ZAACA  403    1 R3 VS V (TB F3)
TB+3 IX
   74 ZAACA  403    1 R3 VS V (TB F3)
TB+4 VI
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Table 2 (*cont.*)

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   72 ACBCA   28  956 BA TB O3
TC+5 VI
   67 STBGA    3    1 R3 VS V (FLUORIDES)
TC+7 IV
   69 AGIEA    8  381 TC2 O7
   71 ZAACA  380  146 TC2 O7
TE+4 IV
   69 ACBCA   25 1551 H3 FE2 TE4 O12 CL
   71 ACBCA   27  602 TI TE3 O8, SN TE3 O8, TE O2,
                      HF TE3 O8, ZR TE3 O8
   71 ACBCA   27  608 U TE3 O9
TE+4 VI
   61 ZKKKA  116  345 TE O2
   71 ACBCA   27  602 M TE3 O8
   71 ACBCA   27  608 U TE3 O9
TE+6 IV
   71 JCSIA 1971 1857 TE(+6)-O
TE+6 VI
   69 ZENBA   24  647 LI6 TE O6
   70 MRBUA    5  199 MG3 TE O6
   69 ACSAA   23 3062 NA2 K4 TE2 O8 (O H)2 (H2 O)14
   64 INOCA    3  634 K TE O (O H)5.H2 O
   64 NATWA   51  552 K TE O O H
   66 ACSAA   20 2138 K4 TE2 O6 (O H)4.H2 O
   70 NATWA   57  393 MG3 TE O6
   70 ZAACA  378  129 SR2 NI TE O6
   70 ACSAA   24 3178 TE (O H)6
   66 ACSAA   20 1535 TE F6
   71 ACBCA   27  815 MG3 TE O6
   65 ZAACA  334  225 K TE O2 (O H)3
   68 CMDBA  267 1435 CU2 TE O6
   69 MOCMB  100 1809 AG2 TE O2 (O H)4
   71 BUFCA   94  172 TE (O H)6
   73 ACBCA   29  643 TE2 O5
   73 ACBCA   29  956 H2 TE2 O6
   73 ACSAA   27   85 TE (O H)6
   74 ACBCA   30 1813 M2 TE O4
   74 ACBCA   30 2095 (N H4)6 (TE MO6 O24) TE (OH)6
                      7H2 O
TH+4 VI
   74 CJCHA   52 2175 R3 VS V
TH+4 VIII
   71 ACBCA   27  829 K5 TH F9
   71 ACBCA   27 2290 K7 TH6 F31
   74 ICHAA    8  273 K TH P3 O10
TH+4 IX
   68 GCJDA 1968  990 (N H4)4 TH F8
   69 ACBCA   25 1958 (N H4)4 TH F8
   68 CCACA   40  147 K TH2 P3 O12
   70 ICHAA    4  571 NA TH2 (P O4)3
   71 ACBCA   27 1823 RB TH3 F13
   73 ACBCA   29 2976 NA3 BE TH10 F45
   70 ACBCA   26 1185 K NA TH F6
   71 ACBCA   27 2279 (N H4)3 TH F7
TH+4 X
   73 ACBCA   29 2687 TH (N O3)4 ((C6 H5)3 P O)2
TH+4 XI
   66 ACCRA   20  842 TH (N O3)4.5H2 O
   66 ACCRA   20  836 TH (N O3)4.5H2 O
TH+4 XII
   65 ACCRA   18  698 MG TH (N O3)6.8H2 O
TI+3 VI
   73 JSSCB    6  213 TI4 O7
   63 PHRVA  130 2230 TI2 O3
   74 JSSCB    9  255 TI2 O3
   74 ACBCA   30  662 CS TI (S O4)2.12H2 O
TI+4 IV
   73 ACBCA   29 2009 BA2 TI O4
   61 ACCRA   14  875 BA2 TI O4
   71 JCSIA 1971 1857 TI(+4)-O
   74 ZAACA  408   60 RB2 TI O3
TI+4 V
   68 ACBCA   24 1327 Y2 TI O5
TI+4 VI
   70 ZKKKA  131  278 Y2 TI2 O7
   71 ACBCA   27  635 NZ H6 TI F6
   71 JSSCB    3  340 TI4 O7
   70 ACACB   26  336 BA TI O3
   64 ACCRA   17  240 CO TI O3
   71 JCPSA   55 3206 TI O2
   72 CSCMC    1    1 BA TI6 O13
   72 ZKKKA  136  273 TI O2
   74 ZKKKA  139  103 K TI P O5
   72 INOCA   11 2989 (TI O(C5 H7 O2)2)2
   74 ICHAA   11  243 (NH4)2 TI O(C2 O4)2.H2 O
   74 ACBCA   30 2894 BA TI2 O5
   74 CJCHA   52 2175 R3 VS V
TI+4 VIII
   66 JCSIA 1966 1496 TI (N O3)4
TL+1 VI
                      R3 VS V (MF)
TL+1 VIII
   75 ACBCA   31  365 TL N O3
TL+3 IV
   71 ZAACA  381  129 LI5 TL O4
   73 ZAACA  396  113 SR4 TL2 O7
   74 ZAACA  405  197 BA2 TL2 O5
TL+3 VI
   68 ZKKKA  126  143 TL2 O3
   74 ZAACA  405  197 BA2 TL2 O5
   75 ZAACA  412   37 RB TL F4
TL+3 VIII
   72 ZAACA  393  223 TL F3
TM+2 VI
      UNPU1            TM I2
TM+2 VII
      UNPU1            TM CL2,TM BR2
TM+3 VI
   63 PHSSA    3 K446 TM2 O3
TM+3 VIII
   70 SSCOA    8 1745 TM3 FE5 O12
   74 ZAACA  403    1 R3 VS V (TM F3)
TM+3 IX
   74 ZAACA  403    1 R3 VS V (TM F3)
U+3  VI
   68 JINCA   30  823 R (U+3)
U+4  VI
   73 JSSCB    8  331 R3 VS V
   67 INUCA    3  327 R (U+4)
   74 CJCHA   52 2175 R3 VS V
U+4  VIII
   70 ACBCA   26   38 (N H4)4 U F8
   73 ACBCA   29 1942 U CL4
U+4  IX
   69 ACBCA   25 1919 K U2 F9
   69 ACBCA   25 2163 K2 U F6
   71 ACBCA   27  245 CS U6 F25
   73 ACBCA   29  480 CS U2 F9
   74 ACBCA   30 1966 B - NH4 U F5
U+5  VI
   67 ACCR4   23  865 CS U F6
   70 JINCA   32 3701 NA U O3
   63 BUFCA   88  214 U CR O4
   67 BUFCA   90  257 U FE O4
U+5  VII
   73 SPHCA   18  323 U2 MO O8
U+6  VI
   68 ACBCA   24  967 CU U O4
   69 ACBCA   25  787 SR U O4, B4 U O4, CA2 U O5,
                      SR2 U O5, CA3 U O6,SR3 U O6
   66 JOPQA   27  726 MN U O4
   62 JOPQA   23  477 CO U O4
   65 ACSAA   19 1955 U F6 (GAS)
   71 INUCA    7  455 U O3
   71 JINCA   33 2867 CR2 U O6
   72 ACBCA   28 3469 U O2 (O H)2
   73 ACBCA   29    7 U F6
U+6  VII
   72 ACBCA   28 3609 U O3
U+6  VIII
   69 ACBCA   25  787 CA U O4
   65 ACCRA   19  205 RB U O2 (N O3)3
V+2  VI
      UNPU5            V F2
V+3  VI
   70 PRVBA    2 3771 V2 O3
   73 JSSCB    6  419 V4 O7
   69 ACBCA   25 1354 V (C5 H7 O2)3
   69 ZAACA  369  106 M V2 O6
   74 MRBUA    9 1091 (VO).99 CRO.01)2 O3
   70 JPCSA   31 2569 V2 O3
V+4  V
   65 ACCRA   19  432 LI V2 O5
   61 JCPSA   35   55 V O (C5 H7 O2)2
   73 ACBCA   29  269 CA V3 O7
   73 ACBCA   29 1335 CA V4 O9
V+4  VI
   72 JSSCB    5  446 CU V O3
   73 JSSCB    6  419 V4 O7
   72 PRVBA    5 2541 V O2 CR
   74 ACBCA   30 2644 V3 O7
   71 JSSCB    3 2675 V6 O13
   70 ACSAA   24  420 VO2
   74 PRVBA   10  490 VO2
V+5  IV
   68 ACBCA   24  292 Y V O4
   68 CHPLB    2   47 ER V O4
   67 ACSAA   21  590 MN2 V2 O7
   70 ZKKKA  131  161 BA3 (V O4)2
   71 JSSCB    3  458 ND V O4
   71 ACBCA   27 2124 NA3 V O4.12H2 O
   70 INOCA    9 2259 CA2 V O4 CL
   71 CJCHA   49 1629 MG3 V2 O8
   73 ACBCA   29 2304 CO3 V2 O8, NI3 V2 O8
   72 JSSCB    4   29 FE V O4
   73 CJCHA   51 1004 ZN2 V2 O7
   71 CJCHA   49 3056 ZN3 V2 O8
   73 JSSCB    6  538 LI3 V O4
   72 CJCHA   50 3944 CU3 V2 O8
   73 CJCHA   51   70 PB2 V2 O7
   73 ACBCA   29  141 Y V O4
   73 ACBCA   29 1338 CU5 V2 O10
   73 CJCHA   51  265 LI V O3
   74 ACBCA   30 1628 NA V O3
   74 NJMMA    5  210 CA5 (V O4)3 O H
V+5  V
   50 ACSAA    4 1119 V2 O5
   71 RVCMA    8  509 LI V2 O5
   74 ACBCA   30 2644 V3 O7
   74 ACBCA   30 2491 MG2 V2 O7
   73 ACBCA   29  567 MG2 V2 O7
   70 CHDCA  270  952 CA V2 O6
V+5  VI
   73 JSSCB    5  432 V P O5
   71 ACSAA   25 2675 V6 O13
   72 CJCHA   50 3619 MG V2 O6
   73 CJCHA   51 2621 V P O5 ALPHA
   74 CJCHA   52 2184 K3 V O2 C2 O4.3H2 O
   73 ACBCA   29 1743 CU V2 O6
W+5  VI
   67 STBGA    3    1 R3 VS V (FLUORIDES)
W+6  IV
   69 ACBCA   25 1704 K2 W O4
   71 SPHDA   15  636 ND2 W O6
   71 SPHCA   15  928 PB W O4
   72 ACBCA   28 3174 SN W O4
   71 JCPSA   55 1093 SR W O4.8A W O4
   71 JCSIA 1971 1857
   74 ACBCA   30 1872 NA2 W O4
   74 ACBCA   30 1878 AL2 (N O4)3
W+6  V
   74 ACBCA   30 2587 CA3 W O5 CL2
W+6  VI
   69 SPHCA   13  933 MG W O4
   69 SSCOA    7 1797 B12 W O6
   70 SPHCA   14  518 K ND (W O4)2
   70 SPHCA   14  515 L12 FE W2 O8
   70 SPHCA   15   28 PR2 W2 O9
   70 ACBCA   26 1020 CU W O4
   70 JSSCB    2  278 LI FE (W O4)2
   66 ACSAA   20 2698 W F6 (GAS)
   72 ZENBA   27  203 SN W O4
   71 SPHCA   15  991 ND4 W3 O15
   74 JSSCB   10    5 FE2 W O6
   74 ACBCA   30 2069 BA W O4
XE+8 IV
   71 JCPSA   52  812 XE O4
   71 JCSIA 1971 1857 XE(+8)-O
XE+8 VI
   64 INOCA    3 1412 NA4 XE O6.8H2 O
   64 INOCA    3 1417 NA4 XE O6.6H2 O
                      K4 XE O6.9H2 O
Y+3  VI
   67 ACCRA   22  354 Y2 BE O4
   68 ZAACA  358  138 SR Y2 O4
   67 SPHCA   11  583 NA Y SI O4
   69 ACBCA   25 2140 Y2 O3
   71 SPHCA   15  806 Y2 SI O5
   74 JCSIA 1974  229 C66 H72 I3 N12 O6 Y
Y+3  VII
   68 INOCA    7 1777 Y(C6H5CO2CH2CO2H)3.H2O
Y+3  VIII
   68 ACBCA   24  292 Y V O4
   57 ACCRA   10  239 Y3 FE5 O12
   68 SPHDA   12 1095 K Y MO2 O8
   69 SPHCA   13  420 K Y W2 O8
   70 ZKKKA  131  278 Y2 TI2 O7
   67 ACCRA   23  939 Y TA O4
   74 ZAACA  403    1 R3 VS V (Y F3)
Y+3  IX
   59 ZKKKA  112  362 Y (C2 H5 S O4)3.9H2 O
   74 ZAACA  403    1 R3 VS V (Y F3)
YB+2 VI
   71 ZAACA  386  221 YB BR2, YB I2
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 SI O5
   70 ACBCA   26  484 YB2 SI2 O7
   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 SI O5
   69 INOCA    8   22 YB (C5 H7 O2)3 (H2 O)
   69 INUCA    8   29 YB (C5 H7 O2)3 (H2 O) 1/2 C6 H6
YB+3 VIII
   70 INOCA    9 1096 YB LI F4
   70 SSCOA    8 1745 YB3 FE5 O12
   74 MRBUA    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+2 IV
   68 SPHDA   12  987 NA2 ZN2 SI2 O7
   69 ACBCA   25 1233 ZN O
   69 PHSSA   32  K91 ZN FE2 O4
   73 ACSAA   27 1541 ZN S O3.2 1/2H2 O
   64 INOCA    3  245 ZN (OPH)2
ZN+2 V
   70 JSSCB    1  120 ZN2 P2 O7
   73 CJCHA   51 1004 ZN2 V2 O7
   71 AMMIA   56 1147 ZN4 AS2 O8 (O H)2.2H2 O
ZN+2 VI
   65 CJCHA   43 1147 ZN2 P2 O7
   68 SPHCA   13  127 ZN W O4
   70 JSSCB    1  120 ZN2 P2 O7
   71 CJCHA   49 3056 ZN3 V2 O8
   71 AMMIA   56 1147 ZN4 AS2 O8 (O H)2.2H2 O
   73 ACBCA   29 2741 ZN SI F6.6H2 O
   73 ACSAA   27 1541 ZN S O3.2 1/2H2 O
ZR+4 IV
   75 JSSCB   13  275 R3 VS V (M+ ZR O4)
ZR+4 V
   69 GCJDA 1969  727 K2 ZR O3
   70 JSSCB    2  410 K2 ZR O3
ZR+4 VI
   69 ACBCA   25 2658 ZR (N AS O4)2.H2 O
   69 ZAACA  371  306 LI2 ZR O3
   70 JSSCB    1  478 K2 ZR2 O5
   68 ACSAA   22 1822 NA ZR2 P3 O12
   73 ACBCA   29 2296 LI2 ZR F6
   71 ACBCA   27 1944 RB5 ZR4 F21
   74 CJCHA   52 2175 R3 VS V
ZR+4 VII
   69 ACBCA   25 2164 NA2 ZR F6
   68 ACBCA   26  417 (N H4)3 ZR F7
   70 JACTA   53  126 ZR O2
   73 ACSAA   27  177 ZR4 (O H)6 (CR O4)5.H2 O
   73 ACSAA   27 2614 ZR (O H)2 S O4.H2 O
   71 ACBCA   27 1944 RB5 ZR4 F21
ZR+4 VIII
   69 ACBCA   25 1558 ZR2 (S O4)4 (H2 O)8.6H2 O
   69 ACBCA   25 1566 ZR2 (S O4)4 (H2 O)8.2H2 O
   69 ACBCA   25 1572 ZR2 (S O4)4.5H2 O
   71 ACBCA   27  638 NZ H6 ZR F6
   71 AMMIA   56  782 ZR SI O4
   63 INOCA    2  243 ZR (ACAC)4
   71 ACBCA   27 1944 RB5 ZR4 F21
   63 INOCA    2  250 NA4 ZR (C2 O4)4.3H2 O

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   UNPU3  C.CALVO,PERSONAL COMMUNICATION
   UNPU4  C.T.PREWITT,PERSONAL COMMUNICATION
   UNPU5  W.H.BAUR,PERSONAL COMMUNICATION

ACACB ACTA CRYST. SECT. A
ACBCA ACTA CRYST. SECT. B
ACCRA ACTA CRYST.
ACIEA ANGEW. CHEM. INT. ED.
ACSAA ACTA CHEM. SCAND.
ADCSA ADV. CHEM. SER.
AMMIA AM. MINER.
ANCPA ANNLS CHIM.
ARKEA ARK. KEMI
BAPCA BULL. ACAD. POL. SCI. SER. SCI. CHIM.
BCSJA BULL. CHEM. SOC. JAPAN
BSCFA BULL. SOC. CHIM. FR.
BUFCA BULL. SOC. FR. MINER. CRISTALLOGR.
CAMIA CAN. MINERALOGIST
CCACA CROAT. CHEM. ACTA
CCJDA CHEM. COMMUN.
CHDAA C. R. HEBD. SEAN. ACAD. SCI. SER. B
CHDCA C. R. HEBD. SEAN. ACAD. SCI. SER. C
CHPLB CHEM. PHYS. LETT.
CIWYA CARNEGIE INST. WASH. YEARBOOK
CJCHA CAN. J. CHEM.
CSCMC CRYST. STRUCT. COMM.
CZYPA CZECH. J. PHYS.
DANKA DOKL. AKAD. NAUK. SSSR
HCACA HELV. CHIM. ACTA
ICHAA INORG. CHIM. ACTA
INOCA INORG. CHEM.
JNOMA RUSS. J. INORG. CHEM.
JNUCA INORG. NUCL. CHEM. LETT.
IVNMA IZV. AKAD. NAUK SSSR, NEORG. CHEM.
JACSA J. AM. CHEM. SOC.
JACGA J. APPL. CRYSTALLOGR.
JACTA J. AM. CERAM. SOC.
JAPIA J. APPL. PHYS.
JCMLB J. CRYST. MOLEC. STRUCT.
JCOMA J. L'SS-COMMON METALS
JCPSA J. CHEM. PHYS.
JCSIA J. CHEM SOC. LOND. (DALTON)
JCSPA J. CHEM. SOC. LOND. (PERKIN II)
JESUA J. ELECTROCHEM. SOC.
JINCA J. INORG. NUCL. CHEM.
JMOSA J. MOLEC. SPECTROSC.
JNBAA J. RES. NAT. BUR. STAND. SECT. A
JOPQA J. PHYS. (FR.)
JPCHA J. PHYS. CHEM.
JPCSA J. PHYS CHEM. SOLIDS
JSSCB J. SOLID STATE CHEM.
JSTCA J. STRUCT. CHEM.
JUPSA J. PHYS. SOC. JAPAN
MNLMB MINERALOG. MAG.
MOCMB MH. CHEM.
MRBUA MATER. RES. BULL.
MSAPA MIN. SOC. AMER. SPEC. PAPER
NATUA NATURE,LOND.
NATWA NATURWISSENSCHAFTEN
NJMIA NEUES JB. MINER. ABH.
NJMMA NEUES JB. MINER. MH.
PEPIA PHYS. EARTH PLANET. INTERIORS
PHSSA PHYS. STATUS SOLIDI
PISAA PROC. INDIAN ACAD. SCI. A
PISBA PROC. INDIAN ACAD. SCI. B
PRLAA PROC. R. SOC. SERIES A
PRVAA PHYS. REV. SECT. A
PRVBA PHYS. REV. SECT. B
PRVVA PHYS. REV.
RTCPB RECL TRAV. CHIM. PAYS-BAS
RVCMA REVUE CHIM. MINER. (FR.)
SCIEA SCIENCE
SPHCA SOVIET PHYS. CRYSTALLOGR.
SPHDA SOVIET PHYS. DOKL.
SSCOA SOLID STATE COMMUN.
STBGA STRUCT. AND BOND.
TFSUA TRANS. FARADAY SOC..
MPMTA TSCHERMAKS MINER. PETROGR. MITT.
UNPU1 (UNPUBLISHED REFERENCE)
ZAACA Z. ANORG. ALLG. CHEM.
ZKKKA Z. KRISTALLOGR. MINER.
ZEPYA Z. PHYS.
ZENBA Z. NATURF.
ZSTKA ZH. STRUKT. KHIM.
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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 $Bi_{4-x}RE_xTi_3O_{12}$ 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 $Bi_2Ru_2O_7$, $Bi_2Ir_2O_7$ and $Bi_2Pt_2O_7$ 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 $Bi_3Fe_5O_{12}$ was estimated to have cell dimensions between those of the hypothetical $Nd_3Fe_5O_{12}$ and $Pr_3Fe_5O_{12}$ (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
$BiLi(MoO_4)_2$	314·7	0·96
$LaLi(MoO_4)_2$	328·7	
$BiNa(MoO_4)_2$	320·5	0·97
$LaNa(MoO_4)_2$	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 (×8)	1·00
La_2MoO_6	267·3	
$BiFeO_3$	62·49 (×6)	1·03
$LaFeO_3$	60·77 (×4)	
$Bi_2Sn_2O_7$	1219·9 (×8)	1·00
$La_2Sn_2O_7$	1225·3	

A similar study of relative cell volumes of isotypic compounds involving the pairs Cu^+-Li^+, Ag^+-Na^+, Tl^+-Rb^+, and Pb^{2+}-Sr^{2+} was used to obtain more reliable estimates of the radii of Cu^+, Ag^+, Tl^+, and Pb^{2+} (Shannon & Gumerman, 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 $r(^{VI}H^-) = 1{\cdot}40$ Å if corrected for cation and anion coordination. The value of $r(^{IV}H^-)$ 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 $Sn_2M_2O_7$ pyrochlores were used in SP 69 to derive $r(^{VIII}Sn^{2+})$, Stewart, Knop, Meads & Parker (1973) and Birchall & Sleight (1975) recently found that the pyrochlore *A* site in $Sn_2Ta_2O_7$ is not fully occupied. Thus, even this example of apparently regular Sn^{2+} polyhedra is not valid.

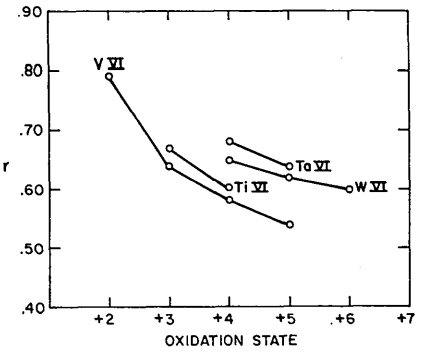


Fig. 1. Effective ionic radius (Å) *vs* oxidation state.

Results and discussion

In Table 1 two sets of radii are included. The first is a set of traditional radii based on $r(^{VI}O^{2-}) = 1{\cdot}40$ Å. The other set is based on $r(^{VI}O^{2-}) = 1{\cdot}26$ and $r(^{VI}F^{-}) = 1{\cdot}19$ Å, 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

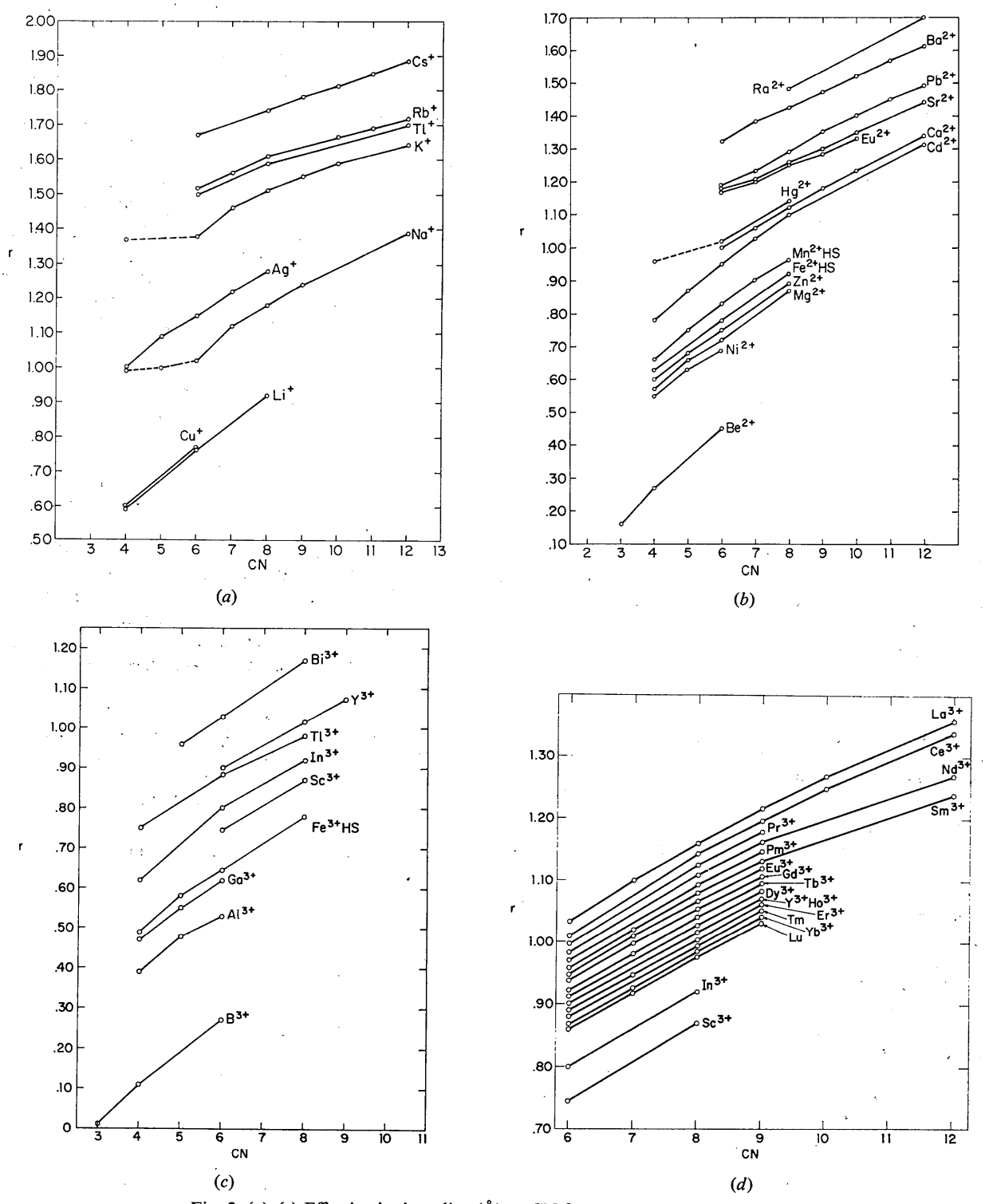
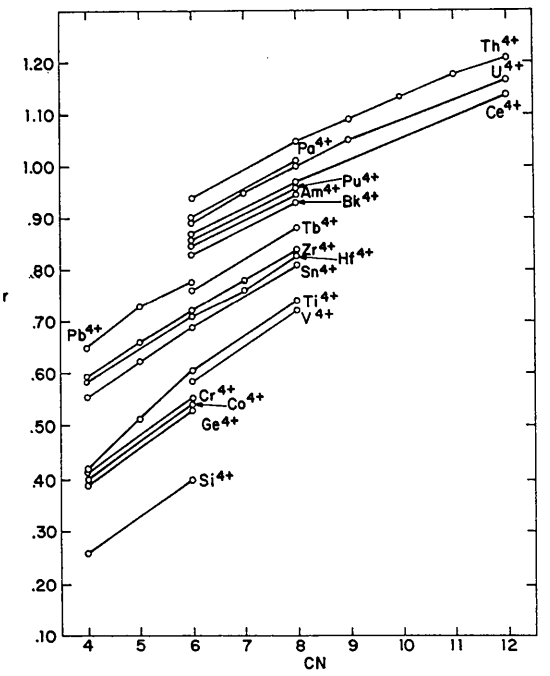


Fig. 2. (*a*)–(*e*) Effective ionic radius (Å) *vs* CN for some common cations.



(*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 $^{VI}Fe^{2+}$LS, $^{VI}Mn^{2+}$LS, $^{VI}Cr^{2+}$LS, $^{VI}V^{2+}$, $^{VI}No^{2+}$, $^{VI}Ni^{3+}$HS, $^{VI}Ir^{3+}$, $^{VI}Mo^{3+}$, $^{VI}Ta^{3+}$, $^{VI}Pa^{3+}$, $^{VI}Ta^{4+}$, $^{IV}Pb^{4+}$, $^{VI}Ir^{5+}$, $^{VI}Os^{5+}$, $^{VI}Re^{5+}$, $^{VI}Pu^{5+}$, $^{VI}Bi^{5+}$, $^{VI}Os^{6+}$, $^{VI}Re^{6+}$, and $^{VI}Os^{7+}$. 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 $^{IV}Na^+$, $^{V}Na^+$, and $^{IV}K^+$. 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):

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

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 Tl^{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 $r(^{IV}Na^+) = 0{\cdot}90$ Å.

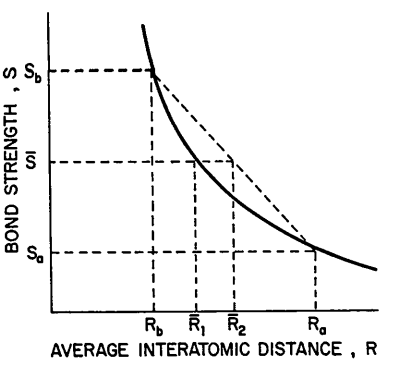


Fig. 3. Typical bond length *vs* bond strength plot.

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.

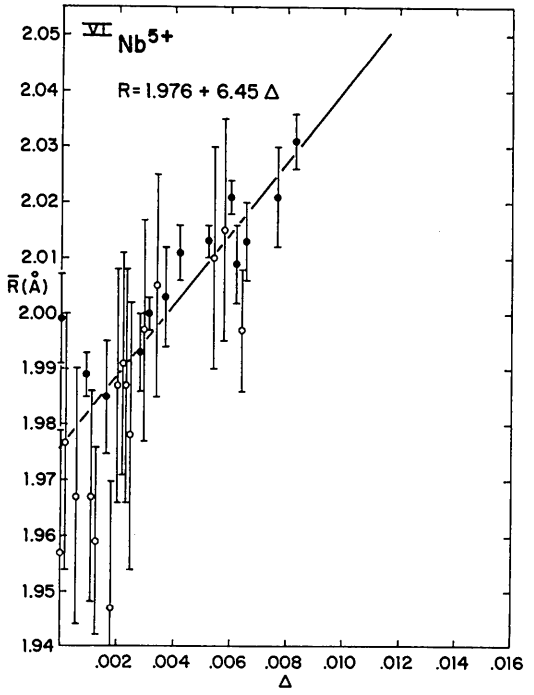


Fig. 4. Mean Nb^{5+}–O bond length *vs* distortion. Vertical bars represent average e.s.d.'s quoted by the authors. Solid circles represent more accurate data.

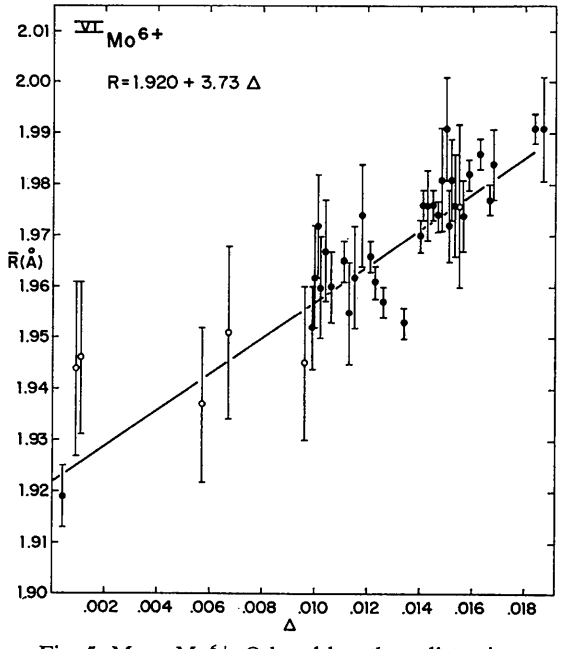


Fig. 5. Mean Mo^{6+}–O bond length *vs* distortion.

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

Compound	$\bar{R}$ (Å)	r (Å)	Reference
(*a*) $^{IV}Na^+$			
Na_2O	2·40	1·02	
$Na_5P_3O_{10}$	2·37	0·99	60 ACCRA 13 263
$NaOH.H_2O$	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
$NaC_6O_7H_7$	2·37	1·01	65 ACCRA 19 561
$Na_4Sn_2Ge_4O_{12}(OH)_4$	2·39	1·02	70 ACSAA 24 1287
$Na_2P_2O_7.10H_2O$	2·48	1·10	64 ACCRA 17 672
$NaHCO_3$	2·44	1·06	65 ACCRA 18 818
$Na_2B_4O_6(OH)_2.3H_2O$	2·41	1·04	67 SCIEA 154 1453
$Na_4P_4O_{12}.4H_2O$	2·415	1·05	61 ACCRA 14 555
$NaAl(SO_4)_2.12H_2O$	2·45	1·10	67 ACCRA 22 182
$NaB(OH)_4.2H_2O$	2·460	1·09	63 ACCRA 16 1233
NaU acetate	2·375	1·025	59 ACCRA 12 526
$C_{10}H_{13}N_5NaO_6P.6H_2O$	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, 1973*a*; Shannon, Gumerman & 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 molybdate. 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 pinakiolite (Shannon, Gumerman & 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 $\Delta=\frac{1}{6}\sum(R_i-\bar{R}/\bar{R})^2$ 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 $\Delta=\langle(\Delta R/R)^2\rangle\times10^4$	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
$Ba_{0.27}Sr_{0.75}Nb_2O_{5.78}$	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 distortion*

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

Compound	$\bar{R}$ (Å)	Distortion $\Delta=\langle(\Delta R/R)^2\rangle\times10^4$	Reference		
$Mo_2(O_2C_6Cl_4)_6$	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
$(C_{15}H_{11}O_2)_2MoO_2$	1·952	99	74 ACBCA	30	300
$(NH_4)_6[Mo_7O_{24}].4H_2O$	1·962	99	75 JCSIA	1975	505
$(NH_4)_6[Mo_7O_{24}].4H_2O$	1·972	101	75 JCSIA	1975	505
$(NH_4)_6[Mo_7O_{24}].4H_2O$	1·960	104	75 JCSIA	1975	505
$LiMoO_2AsO_4$	1·967	104	70 ACSAA	24	3711
$(NH_4)_6Mo_8O_{27}.4H_2O$	1·960	106	74 ACBCA	30	48
$HgMoO_4$	1·965	111	73 ACBCA	29	869
$(NH_4)_6[Mo_7O_{24}].4H_2O$	1·955	113	75 JCSIA	1975	505
$(NH_4)_6[Mo_7O_{24}].4H_2O$	1·962	115	75 JCSIA	1975	505
$(NH_4)_6[Mo_7O_{24}].4H_2O$	1·974	118	68 JACSA	90	3275
$MoO_3.2H_2O$	1·966	121	72 ACBCA	28	2222
$MoO_3.2H_2O$	1·961	123	72 ACBCA	28	2222
$MoO_3.2H_2O$	1·957	126	72 ACBCA	28	2222
$MoO_3.2H_2O$	1·953	134	72 ACBCA	28	2222
$(NH_4)_5[MoO_3)_5(PO_4)\ (HPO_4)].3H_2O$	1·970	140	74 JCSIA	1974	941
$Na_3(CrMo_6O_{24}H_6).8H_2O$	1·976	141	70 INOCA	9	2228
$(NH_4)_6Mo_8O_{27}.4H_2O$	1·976	141	74 ACBCA	30	48
$Na_3CrMo_6O_{24}H_6.8H_2O$	1·976	143	70 INOCA	9	2228
$(NH_4)_5[(MoO_3)_5(PO_4)\ (HPO_4)].3H_2O$	1·974	145	74 JCSIA	1974	941
$(NH_4)_6[TeMo_6O_{24}].Te(OH)_6.7H_2O$	1·981	147	74 ACBCA	30	2095
$CoMoO_4$	1·991	150	65 ACACA	19	269
$(NH_4)_6Mo_8O_{27}.4H_2O$	1·972	151	74 ACBCA	30	48
MoO_3	1·981	151	63 ARKEA	21	357
$(NH_4)_6[Mo_7O_{24}].4H_2O$	1·976	152	68 JACSA	90	3275
$K_2\{[MoO_2(C_2O_4)\ (H_2O)]_2O\}$	1·976	152	64 INOCA	3	1603
$(NH_4)_6Mo_8O_{27}.4H_2O$	1·974	152	74 ACBCA	30	48
$(NH_4)_5[(MoO_3)_5(PO_4)\ (HPO_4)].3H_2O$	1·982	159	74 JCSIA	1974	941
$Na_3CrMo_6O_{24}H_6.8H_2O$	1·986	163	70 INOCA	9	2228
$(NH_4)_5[(MoO_3)_5(PO_4)\ (HPO_4)].3H_2O$	1·977	167	74 JCSIA	1974	941
$MoO_3.H_2O$	1·984	167	74 ACBCA	30	1795
$(NH_4)_5[(MoO_3)_5(PO_4)\ (HPO_4)].3H_2O$	1·991	186	74 JCSIA	1974	941
$(NH_4)_6[Mo_7O_{24}].4H_2O$	1·991	189	75 JCSIA	1975	505
$(NH_4)_6[Mo_7O_{24}].4H_2O$	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 $\Delta\times10^4$	N*	R_0†	r_0‡	m	Correlation coefficient	Goodness of fit ($\times10^3$)
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

† $R=R_0+m\Delta$.

‡ $r=r_0+m\Delta$.

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 α-Li_5GaO_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 $Sr_{0.84}Na_{0.03}\square_{0.13}Al_{1.69}Si_{2.29}O_8$ reported by Grundy & Ito (1974). The mean Sr–O distance in this compound is 0·03 Å greater than in the stoichiometric $SrAl_2Si_2O_8$ (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.* chlorides, 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(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*) $^{IV}Li^+$					
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
$LiAlSi_2O_6$ 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
$Li_2Al_2Si_3O_{10}$	0·40	2·064 (4)	70 ZKKKA	132	118
$LiAlSi_2O_6$ III	0·33	2·068 (5)	68 ZKKKA	127	327
α-Li_5GaO_4	0·00	2·11	71 ACBCA	27	616
$LiAlSiO_4$	0·00	2·11	72 ZKKKA	135	175
(*b*) $^{VI}Na^+$					
Typical	1·00	2·42	Table 1		
$Na_2Fe_2Al(PO_4)_3$ (wyllieite)	0·91	2·533 (6)	74 AMMIA	59	280
$NaSbO_3$	0·82	2·74	74 JSSCB	9	345
$Na_2Fe_2Al(PO_4)_3$ (wyllieite)	0·70	2·723 (6)	74 AMMIA	59	280
$NaAlSi_3O_8$ (high albite)	0·50	2·600 (9)	69 ACBCA	25	1503
$NaAl_{11}O_{17}$ (β-Al_2O_3)	0·35	2·839 (1)	68 ZKKKA	127	94
$NaSbO_3$	0·29	2·65	74 JSSCB	9	345
$Na_{2.58}Al_{21.81}O_{34}$ (β-Al_2O_3)	0·25	2·88	71 ACBCA	27	1826
(*c*) $^{VI}Ag^+$					
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
$Ag_{2.4}Al_{22}O_{34.2}$	0·22	2·83	72 JSSCB	4	60

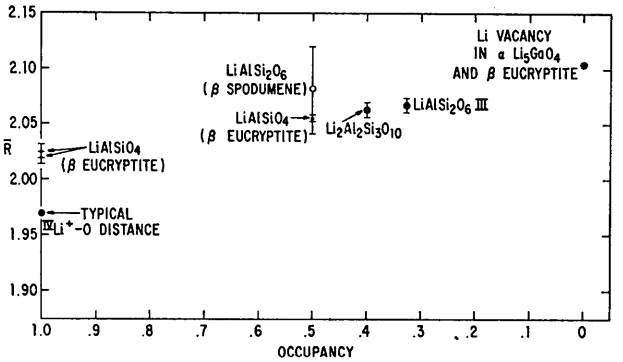


Fig. 6. Mean Li^+–O bond length *vs* partial occupancy.

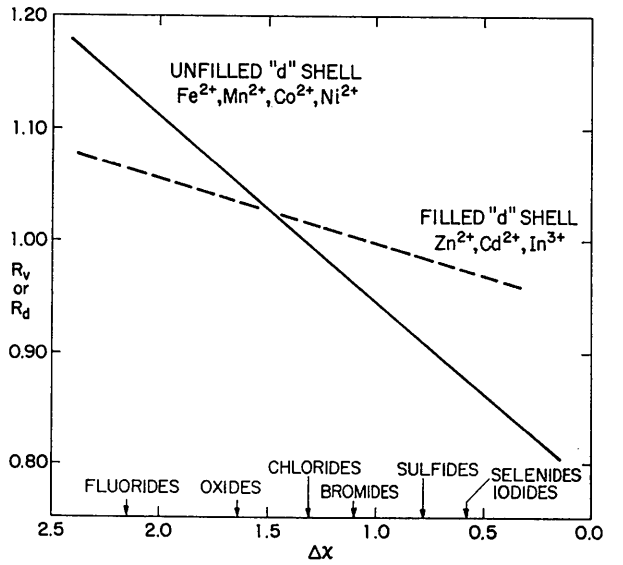


Fig. 7. Covalency contraction parameter, R_v or R_d, *vs* $\Delta\chi$ for filled and unfilled *d* shell cations.

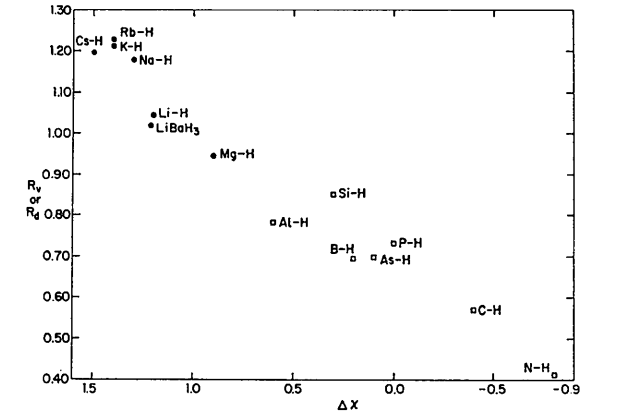


Fig. 8. Covalency contraction parameter, R_v or R_d, *vs* $\Delta\chi$ for hydrides. Solid circles represent ratios of cell volumes of isotypic compounds. Squares represent ratios of the cubed M–H distances to the cubed M–F distances.

dependence of R_v on $\Delta\chi$. For Fe^{2+}-Mg^{2+} the Fe^{2+} fluoride volumes are ~110% of the corresponding Mg^{2+} fluoride volumes whereas the Fe^{2+} sulfide volumes are ~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–$\Delta\chi$ plots for the pairs Cu^+-Li^+ and Ag^+-Na^+ (Shannon & Gumerman, 1975). The Cu^+-Li^+ and Ag^+-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 M^+–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 isotypic fluorides. The results of this analysis are shown in Fig. 8. The solid circles represent volume ratios, $R_v = V(M_mH_n)/V(M_mF_n)$; open squares represent ratios of typical distances $R_d = d(M\text{–}H)^3/d(M\text{–}F)^3$. 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, 1973*b*). 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, 1973*b*), 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-$NaFeO_2$ $\bar{R}=1{\cdot}86$ Å and $\delta=0{\cdot}18$ mm s^{-1} relative to α Fe whereas in $Bi_3(FeO_4)(MoO_4)_2$ $\bar{R}=1{\cdot}909$ Å and $\delta=0{\cdot}282$ 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.* $r(^{VI}V^{3+})=0{\cdot}64$ and $r(^{VI}Cr^{3+})=0{\cdot}615$ 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 $K_4[Re_2O_2(C_2O_4)_4].3H_2O$ (Lis, 1975) of 2·021 (10) Å ($r=0{\cdot}671$ Å) is greater than the estimated mean distance in metallic ReO_2 of 1·99 Å ($r=0{\cdot}63$ Å). Knop & Carlow's (1974) value of $r=0{\cdot}662$ Å derived from cell volumes of the insulating Cs_2ReF_6 phases is consistent with the radius of Re^{4+} from $K_4[Re_2O_2(C_2O_4)_4].3H_2O$. The Re^{5+}–O distance in $Nd_4Re_2O_{11}$ (Wilhelmi, Lagervall & Muller, 1970) of 1·987 (12) Å ($r=0{\cdot}607$ Å) is significantly greater than the distance in metallic $Cd_2Re_2O_7$ (Sleight, 1975) of 1·93 (2) Å ($r=0{\cdot}55$ Å). The radii of 0·58 Å derived from XeF_5RuF_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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