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

By R. D. Shannon

Central Research and Development Department, Experimental Station, E. I. Du Pont de Nemours and Company, Wilmington, Delaware 19898, *U.S.A.*

The effective ionic radii of Shannon & Prewitt [*Acta Cryst.* (1969), B**25**, 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

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* 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 ($+0\cdot030$ Å to $^{IX}La^{3+}$, $^{IX}Ce^{3+}$, $^{IX}Pr^{3+}$, and $^{IX}Nd^{3+}$; $+0\cdot025$ Å to all other Greis & Petzel $^{IX}RE^{3+}$ radii, and $0\cdot015$ 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 $^{VIII}U^{6+}$.

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'	
AC+3	6P 6	VI		1.26	1.12	R
AG+1	4D10	II		.81	.67	
		IV		1.14	1.00	C
		IVSQ		1.16	1.02	
		V		1.23	1.09	C
		VI		1.29	1.15	C
		VII		1.36	1.22	
		VIII		1.42	1.28	
AG+2	4D 9	IVSQ		.93	.79	
		VI		1.08	.94	
AG+3	4D 8	IVSQ		.81	.67	
		VI		.89	.75	R
AL+3	2P 6	IV		.53	.39	*
		V		.62	.48	
		VI		.675	.535	R*
AM+2	5F 7	VII		1.35	1.21	
		VIII		1.40	1.26	
		IX		1.45	1.31	
AM+3	5F 6	VI		1.115	.975	R
		VIII		1.23	1.09	
AM+4	5F 5	VI		.99	.85	R
		VIII		1.09	.95	
AS+3	4S 2	VI		.72	.58	A
AS+5	3D10	IV		.475	.335	R*
		VI		.60	.46	C*
AT+7	5D10	VI		.76	.62	A
AU+1	5D10	VI		1.51	1.37	A
AU+3	5D 8	IVSQ		.82	.68	
		VI		.99	.85	A
AU+5	5D 6	VI		.71	.57	
B +3	1S 2	III		.15	.01	*
		IV		.25	.11	*
		VI		.41	.27	C
BA+2	5P 6	VI		1.49	1.35	
		VII		1.52	1.38	C
		VIII		1.56	1.42	
		IX		1.61	1.47	
		X		1.66	1.52	
		XI		1.71	1.57	
		XII		1.75	1.61	C
BE+2	1S 2	III		.30	.16	
		IV		.41	.27	*
		VI		.59	.45	C
BI+3	6S 2	V		1.10	.96	C
		VI		1.17	1.03	R*
		VIII		1.31	1.17	R
BI+5	5D10	VI		.90	.76	E
BK+3	5F 8	VI		1.10	.96	R
BK+4	5F 7	VI		.97	.83	R
BR-1	4P 6	VI		1.82	1.96	P
BR+3	4P 2	IVSQ		.73	.59	
BR+5	4S 2	IIIPY		.45	.31	
BR+7	3D10	IV		.39	.25	
		VI		.53	.39	A
C +4	1S 2	III		.06	-.08	P
		IV		.29	.15	P
		VI		.30	.16	A
CA+2	3P 6	VI		1.14	1.00	*
		VII		1.20	1.06	*
		VIII		1.26	1.12	*
		IX		1.32	1.18	*
		X		1.37	1.23	C
		XII		1.48	1.34	C
CD+2	4D10	IV		.92	.78	
		V		1.01	.87	
		VI		1.09	.95	
		VII		1.17	1.03	C
		VIII		1.24	1.10	C
		XII		1.45	1.31	
CE+3	6S 1	VI		1.15	1.01	R
		VII		1.21	1.07	E
		VIII		1.283	1.143	R
		IX		1.336	1.196	R
		X		1.39	1.25	
		XII		1.48	1.34	C
CE+4	5P 6	VI		1.01	.87	R
		VIII		1.11	.97	R
		X		1.21	1.07	
		XII		1.28	1.14	
CF+3	6D 1	VI		1.09	.95	R
CF+4	5F 8	VI		.961	.821	R
		VIII		1.06	.92	
CL-1	3P 6	VI		1.67	1.81	P
CL+5	3S 2	IIIPY		.26	.12	
CL+7	2P 6	IV		.22	.08	*
		VI		.41	.27	A
CM+3	5F 7	VI		1.11	.97	R
CM+4	5F 6	VI		.99	.85	R
CO+2	3D 7	IV	HS	.72	.58	
		V		.81	.67	C
		VI	LS	.79	.65	R
			HS	.885	.745	R*
		VIII		1.04	.90	
CO+3	3D 6	VI	LS	.685	.545	R*
			HS	.75	.61	
CO+4	3D 5	IV		.54	.40	
		VI	HS	.67	.53	R
CR+2	3D 4	VI	LS	.87	.73	E
			HS	.94	.80	R
CR+3	3D 3	VI		.755	.615	R*
CR+4	3D 2	IV		.55	.41	
		VI		.69	.55	R
CR+5	3D 1	IV		.485	.345	R
		VI		.63	.49	ER
		VIII		.71	.57	
CR+6	3P 6	IV		.40	.26	
		VI		.58	.44	C
CS+1	5P 6	VI		1.81	1.67	
		VIII		1.88	1.74	
		IX		1.92	1.78	
		X		1.95	1.81	
		XI		1.99	1.85	
		XII		2.02	1.88	
CU+1	3D10	II		.60	.46	
		IV		.74	.60	E
		VI		.91	.77	E
CU+2	3D 9	IV		.71	.57	
		IVSQ		.71	.57	*
		V		.79	.65	*
		VI		.87	.73	
CU+3	3D 8	VI	LS	.68	.54	
D +1	1S 0	II		.04	-.10	
DY+2	4F10	VI		1.21	1.07	
		VII		1.27	1.13	
		VIII		1.33	1.19	
DY+3	4F 9	VI		1.052	.912	R
		VII		1.11	.97	
		VIII		1.167	1.027	R
		IX		1.223	1.083	R
ER+3	4F11	VI		1.030	.890	R
		VII		1.085	.945	
		VIII		1.144	1.004	R
		IX		1.202	1.062	R
EU+2	4F 7	VI		1.31	1.17	
		VII		1.34	1.20	
		VIII		1.39	1.25	
		IX		1.44	1.30	
		X		1.49	1.35	
EU+3	4F 6	VI		1.087	.947	R
		VII		1.15	1.01	
		VIII		1.206	1.066	R
		IX		1.260	1.120	R
F -1	2P 6	II		1.145	1.285	
		III		1.16	1.30	
		IV		1.17	1.31	
		VI		1.19	1.33	
F +7	1S 2	VI		.22	.08	A
FE+2	3D 6	IV	HS	.77	.63	
		IVSQ	HS	.78	.64	
		VI	LS	.75	.61	E
			HS	.920	.780	R*
		VIII	HS	1.06	.92	C
FE+3	3D 5	IV	HS	.63	.49	*
		V		.72	.58	
		VI	LS	.69	.55	R
			HS	.785	.645	R*
		VIII	HS	.92	.78	
FE+4	3D 4	VI		.725	.585	R
FE+6	3D 2	IV		.39	.25	R
FR+1	6P 6	VI		1.94	1.80	A
GA+3	3D10	IV		.61	.47	*
		V		.69	.55	
		VI		.760	.620	R*
GD+3	4F 7	VI		1.078	.938	R
		VII		1.14	1.00	
		VIII		1.193	1.053	R
		IX		1.247	1.107	RC
GE+2	4S 2	VI		.87	.73	A
GE+4	3D10	IV		.530	.390	*
		VI		.670	.530	R*
H +1	1S 0	I		-.24	-.38	
		II		-.04	-.18	
HF+4	4F14	IV		.72	.58	R
		VI		.85	.71	R
		VII		.90	.76	
		VIII		.97	.83	
HG+1	6S 1	III		1.11	.97	
		VI		1.33	1.19	
HG+2	5D10	II		.83	.69	
		IV		1.10	.96	
		VI		1.16	1.02	
		VIII		1.28	1.14	R
HO+3	4F10	VI		1.041	.901	R
		VIII		1.155	1.015	R
		IX		1.212	1.072	R
		X		1.26	1.12	
I -1	5P 6	VI		2.06	2.20	A
I +5	5S 2	IIIPY		.58	.44	*
		VI		1.09	.95	
I +7	4D10	IV		.56	.42	
		VI		.67	.53	
IN+3	4D10	IV		.76	.62	
		VI		.940	.800	R*
		VIII		1.06	.92	RC
IR+3	5D 6	VI		.82	.68	E
IR+4	5D 5	VI		.765	.625	R
IR+5	5D 4	VI		.71	.57	EM
K +1	3P 6	IV		1.51	1.37	
		VI		1.52	1.38	
		VII		1.60	1.46	
		VIII		1.65	1.51	
		IX		1.69	1.55	
		X		1.73	1.59	
		XII		1.78	1.64	
LA+3	4D10	VI		1.172	1.032	R
		VII		1.24	1.10	
		VIII		1.300	1.160	R
		IX		1.356	1.216	R
		X		1.41	1.27	
		XII		1.50	1.36	C
LI+1	1S 2	IV		.730	.590	*
		VI		.90	.76	*
		VIII		1.06	.92	C
LU+3	4F14	VI		1.001	.861	R
		VIII		1.117	.977	R
		IX		1.172	1.032	R
MG+2	2P 6	IV		.71	.57	
		V		.80	.66	
		VI		.860	.720	*
		VIII		1.03	.89	C
MN+2	3D 5	IV	HS	.80	.66	
		V	HS	.89	.75	C
		VI	LS	.81	.67	E
			HS	.970	.830	R*
		VII	HS	1.04	.90	C
		VIII		1.10	.96	R
MN+3	3D 4	V		.72	.58	
		VI	LS	.72	.58	R
			HS	.785	.645	R*
MN+4	3D 3	IV		.53	.39	R
		VI		.670	.530	R*
MN+5	3D 2	IV		.47	.33	R
MN+6	3D 1	IV		.395	.255	
MN+7	3P 6	IV		.39	.25	
		VI		.60	.46	A
MO+3	4D 3	VI		.83	.69	E
MO+4	4D 2	VI		.790	.650	RM
MO+5	4D 1	IV		.60	.46	R
		VI		.75	.61	R
MO+6	4P 6	V		.55	.41	R
		VI		.60	.50	
		VII		.73	.59	R*
		VII		.87	.73	
N -3	2P 6	IV		1.32	1.46	
N +3	2S 2	VI		.30	.16	A
N +5	1S 2	III		.044	-.104	A
		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*
			HS	.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 C
		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 2P 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*
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
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+}

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* 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  754 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 AL4 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 1544 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 IN H+12 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 AMLIA   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 NM4 H2 AS O4
AS+5 VI
  71 CJCHA   49 2539 CL F2 AS F6
  73 JSSCB    6   80 MG8.5 AS3 O16
  70 CJCHA   48 3124 CO8 AS3 U16
  73 ACACO   29  266 CALCULATED
  74 INOCA   13  780 K6 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.X AU O2.XB AU O2
  70 JCSIA 1970 3092 K AU (NO3)4
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 I3
  71 SPHDA   15  802 K BE2 B O3 F2
  71 ACBCA   27  672 ZN B4 O7
  7U ACBCA   26 1189 K B O2
  71 ACBCA   27  904 LI3 B O3
  70 ZKKKA  132  241 CA B3 O5 (OH)
  71 JACGA    4  284 LU B O3
  74 JCPSA   60 1899 MN B4 O7
  74 MRBUA    9 1661 ND AL3 (B O3)4
B +3 VI
  68 ACBCA   24  869 B2 U3 II
  68 ACBCA   26 1703 NA B F4
  69 CLCHA   47 2579 M B F4
  71 ACACA   47  677 CU B2 O4
  71 ACBCA   27 1102 M H4 B F4
  7U ZKKKA  132  241 CA B3 O5 O H
  63 ACCRA   16 1233 NA B (U H)4.2 H2 U
  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
  73 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 NB6 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 CHOCA 268C 1694 BA NI2 AS2 O8
  75 AC6CA   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 ACBCA   28 1899 AL2 BE3 SI6 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 (SI16 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  697 NA2 C O3.H2 O
CA+2 VI
  68 NJMAA 1968   80 CA AL B O4
  69 ACBCA   25 1933 CA NA (H2 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 CR 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 O3 (O)2/2 (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 O1C H2 C O O)2.3 1/2 H2 O
                      CD O1C H2 C O O)2.3 H2 O
  74 JCSIA 1974 1922 CD C13 H5 O5
CD+2 VIII
  55 PRVBA   98  903 CD2 NB2 O7
  69 ACBCA   25 1804 CD (N O3)2.4 O2 U
  74 JCSIA 1974  674 CD C4 H6 O6
CE+3 VIII
  74 ZAACA  403    1 R3 VS V (CE F3)
  74 JCSIA 1974 1165 C4L 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 (CE+4)
CE+4 VIII
  69 INUCA    8   33 IN M+12 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).12 H2 O
CF+3 VI
  74 JINCA   36 2023 R3 VS V (CF2 (S O4)3 )
CL+5 III
  73 MRBUA    8  791 RB CL O3
CL+7 IV
  72 ACBCA   28  839 TMPO CL O4
  32 ZKKKA   84   65 K CL O4
  60 ACCRA   13  855 H U2 CL O4.M CL O4,
                      H CL O4.H2 O,LI CL O4.3 H2 O
  54 JPCHA   63  279 H 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 ACCRA   15 1201 N H4 CL O4
  71 JCSIA 1971 1371 CU (CL0 H9 N3)2 (CL O4)2
  70 ACBCA   26 1928 N2 H5 CL O4
  71 ACBCA   27  898 H CL O4.2 1/2 H2 O
  73 ICHAA    7  477 (C NI2-TRIEN-CU CL O4
  71 ACBCA   27  898 H 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 VII
  67 INUCA    3  327 R (CM+4)
CO+2 IV
  69 ZAACA  369  306 CO V2 O4
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
  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 CCJDA 1968  871 CO (N O3)3
  68 CJCHA   46 3472 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 O4
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 H61.8 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   54 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 ZN4 (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 M4J3 F10
  69 SPHCA   13  930 CS2 BE F4
CS+1 XI
  69 INOCA    8 1665 CS4 M4J3 F10
CS+1 XII
  67 ACCRA   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 ACCRA   10  554 CU CR2 O4
  71 ACIEA   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 H5(C H3)2 C3 O2I2
  66 PRLAA   16  517 CU (C10 H9 O2)2
  67 JCSIA 1967  309 CU (O4 CI2 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 O6 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((C H312 N12 -
                      )P(O12 O)13) (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
  UNPU1              DY I2
DY+2 VII
  UNPU1              DY CL2, DY BR2
DY+2 VIII
  UNPU1              DY CL2
DY+3 VI
  73 MSSSA    3 K446 DY2 O3
DY+3 VIII
  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
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Table 2 (cont.)

```
74 ZAACA  403    1 R3 VS V (DY F3)
ER+3 VI
7u ACBCA  26  484 ER2 S12 07
ER+3 VII
70 SPHCA  15   36 ER2 GE2 07
72 JCMLB   2  197 ER8 U (THD)10 (O H)12
ER+3 VIII
68 CHPLB   2   47 ER P O4, ER V O4
70 INOCA   9 2100 ER (C2 O4) (H C2 O4).3H2 O
70 SSCOA   8 1745 ER3 FE5 012
71 ACSAA  25  372 ER (H U C H2 C O O)3.2H2 O
74 ZAACA  403    1 R3 VS V (ER F3)
72 JCMLB   2  197 ER8 U (THD)10 (O H)12
ER+3 IX
59 ZKKKA 112  362 EK (C2 H5 S O4)3.9H2 O
74 ZAACA  403    1 R3 VS V (ER F3)
EU+2 VI
70 ZAACA  374  201 LI EU3 O4
EU+2 VII
70 ZAACA  374  201 LI EU3 O4
69 ACBCA  25 1104 EU I2
73 REF 3              LI2 EU5 08
EU+2 VIII
       UNPUI          EU FZ, EU 8RZ
EU+2 IX
73 RVCMA  10   7? EU CL2
       UNPUI          EU F2
EU+2 X
71 NATWA  58  218 EU2 SI 04
EU+3 VII
68 REF 4              EU4 AL2 09
70 ZAACA  374  201 LI EU3 O4
73 REF 3              LI2 EU5 08
EU+3 VII
68 REF 4              EU4 AL2 09
73 REF 3              LI2 EU5 08
EU+3 VIII
68 JCPSA  48 1094 EU3 FE2 GA3 012
74 ZAACA  403    1 R3 VS V (EU F3)
73 ACSAA  27 2827 EU2 (C3 H2 O4)3.8H2 O
EU+3 IX
74 ZAACA  403    1 R3 VS V (EU F3)
73 ACSAA  27 2827 EU2 (C3 H2 O4)3.8H2 O
71 ACSAA  25 3347 EU TRISGLYCOLATE
FE+2 IV SQ  HS
74 AMMIA  59 1166 BA FE SI4 010
FE+2 IV   HS
69 SCIEA 166 1399 (NA,K)2 FE4 S112 030.H2 O
69 ZAACA 369  306 FE V2 O4
71 JUPSA  31  452 FE2 TI O4
72 JUPSA  33 1296 FE2 MO O4
FE+2 VI  LS
69 ACBCA  25  925 R VS A (FE S2)
FE+2 VI   HS
69 NJMMA 1969  430 FE AL2 (P O4)2 (O H)2 (O H2)6
                     .2H2 O
70 BUFCA  93  190 FE S O4
71 SPHCA  15  999 FE3 BE S13 09 (F,O H)2
67 ACCRA  22  775 FE (NH4)2(S O4)2.6H2 O
68 CIMYA  68  290 LI FE P O4
74 AMMIA  59  486 FE2 SI O4
FE+2 VIII
71 AMMIA  56  791 GARNETS
71 ZKKKA 134  333 FE3 AL2 SI3 012
73 ACACB  29  266 CALCULATED
FE+3 IV   HS
70 ACBCA  26 1469 CA2 FE2 05
70 SSCOA   8 1745 M3 FE5 012
71 ACBCA  27 1263 BA FE2 O4
71 MRBUA   6  725 BA CA FE4 08
71 ACSAA  25 3616 CA2 FE2 05
73 ACBCA  29  832 BA FE2 O4
FE+3 V
71 JSSCB   4    1 FE V O4
FE+3 VI   HS
70 ACBCA  26 1469 CA2 FE2 05
70 SSCOA   8 1745 M3 FE5 012
71 SSCOA   9  335 K FE F4
71 JSSCB   4    1 FE V O4
71 JPCSA  32 1315 B1 FE O3
71 ACSAA  25 3616 CA2 FE2 05
67 ACCRA  23  239 FE (C5 H7 O2)3
69 CCJDA 1969  440 FE (C7 H5 O2)3
FE+3 VIII
73 JSSCB   8  331 ESTIMATED
FE+4 VI
73 JSSCB   8  331 R3 VS V (PEROVSKITES)
                   R3 VS V (SR FE O3)
FE+6 IV
73 JSSCB   8   43 K2 FE O4
                   R3 VS V (K2 FE O4)
GA+3 IV
71 ACBCA  27  616 LI5 GA O4
75 ACBCA  31  560 SR GA2 S12 08
GA+3 VI
74 ACBCA  30 1364 C15 H21 O6 GA
GD+3 VII
70 ACBCA  26  484 GD2 S12 07
72 SPHCA  28   60 GD2 MO3 012
72 SPHCA  16  790 GD2 GE2 O7
69 IVNMA   5 1823 GD9.33 S16 026
72 JSSCB   5  266 GD9.33 S16 026
GD+3 VIII
71 SPHCA  15  926 NA GD SI O4
72 SPHCA  16  790 GD2 GE2 O7
74 ZAACA  403    1 R3 VS V (GD F3)
GD+3 IX
72 SPHCA  16  790 GD2 GE2 O7
69 IVNMA   5 1823 GD9.33 S16 026
74 ZAACA  403    1 R3 VS V (GD F3)
GE+4 IV
68 ZKKKA 126  299 CO GE O3
69 SCIEA 165  586 MN2 GE O4
69 ZKKKA 129  427 MN3 FE2 GE3 012
72 JSSCB   2  612 MG28 GE10 O48
71 SPHCA  15  924 NA SM GE O4
70 ACSAA  24 1287 NA4 SN2 GE4 012 (O H)4
67 ACSAA  21 1281 NA8 SN4 GE10 030 (O H)4
70 MOCMB 102  964 NA2 GE O3
71 SPHCA  17  244 CO GE O3
72 MOCMB 103 1560 GE5 O (P O4)6
GE+4 VI
70 SSCOA   1  557 CA2 GE O4
70 JSSCB   2  612 MG28 GE10 O48
72 MOCMB 102 1245 K2 GE4 O9
71 ACACA  27 2133 GE O2
72 AMMIA  57   62 MN2 GE O4 DELTA
72 ZKKKA 136  387 GE.10 MI P O4
72 MOCMB 103 1560 GE5 O (P O4)6
H+1 I
57 JMOSA   1   43 T F
56 JCPSA  25  275 H F
HF+4 IV
75 JSSCB  13  275 R3 VS V (M4 HF O4)
HF+4 VII
70 JACTA  53  126 HF O2
69 ACSAA  23 3541 HF (O H)2 S O4.H2 O
74 ACSAA  27 3467 HF4 (DH)8 (CH O4)4.H2 O
HF+4 VIII
73 ACSAA  27 2455 HF (O H)2 S O4
HG+1 VI
71 CCJDA 1971  466 HG2 F2
HG+2 II

73 ACBCA  29  869 HG MO O4
HO+3 VIII
74 ACBCA  30 2049 K HO BE F6
70 SSCOA   8 1745 HO3 FE5 012
72 BUFCA  95  437 HO P5 014
74 ZAACA  403    1 R3 VS V (HO F3)
HO+3 IX
74 ZAACA  403    1 R3 VS V (HO F3)
74 ACBCA  30 2613 HO(C2 H5 S O4)3.9H2 O
HO+3 X
74 INOCA  13 2535 HO(H2 O)4 (H C O3)3.2H2 O
75 CJCHA  53  83L (N O)2(HO(N O3)5)
I+5 III
71 JCPSA  54 2556 N H4 I O3
66 ACCRA  20  758 LI (I O3)
66 ACCRA  21  841 LI I O3
58 ACCRA   9 1015 CE (I O3)4
58 ACCRA  11  794 CE (I O3)4.H2 O
43 RTCPB  62  729 N H4 I O3
I+5 VI
71 JCPSA  54 2556 N H4 I O3
I+7 IV
70 ACBCA  26 1782 NA I O4
26 ZEPYA  39  308 K I O4
71 JCSIA 1971 1857 II+7J-U
I+7 VI
66 ACCRA  20  765 H5 I U6
65 ACCRA  19  629 K4 H2 I2 O10.8H2 O
37 JACSA  59 2036 (N H4)2 H3 I U6
IN+3 IV
74 ZAACA  409   97 RB2 IN4 O7
73 ZAACA  395  280 SR2 IN2 O5
IN+3 VI
74 ZAACA  409   97 RB2 IN4 O7
61 ACSAA  15 1437 IN O H S O4.(H2 O)2
68 ACBCA  24  388 CU2 IN2 O5
70 ACSAA  24 1662 IN O O H
69 INOCA   8 1985 IN2 O3
74 ACBCA  30 1882 NA IN SI2 O6
74 SPHDA  18  761 IN2 GE2 O7
IR+4 VI
71 JSSCB   3  174 SR IR O3
IR+5 VI
74 MRBUA   9 1177 R3 VS V (CO2 IR2 O7)
K+1 IV
68 ZAACA 358  241 K AG O
       REF 2           K2 O
K+1 VI
51 ZAACA 264  144 K SB F6
68 SPHDA  12 1095 K Y MO2 08
69 CCJDA  11  606 K2 ZR2 O5
69 ACBCA  25 1919 K U2 F9
K+1 VII
68 CJCHA  46  935 K2 CR2 O7
69 JCSIA 1969  849 K2 MO O4
71 SSCOA   9  335 K FE F4
K+1 VIII
30 ZKKKA  74  306 K H2 P O4
62 ZKKKA 117  411 K2 TI6 O13
37 ZKKKA  98  266 K H2 (M3 O) 85 010
71 INUCA   7  873 K H C2 O4
68 CJCHA  46  935 K2 CR2 O7
70 JCSIA 1970 3092 K AU (N O3)4
65 ACCRA  19  629 K4 H2 I2 O10.8H2 O
K+1 IX
70 ZKKKA 132   27 K1.4 NA5.5 CAO.3 AL7.5
                    L18.5 O32
69 ACBCA  25  600 K CE F4
69 ACBCA  25 1919 K U2 F9
K+1 X
73 CJCHA  51 2613 K AL P2 O7
K+1 XII
68 SPHCA  13  420 K Y W2 08
71 INOCA  10 1264 K2 PB CU (N O2)6
67 INOCA   5  514 K2 BA CO (N O2)6
74 JACSA  96 6606 K2 CA CU (N O2)6
75 ACBCA  31  596 K2 BA CU (N O2)6
57 PISAA  56  143 K CL O4
LA+3 VI
69 ZAACA 259  259 CU LA O2
73 MRBUA   8 1269 R3 VS V (RE2 W3 O12)
LA+3 VIII
74 AMMIA  59 1277 LA4 MG2 TI3 SI4 022
73 ACBCA  29 2074 LA2 MO3 012
68 INOCA   7 2295 LA (C5 H7 O2)3 (H2 O)2
74 ZAACA  403    1 R3 VS V (LA F3)
74 SPHCA  18  675 LA2 SR3 (B O3)4
LA+3 IX
71 MRBUA   6   23 LA FE O3
74 ZAACA  403    1 R3 VS V (LA F3)
74 AMMIA  59 1277 LA4 MG2 TI3 SI4 022
LI+1 IV
39 ZKKKA 1G2  119 LI O H.H2 O
70 ZAACA 379  157 LI2 CU O2
70 INOCA   9 1096 YB LI F4
71 AMMIA  56   18 NA3 AL2 LI3 F12
71 ACBCA  27  616 LI5 GA O4
73 JSSCB   6  538 LI3 V O4
73 ACBCA  29 2625 LI (N2 H5) BE F4
73 ACBCA  29 2628 LI H N3 O H S O4
64 ACCRA  17  783 LI2 C2 O4
74 ACBCA  30 2434 LI2 BE SI O4
LI+1 VI
68 ACBCA  24  225 LI3 AL F6
69 ZAACA 371  306 LI2 ZR O3
70 ZKKKA 132  118 LI2 AL2 SI3 O10
71 MRBUA   6  555 LI2 MO F6
65 ACCRA  19  561 LI C6 07 H7
74 ACIEA  86  819 LI NB O2
68 CIMYA  68  290 LI FE P O4
74 ACSAA  25 3337 LI M3 08
73 CJCHA  51  265 LI V O3
73 ACBCA  29 2294 LI2 ZR F6
LU+3 VI
70 ZAACA 377   70 CA LU2 O4
74 ZAACA  403    1 R3 VS V (LU F3)
LU+3 VIII
74 ZAACA  403    1 R3 VS V (LU F3)
LU+3 IX
74 ZAACA  403    1 R3 VS V (LU F3)
MG+2 IV
72 ACBCA  28  267 K2 MG5 SI12 U30
32 ACCRA   5  684 MG AL2 O4
72 ACBCA  28 3583 MG2 FE3 NA16 015
74 ACBCA  30 2667 K6 MG U4
MG+2 V
68 ACSAA  22 1966 MG3 P2 08
66 NJMMA 1966  142 MG B4 O7
       UNPU3          MG3 P2 08
       UNPU3          MG2 P2 07
MG+2 VI
65 CJCHA  43 1139 MG2 P2 O7
63 BAPCA  11  361 MG2 AS2 O7
70 ACBCA  26 1429 MG M H4 P O4
71 CJCHA  49 1630 MG3 V2 O8
69 INOCA   8 1665 CS4 MG3 F10
72 AMMIA  57   65 MG SI O3
69 SPHCA  13  933 MG N O4
70 JSSCB   2  612 MG28 GE10 O48
65 NNLMO 1965  196 MG AL B O4
74 INOCA  13 2715 R3 VS V (MG2 SI O4).H2 O
71 ACBCA  27  815 MG3 TE O6
68 ACSAA  22 1466 MG3 P2 O8
70 REF 1            CA MG SI O4

74 ACBCA  30 2491 MG2 V2 O7
71 AMMIA  56 1553 MG (B6 O7 (O H)6).2H2 O
73 AMMIA  58 1029 MG C O3
74 CJCHA  52 1155 CA18 MG2 H2 (P O4)14
70 INOCA   9  181 MG (OMPA)3 (CL O4)2
72 CJCHA  50 3619 MG V2 U6
73 ACBCA  29 2611 MG3 AS2 08
MG+2 VIII
73 ACACB  29  266 CALCULATED
MN+2 IV   HS
70 AMMIA  53 1489 MN7 S8 AS 012
69 ZAACA 369  306 MN V2 O4
71 ACBCA  27 1044 MN CO CR O4
69 PHSSA  32  K91 MN CR2 O4
73 ACACB  29  266 CALCULATED
MN+2 V   HS
68 AMMIA  53 1841 MN2 O H AS O4
74 MPRTA  21  246 MN2 AS O4 OH
MN+2 VI  LS
69 ACBCA  25  925 R VS O ELECTRONS
MN+2 VI   HS
69 SCIEA 165  586 MN2 GE U4
69 JCPSA  51 4928 BA MN F4
70 ZKKKA 132    1 MN5 (O H)2 S12 O8
69 AMMIA  54 1312 MN FE2 (P O4)2 (OH)2.8H2 O
70 NJMIA 113    1 MN7 NA12 (S O4)13.15H2 O
65 ACCRA  19  854 MN S O4
72 AMMIA  57  621 MN2 GE O4
67 PRLAA  92  125 MN N C O3
67 HCACA  50 2023 MN5 08
MN+2 VII
72 AMMIA  57  621 MN2 GE O4
MN+2 VIII
69 ZKKKA 129  427 MN3 FE2 GE3 012
71 AMMIA  56  791 GARNETS
73 SSCOA  12  109 MN3 AL2 GE3 012
74 JCPSA  60 1899 MN B4 O7
MN+3 VI   HS
67 ACSAA  21 2871 MN2 O3
67 ZKKKA 124  428 MN2 O3
68 ACBCA  24 1233 MN O O H
69 JCPSA  50 1066 (N M412 MN F5
63 PHSSA   3 K446 MN2 O3
68 BUFCA  91  339 T8 MN O3, PR MN O3, ND MN O3
71 JSSCB   3  238 LA MN O3, MM3 O4,
                    LA.95 CA.05 MN O3
73 JSSCB   6   16 NA MN7 O12
74 AMMIA  59  985 MG2 MN B 05
68 ACBCA  24 1114 NA4 MN4 TI5 O18
74 INOCA  13 1854 MN (C7 H5 O2)3.1/4 C6 H5 CH3
74 INOCA  13 1864 MN (ACAC)3
MN+4 IV
75 JSSCB  13  275 R3 VS V (M4 MN O4)
MN+4 VI
73 JSSCB   8  234 BA MN O3
69 INOCA   8  335 NA12 MN NB12 038.50H2 O
63 CZYPA  13  398 NA7 H4 MN (I O6)3.17H2 O
67 HCACA  50 2023 MN5 08, CO2 MN3 08
MN+6 IV
72 ACBCA  28 2845 K2 MN O4
MN+7 IV
68 ACBCA  24 1053 AG MN O4
MU+3 VI
69 ACBCA  25  400 KJ MO CL6
69 INOCA   8 2694 K3 MO F6
MO+4 VI
71 MRBUA   6  555 LI2 MO F6
MO+5 VI
74 INOCA  13 2715 R3 VS V (RE MO O4)
MO+5 VI
71 INOCA  10  922 BA2 ND MO O6
MO+6 IV
68 JCPSA  48 2619 CU MO O4
68 SPHDA  12 1095 K Y MO2 08
69 JCSIA 1969  849 K2 MO O4
72 ACBCA  28   60 GU2 MO3 O12
69 JCPSA  50   86 ND2 MO3 012
71 SPHCA  15  611 LI3 FE MO3 012
72 SPHCA  15  829 K AL MO2 08, K FE MO2 08
72 JCPSA  55 1093 CA MO O4, SR MO O4
73 ACBCA  29 2074 LA2 MO3 012
71 JCSIA 1971 1857 MOI+61 -0
MO+6 V
67 CCJDA 1967  374 K2 MO3 O10
69 JCSIA 1968 1398 K2 MO3 010
MO+6 VI
68 JCSIA 1968 1398 K2 MO3 010
70 JSSCB   1  484 AG6 MO10 033
70 INOCA   9 2228 NA3 (CR MO O6 O24 H6).8H2 O
70 ACSAA  24 3711 LI MO O2 AS O4
66 ACSAA  20 2698 MO F6 (GAS)
70 CCJDA 1970  350 MO (O H)2 O)2
72 ACBCA  28 2222 MO O3.2H2 O
64 INOCA   3 1603 K2 (MO O2 (C2 O4) H2 O)2 O
73 ACBCA  29  869 HG MO O4
74 ACBCA  30 1795 MO 039H2 O
N-3 IV
       REF 6          MG3 N2,SI3 N4,B N3TI N
N+5 III
       REF 6          NH4 N O3,NA N O3,K N O3,
                      BAIN O3I2,TIIN O3I4
NA+1 IV
74 ZAACA  409   69 NA6 ZN O4
       REF 2          NA2 O
NA+1 V
68 ACBCA  24 1077 NA2 S12 05
68 SPHDA  12  987 NA2 ZN2 S12 07
64 ZAACA 329  110 NA2 HG O2
NA+1 VI
70 ACSAA  24 1287 NA4 SN2 GE4 012 (O H)4
65 ACCRA  19  561 NA C6 O7 H7
73 ACCRA  14 1233 NA B (OH)4.2H2 O
60 ZKKKA 113  430 NA2 AL2 SI3 010.2H2 O
58 ZKKKA 111  241 NA CL O3
56 ACCRA   9  811 (NA AS O3)X
53 ARKEA   8   77 NA S8 F*
59 ACCRA  12  526 NA U ACETATE
30 ACBCA  31  890 NA2 C O3.H2 O
NA+1 VII
71 SPHCA  15  926 NA GD SI O4
70 NJMIA 113    1 MN7 NA12 (S O4)13.15H2 O
73 ACBCA  29  890 NA2 CR2 O7 ALPHA
NA+1 VIII
68 ACBCA  24 1703 NA B F4
68 SPHDA  12  987 NA2 ZN2 S12 07
74 AMMIA  56   18 NA3 AL2 LI3 F12
NA+1 XII
71 JSSCB   3   89 NA13 NB35 O94
32 ZKKKA  81  135 NA AL SI O4
NB+3 VI
74 ACIEA  86  819 LI N8 O2
NB+4 VIII
78 JACSA  97 2713 NB(DPM)4
NB+5 VI
68 JCPSA  48 5048 BA27 SR7.5 NB2 05.78
70 JSSCB   1  419 M -NB2 05
70 JSSCB   1  454 NA2 NB4 O11
70 AMMIA  55   90 CA NB2 O6
55 PRVAA  98  903 CD2 NB2 O7
71 JSSCB   3   89 NA13 NB35 O94
73 ZAACA 380  119  MN NB2 O6
74 JINCA  36 1965 CA2 NB2 O7
71 JCSIA 1971 1280 B13 NB17 O47
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Table 2 (cont.)

```
70 ACBCA    26  105 BA3 SI4 NB6 O26
71 ACSAA    25 3347 LI NB3 O8
59 SPHCA     4  796 IY, YB1 NB O4
73 JSSCB     8  150 BI NB O4
66 ACSAA    20   72 NB P O5
74 BUFCA    97    3 NA3 NB O4
NB+5 VII
71 JSSCB     1  454 NA2 NB4 O11
71 JSSCB     3   89 NA13 NB95 O94
71 ACBCA    27 1610 (NH413 NB O (C2 O413.H2 O
75 ACBCA    31  673 NB2 O5
NO+2 VIII
  UNPUI               NO I2
NO+2 IX
  UNPUI               NO CL2, NO BR2
ND+3 VI
71 INOCA    10  922 BA2 ND MO O6
74 MRBUA     9 1661 ND 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 T12 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 ACCCA    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 O H C O3
74 AMMIA    59 1277 ND4 MG2 T13 SI4 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 (DPM12
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 F412
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 PHSSA   438  125 NI (O H12
70 REF 1            NI2 SI O4
64 ACCRA    17 1481 NI (C5 H7 O212.2H2 O
73 ACBCA    29 2741 NI SI F6.6H2 O
63 ZKKKA   118  291 NI (H C O O12.2H2 O
74 JCPSA    61  852 NI C4 O4.2H2 O
73 JCMLB     3  181 NI (C5 H7 O212.(C2 H5 O H12
73 ACBCA    29 2304 NI3 V2 O8
NI+3 VI  LS
74 ZAACA   405  167 M2 M7 NI F6
71 CHOCA   272 2163 HQ NI O3
NI+3 VI  MS
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 JACBA    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-11=R(F-11+.04
OH-1 III
71 AMMIA    56 1155 MG6.6 FE.4 SI3 O12 F O H,
                    R(OH-1)=R(F-11+.04
OH-1 IV
                    R(OH-1)=R(F-11+.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    28 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 O412 (O H15.H2 O
69 ZKKKA   130  148 K ZR2 (P O413
71 ACBCA    27 2124 NA3 P O4.12H2 O
68 ACBCA    22 1822 NA ZR2 P3 O12
68 ZKKKA   127   21 AL3 P2 O8.5H2 O
68 CINYA    68  290 LI FE P O4
70 ACBCA    26 1826 H3 P O4
72 AMMIA    57   45 MN.65 FE.35 P O4
72 ACUCA    28 2065 (N MH12 H P O4
73 ACBCA    29  141 LU P O4
71 ACBCA    27 2247 CA (H2 P O412.H2 U
73 ACBCA    29 2292 AL P O4.2H2 O
71 ACSAA    25  512 K H5 (P O412
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 CCJDA  1972  676 ET3 N H H (C6 H4 O213 P
73 ACACB    29  266 CALCULATED
PA++ VI
67 INUCA     3  327 R (PA++1
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
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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 CJCHA    51   70 PB2 V2 O7
72 MRBUA     7 1025 BI TITANATES
PB+2 IX
67 ACCRA    22  744 PB F2
73 CJCHA    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 O312
                   R3 VS V (BA S O4)
70 ZKKKA   132  228 PB3 P2 O8
71 INOCA    10 1264 K2 PB CU (N O216
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 CH1C O1212
68 JSTCA     9  166 PD ((C6 H512 CH C2 O212
PD++ 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++ VII
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 O121
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 O413.9H2 O
74 ZAACA   403    1 R3 VS V (PR F3)
PR++ VI
72 ACBCA    28  956 BA PR U3
75 ACBCA    31  971 PR7 O12
73 JSSCB     8  331 R (PR++)
74 CJCHA    52 2175 R3 VS V
PT+2 IV SQ
72 REF 5            PT3 CD O6
PT++ VI
69 JINCA    31 3803 PT O2
                   R3 VS V (M2 PT2 O71
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+31
PU++ 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 O312
RE++ VI
68 INOCA     1  108 LA4 RE6 O19
74 CJCHA    52 2175 R3 VS V
RE+5 VI
70 ACSAA    24 3406 ND4 RE2 O11
  UNPU2            CO2 RE2 O7
68 ACBCA    24  874 RE 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 H212
71 JCSIA  1971 1857 RE(+71 -O
70 CJCHA    48  219 (RE2 (N-C4 H7 O212) (RE O412
RE+7 VI
68 ACIEA     7  295 RE2 O7 (H2 O12
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 O31
RU++ 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            K3 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 U
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 H4 H S O4
70 NJMIA   113    1 MN7 NAI2 (S O413.15H2 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 ACUCA    28 2845 K2 S O4
73 JSTCA    14  499 TL2 S O4
74 ACUCA    3U  921 CA S O4.2H2 O
74 NJMIA   121  208 FE2 (S O413
S+6 VI
73 ACACB    29  266 CALCULATED
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SB+3 IV
70 ACSAA    24  320 SB P O4
SB+5 VI
70 AMMIA    55 1489 MN7 SB A5 O12
71 JCSIA  1971  942 AS SB F8
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 (C5 H7 O213
73 ACBCA    29 2615 NA SC SI2 O6
74 INOCA    13  158 SC (C7 H5 O213
73 ACSAA    27 2841 SC U M (C3 H2 O41.2H2 O
69 SPHOA    14    9 NA3 SC SI2 O7
SC+3 VIII
74 INUCA    10  137 SC H (C7 H5 O214
72 ACSAA    26 1337 SC2 (C2 O413.6H2 O
74 INOCA    13 1886 H SC (C7 H5 O214
74 INOCA    13 1880 H SC (C7 H5 O214
SE+6 VI
68 ZAACA   358  125 MN SE O4, CO SE O4, NI SE O4
51 JCSIA   217  168 H2 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 H314 SE O4
71 JSCIA  1971 1857 SE(+61 -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 (U HI2 SI2 O8
5B ACCRA    11  437 CA3 AL2 SI3 O12 (GROSSULARITE)
71 AMMIA    56  193 CU2 CA2 SI3 O10.2H2 O
71 SPHCA    15  926 NA GU SI O4
71 SPHCA    15  806 Y2 SI O5
71 NATWA    58  218 EU2 SI O4
70 PEPIA     3  161 CU2 SI O4
70 ACBCA    26  105 BA3 SI4 NB6 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 G6
                    CA MG SI2 O6
69 MSAPA     2   95 FE6.1 MN.1 MG.8 CA.1 SI8
                    O22.1 (OH11.4 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 OT (C O312
71 ACBCA    27 2269 NA2 SI O13.6H2 O
72 SPHCA    16 1021 BE2 SI O6
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 H16.12H2 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 O313.9H2 O
70 SPHCA    15  214 SM2 SI2 O7
74 INOCA    13  290 N H4 SM (S O412.4H2 O
74 ZAACA   403    1 R3 VS V (SM F3)
SM+3 XII
72 JSSCB     4   11 SM AL O3
SN+4 VI
75 ACBCA    31  511 K4 SN O4
72 JCSIA  1972 2448 R3 VS V (NA4 SN O41)
73 ACACB    29  266 CALCULATED
SN++ V
70 AMMIA    55  367 SN TA2 O7
70 JSSCB     2  410 K2 SN O3
SN++ VI
69 ZAACA   368  248 LI8 SN O6
70 ACSAA    24 1287 NA4 SN2 GE4 O12 (O H12
74 CJCHA    52 2175 R3 VS V
SN+4 VIII
67 JCSIA  1967 1949 SN (N O314
SR+2 VI
70 ZAACA   379  113 SR CU2 O2
72 ZAACA   393  266 SR AG6 O4
SR+2 VIII
68 ZAACA   358  138 SR Y2 O4
71 ACPSA    55 1093 SR MO O4, SR W O4
71 AMMIA    56  758 SA C O3
71 ACBCA    27 2429 SR (H C O O12.2H2 O
74 SPHCA    18  S75 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 (1 O312.H2 O
72 ACBCA    28 3668 SR5 (P O413 O H
74 SPHCA    18  675 LA2 SR3 B4 O12
SR+2 X
70 AMMIA    55 1911 SR CA B14 O20 (O H16.5H2 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 IK O3
71 NJMMA  1971  241 SR AL3 (P O412 (O H15.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
70 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 VII
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 T8 O3
TC+5 VI
67 STBGA     3     1 R3 VS V (FLUORIDES)
TC+7 IV
69 ACIEA     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 K 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
66 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 CHDBA   267  1435 CUZ 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 H2 TE O6
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   879 K5 TH F9
71 ACBCA    27  2290 K7 TH6 F31
74 ICHAA     8   273 K TH P3 O10
TH+4 IX
68 CCJDA  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 N2 H6 TI F6
71 JSSCB     3   340 TI4 O7
70 ACACB    26   336 BA TI O3
64 ACCRA    17   240 CO TI O3
72 CSCMC     1     1 BA TI6 O13
72 ZKKKA   136   273 TI O2
74 ZKKKA   139   103 K TI P O5
74 INOCA    11  2989 (TI OICS H7 O2)2I2
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   390   113 SR4 TL2 O7
74 ZAACA   405   197 BA2 TL2 O5
TL+3 VI
68 ZKKKA   143   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 VII
       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   460 CS U2 F9
74 ACBCA    30  1966 B - NH4 U F5
U+5 VI
67 ACCRA    23   865 CS U F6
70 JINCA    32  3701 NA U O3
65 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 CA U O4, BA U O4, CA2 U O5,
                     SR2 U O5, CA3 U O6,SR3 U O6
66 JOPQA    27   726 MN U O4
62 JOPQA     3   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   306 M V2 O4
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 ACSAA    25  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 JACTA    21   590 MN2 V2 O7
71 ZKKKA   131   161 BA3 (V O4)2
71 JSSCB     3   458 NO 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
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   518 LI3 V O4
72 CJCHA    50  3944 CU3 V2 O8
73 CJCHA    51    70 PB2 V2 O7
73 CJCHA    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
71 ACSAA    25  2491 MG2 V2 O7
73 ACBCA    29   567 HG2 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
71 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 ALZ (W O4)3
W+6 VI
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 LI2 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 O6
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(C6H5COCHCOCH3)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 MO2 O8
70 ZKKKA   131   278 Y2 TI2 O7
67 ACCRA    23   939 Y TA O6
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 INOCA     8    29 YB (C5 H7 O2)3 (H2 O) 1/2 C6 H6
YB+3 VIII
70 SPHCA     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 (OPN)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 O6
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 (K4 ZR O4)
ZR+4 V
69 CCJDA  1969   727 K2 ZR O3
70 JSSCB     2   410 K2 ZR O3
ZR+4 VI
69 ACBCA    25  2650 ZR (H 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  2294 LI2 ZR F6
71 ACBCA    27  1944 RB5 ZR4 F21
74 CJCHA    52  2175 R3 VS V
ZR+4 VII
75 ACBCA    25  2164 NA2 ZR F6
70 ACBCA    26   417 (N H4)3 ZR F7
70 JACTA    53   126 ZR O2
73 ACBCA    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 N2 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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REF 1  G. E. BROWN, PH.D. THESIS, VIRGINIA
       POLYTECH.INST.,UNIV.MICROFILMS,74-498
REF 2  R.W.G.WYCKOFF,CRYSTAL STRUCTURES,WILEY,
       N.Y.,1965
REF 3  H.BARNIGHAUSEN ET AL.,PROC.10TH R.E.
       RES.CONF.,CAREFREE,ARIZ(1973)P.490
REF 4  C.BRANDLE+H.STEINFINK,PROC.7TH R.E.
       RES.CONF.,CORONADO,CAL.OCT 28,1968
REF 5  R.D.SHANNON,U.S.PAT.3663181,MAY16,1972
REF 6  W.H.BAUR,NITROGEN,HANDBOOK OF GEOCHEM.
       SPRINGER-VERLAG,N.Y.1974
REF 7  A.W.SLEIGHT,U.S.PAT.3849544,NOV 19,1974
UNPU1  H.BARNIGHAUSEN,PERSONAL COMMUNICATION
UNPU2  A.W.SLEIGHT,PERSONAL COMMUNICATION
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.
CHDBA  C. R. HEBD. SEAN. ACAD. SCI. SER. B
CHDLA  C. R. HEBD. SEAN. ACAD. SCI. SER. C
CHPLB  CHEM. PHYS. LETT.
CIHYA  CARNEGIE INST. WASH. YEARBOOK
CJCHA  CAN. J. CHEM.
CSCMC  CRYST. STRUCT. COMMUN.
CZYPA  CZECH. J. PHYS.
DANKA  DOKL. AKAD. NAUK. SSSR
HCACA  HELV. CHIM. ACTA
ICHAA  INORG. CHIM. ACTA
INOCA  INORG. CHEM.
INOMA  RUSS. J. INORG. CHEM.
INUCA  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. CHEM.
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
PHRVA  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.
ZEPYA  Z. PHYS.
ZENBA  Z. NATURF.
ZKKKA  Z. KRISTALLOGR.
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.

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 $1\cdot61$ Å, between that of Rb^+ ($1\cdot52$ Å) and Cs^+ ($1\cdot67$ 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: $2\cdot08$ (Pauling, 1960); $1\cdot40$ (Gibb, 1962); and $1\cdot53$ 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 $r(^{VI}H^-)=1\cdot40$ Å if corrected for cation and anion coordination. The value of $r(^{IV}H^-)$ was taken to be $1\cdot22$ 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.

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* 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.

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	

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 $r(^{VI}O^{2-}) = 1\cdot40$ Å. The other set is based on $r(^{VI}O^{2-}) = 1\cdot26$ and $r(^{VI}F^{-}) = 1\cdot19$ 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
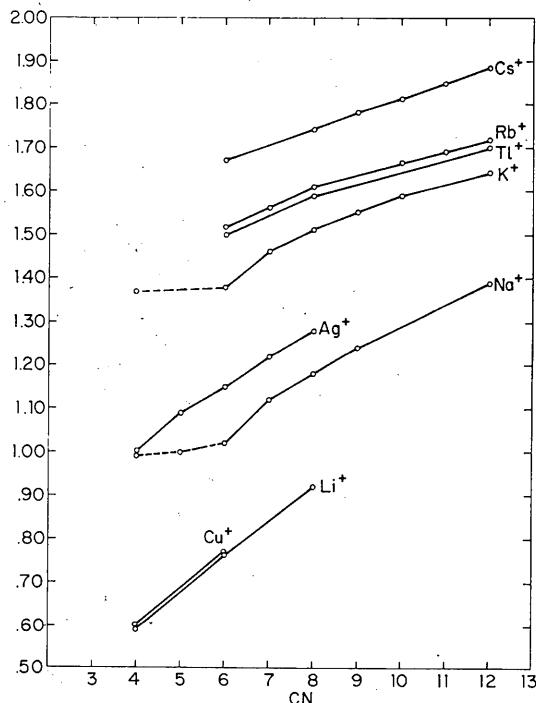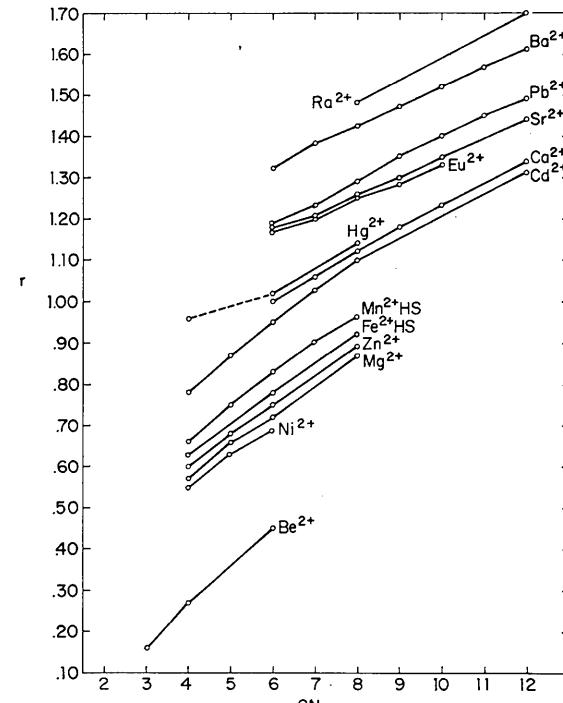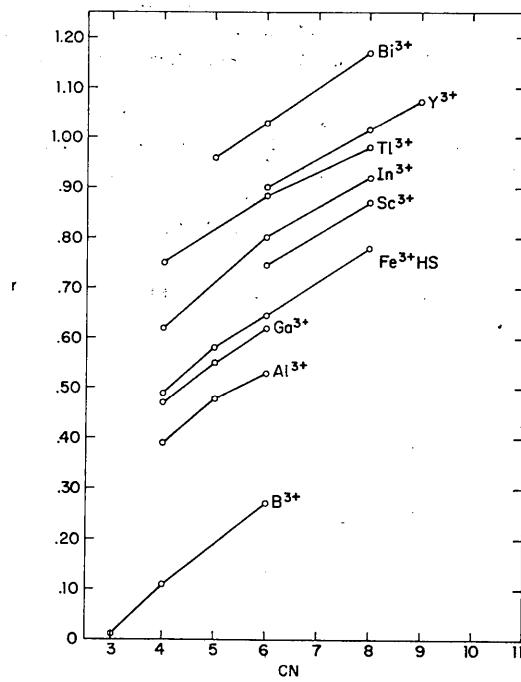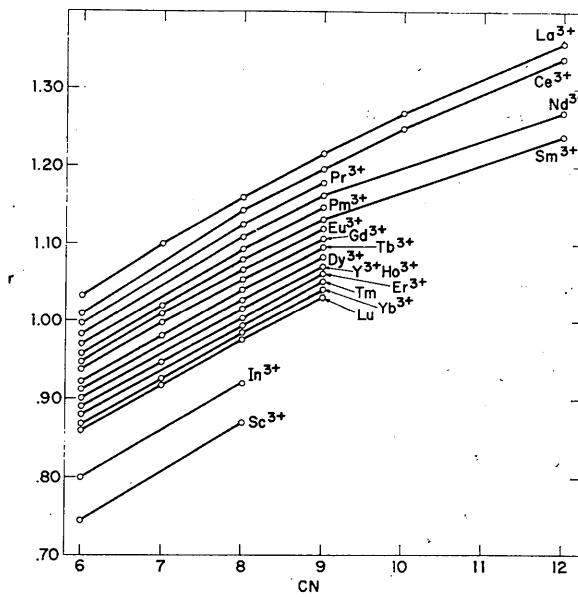
Fig. 2. (a)–(e) Effective ionic radius (Å) vs CN for some common cations.

(e)
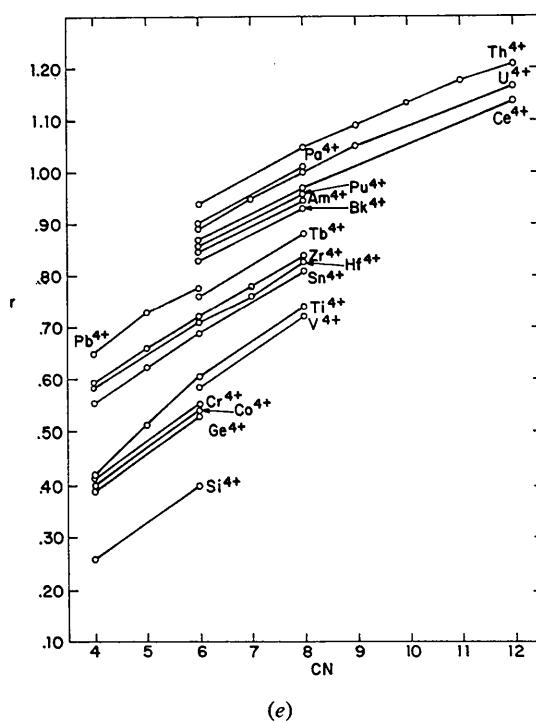
Fig. 2. (cont.)

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

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* Extrapolation of the Na curve gives $r(^{IV}Na^+) = 0.90$ Å.
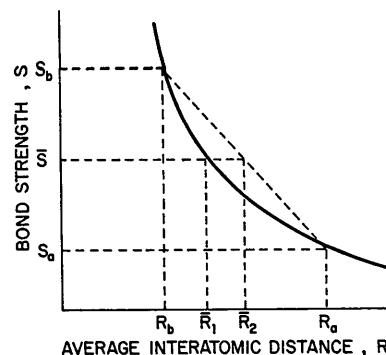
Fig. 3. Typical bond length vs bond strength plot.

repulsion effects. A similar comparison with Fe^{2+} and Ni^{2+} cannot be made because of electron distribution changes from tetrahedral to square planar coordination.
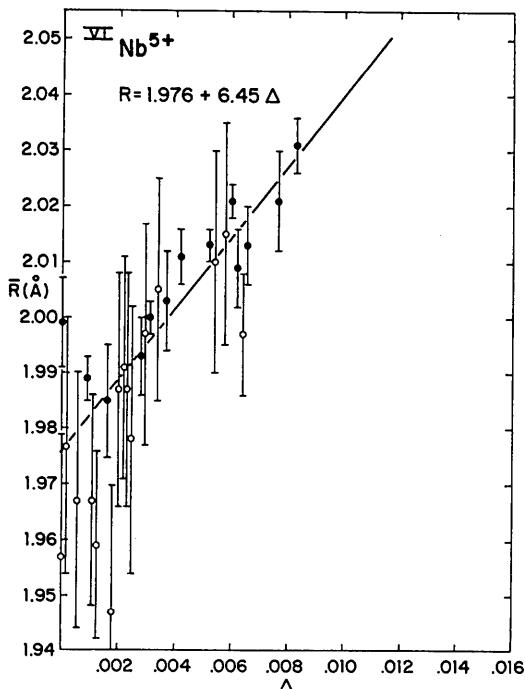
Fig. 4. Mean Nb^{5+}–O bond length vs distortion. Vertical bars represent average e.s.d.'s quoted by the authors. Solid circles represent more accurate data.
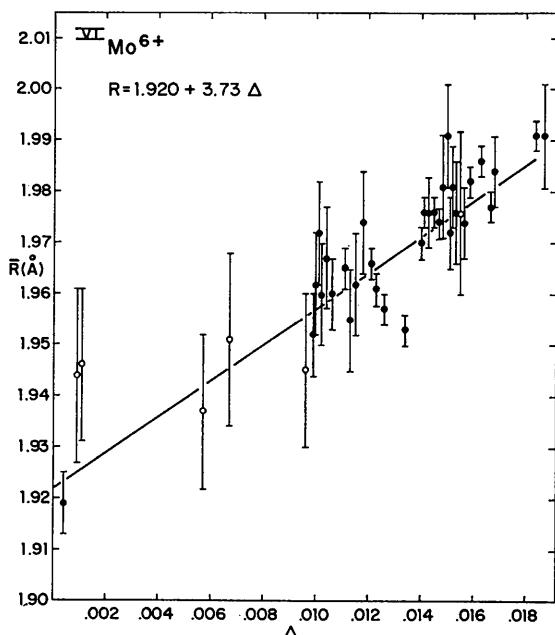
Fig. 5. Mean Mo^{6+}–O bond length vs distortion.

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

Compound	$\bar{R}$ (Å)	r (Å)	Reference	
(a) $^{IV}Na^+$				
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, 1973a; 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 molyb-

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* 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.

date. In fact, the Mo^{6+}–O octahedra in $Mo_2(O_2C_6Cl_4)_6$ with a very small distortion have the short mean distance of 1·919 Å.

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

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

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

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

Compound	$\bar{R}$ (Å)	Distortion $\Delta = \langle(\Delta R/R)^2\rangle \times 10^4$	Reference		
$Hg_2Nb_2O_7$	1·999	0	68 INOCA	7	1704
$Cd_2Nb_2O_7$	1·957	0	72 CJCHA	50	3648
$Na_2Nb_4O_{11}$	1·977	1	70 JSSCB	1	454
$Ba_{0.27}Sr_{0.75}Nb_2O_{5.78}$	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 $\Delta = \langle(\Delta R/R)^2\rangle \times 10^4$		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 $\Delta \times 10^4$	N^*	R_0†	r_0‡	m	Correlation coefficient	Goodness of fit ($\times 10^3$)
Mo^{6+}	212	38	1·920		3·73	0·74	67
				0·572	3·01	0·63	70
W^{6+}	122	7	1·925		3·30	0·75	19
				0·565	3·28	0·66	24
V^{5+}	576	16	1·887		2·62	0·98	8
Nb^{5+}	83	29	1·976		6·45	0·69	71
				0·599	6·83	0·44	99
Ta^{5+}	79	6	1·984		6·70	0·81	18
				0·617	3·79	0·15	46
Mn^{3+}	71	15	1·994		7·08	0·82	30
				0·624	6·15	0·54	50
Cu^{2+}	316	26	2·085		3·99	0·82	77
Mg^{2+}	156	28	2·094		8·31	0·72	21
				0·728	8·86	0·77	18
Co^{2+}	46	15	2·106		7·38	0·42	19
				0·734	11·70	0·70	16
Zn^{2+}	71	16	2·099		7·70	0·64	21
				0·736	8·20	0·74	16
Li^+	148	11	2·159		8·42	0·81	30
				0·784	9·02	0·79	35

* N = number of independent octahedra
† $R = R_0 + m\Delta$.
‡ $r = r_0 + m\Delta$.

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:

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

where $d(Fe-X) = $ mean Fe–X distance.
A similar parameter

$$R_v = \frac{V(Fe_mX_n)}{V(Mg_mX_n)}$$

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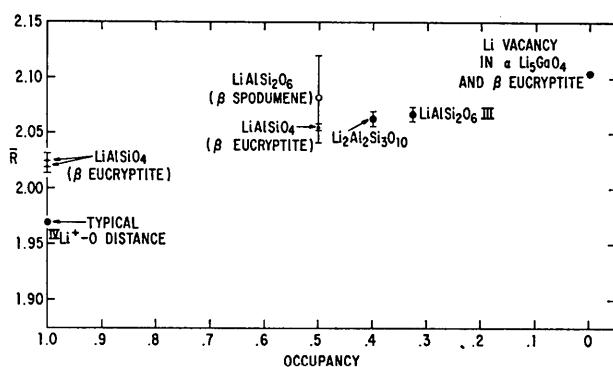
Fig. 6. Mean Li$^+$–O bond length vs partial occupancy.
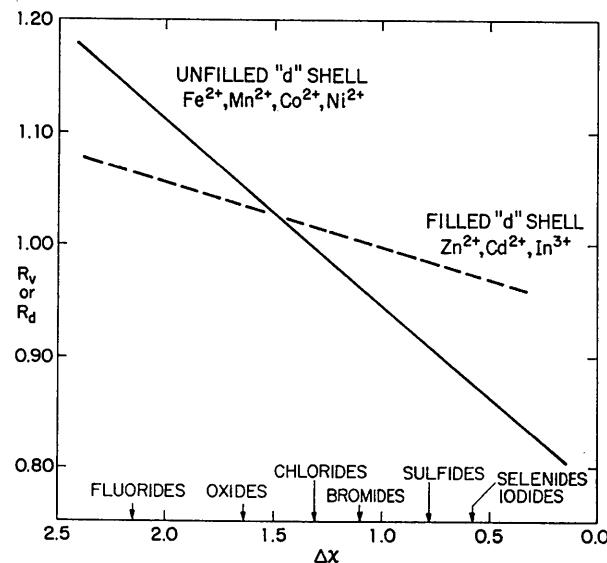
Fig. 7. Covalency contraction parameter, R_v or R_d, vs $\Delta\chi$ for filled and unfilled d shell cations.
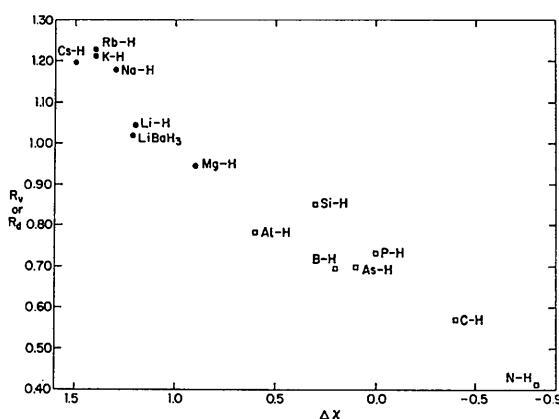
Fig. 8. Covalency contraction parameter, R_v or R_d, vs $\Delta\chi$ for hydrides. Solid circles represent ratios of cell volumes of isotypic compounds. Squares represent ratios of the cubed M–H distances to the cubed M–F distances.

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

These relations show that effective ionic radii derived primarily from oxides are not strictly applicable to fluorides – note the change in R_v for Fe^{2+}, Co^{2+}, Ni^{2+}, and Mn^{2+} from fluorides to oxides. This effect is particularly noticeable in R_v–$\Delta\chi$ 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 $R_d = d(M-H)^3/d(M-F)^3$. In the more ionic hydrides of Cs, Rb, K, and Na, hydride volumes are considerably larger than those of the fluorides. For the Li and Mg compounds, hydride and fluoride volumes are approximately equal, whereas the more covalent hydrides have increasingly smaller relative volumes than the corresponding fluorides. Fig. 8 partly explains the differences in reported radii. The Morris & Reed (1965) value of 1·53 Å was derived essentially from the large alkali halides, while Gibb's value of 1·40 Å was derived primarily from hydrides of the more electronegative

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

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

The evidence for covalent shortening of $^{IV}Fe^{3+}$–O bonds is more direct. Jeitschko, Sleight, McClellan & Weiher (1976) have found a good correlation between (1) the Fe Mössbauer isomer shift and mean Fe–O distance and (2) $\bar{\chi}$ and mean Fe–O distance ($\bar{R}$). Thus, in β-NaFeO$_2$ $\bar{R} = 1.86$ Å and $\delta = 0.18$ mm s^{-1} relative to α Fe whereas in Bi$_3$(FeO$_4$) (MoO$_4$)$_2$ $\bar{R} = 1.909$ Å and $\delta = 0.282$ mm s^{-1}.

4. Effects of electron delocalization

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

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

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

A further example of delocalization effects occurs in the compound NaVS$_2$ (Weigers, van der Meer, van Heinigen, Kloosterboer & Alberink, 1974). The molecular volume of Pauli paramagnetic NaVS$_2$ I (67.9 Å^3) is significantly less than that of NaVS$_2$ II (72.7 Å^3). NaVS$_2$ II is characterized by localized electrons (Jellinek, 1975) and its molecular volume is consistent with that of isotypic NaCrS$_2$ (71.1 Å^3).

If electron delocalization in oxides results in reduced metal–oxygen distances and thereby an effective increase in valence, radii derived for the ions Mo^{4+}, Tc^{4+}, Ru^{4+}, Rh^{4+}, W^{4+}, Re^{4+}, Os^{4+}, and Ir^{5+} from metallic oxides may not be reliable when applied to insulating oxides. Thus, radii obtained from distances in the metallic phases, e.g. RhO$_2$, ReO$_2$, and Cd$_2$Ir$_2$O$_7$, 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$_2$O$_2$(C$_2$O$_4$)$_4$].3H$_2$O (Lis, 1975) of 2.021 (10) Å ($r = 0.671$ Å) is greater than the estimated mean distance in metallic ReO$_2$ of 1.99 Å ($r = 0.63$ Å). Knop & Carlow's (1974) value of $r = 0.662$ Å derived from cell volumes of the insulating Cs$_2$ReF$_6$ phases is consistent with the radius of Re^{4+} from K$_4$[Re$_2$O$_2$(C$_2$O$_4$)$_4$].3H$_2$O. The Re^{5+}–O distance in Nd$_4$Re$_2$O$_{11}$ (Wilhelmi, Lagervall & Muller, 1970) of 1.987 (12) Å ($r = 0.607$ Å) is significantly greater than the distance in metallic Cd$_2$Re$_2$O$_7$ (Sleight, 1975) of 1.93 (2) Å ($r = 0.55$ Å). The radii of 0.58 Å derived from XeF$_5$RuF$_6$ 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$_2$Ru$_2$O$_7$. In contrast, however, the Mo^{4+} radius of 0.64 Å derived from insulating Li$_2$MoF$_6$ (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.

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

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References

AHRENS, L. H. (1952). *Geochim. Cosmochim. Acta*, 2, 155–169.
BARTLETT, N., GENNIS, M., GIBLER, D., MORRELL, B. & ZALKIN, A. (1973). *Inorg. Chem.* 12, 1717–1721.
BAUR, W. H. (1972). *Amer. Min.* 57, 709–731.
BAUR, W. H. (1974). *Acta Cryst.* B30, 1195–1215.
BIRCHALL, T. & SLEIGHT, A. W. (1975). *J. Solid State Chem.* 13, 118–130.
BONAMICO, M., DESSY, G., FARES, V. & SCARAMUZZA, L. (1974). *J. Chem. Soc. Dalton*, pp. 1258–1263.
BRANDT, B. G. & SKAPSKI, A. C. (1967). *Acta Chem. Scand.* 21, 661–667.
BROWN, I. D. (1975). Private communication.
BROWN, I. D. & SHANNON, R. D. (1973). *Acta Cryst.* A29, 266–282.
BRUGGEN, C. F. VAN (1969). Ph.D. Thesis, Univ. of Groningen.
BRUNTON, G. (1971). *Mater. Res. Bull.* 6, 555–560.
CHIARI, G., CALLERI, M., BRUNO, E. & RIBBE, P. H. (1975). *Amer. Min.* 60, 111–119.
Codens for Periodical Titles (1966). Vol. II. ASTM Data series DS23A, Philadelphia.
DEMPSEY, M. J. & STRENS, R. G. J. (1975). Proc. NATO Conf. on Petrophysics, Newcastle-upon-Tyne, April 22–26.
EVANS, H. T. JR (1951). *Acta Cryst.* 4, 377.
FLYGARE, W. H. & HUGGINS, R. A. (1973). *J. Phys. Chem. Solids*, 34, 1199–1204.
FUKUNAGA, O. & FUJITA, T. (1973). *J. Solid State Chem.* 8, 331–338.
FUMI, F. G. & TOSI, M. P. (1964). *J. Phys. Chem. Solids*, 25, 31–43.
GELLER, S., WILLIAMS, H. J., ESPINOSA, G. P., SHERWOOD, R. C. & GILLEO, M. A. (1963). *Appl. Phys. Lett.* 3, 21–22.
GIBB, T. R. P. (1962). *Prog. Inorg. Chem.* 3, 315–509.
GREIS, O. & PETZEL, T. (1974). *Z. anorg. allgem. Chem.* 403, 1–22.
GRUNDY, H. D. & ITO, J. (1974). *Amer. Min.* 59, 1319–1326.
HAWTHORNE, F. C. (1973). *The Crystal Chemistry of the Clino-Amphiboles*, Ph.D. Thesis, McMaster Univ.
JAYARAMAN, A., NARAYANAMURTI, V., BUCHER, E. & MAINES, R. G. (1970). *Phys. Rev. Lett.* 25, 1430–1433.

JEITSCHKO, W., SLEIGHT, A. W., McCLELLAN, W. R. & WEIHER, J. F. (1976). *Acta Cryst.* B32, 1163–1170.
JELLINEK, F. (1975). Private communication.
KÁLMÁN, A. (1971). *Chem. Commun.* pp. 1857–1859.
KHAN, A. A. & BAUR, W. (1972). *Acta Cryst.* B28, 683–693.
KNOP, O. & CARLOW, J. S. (1974). *Canad. J. Chem.* 52, 2175–2183.
LIS, T. (1975). *Acta Cryst.* B31, 1594–1597.
McCARTHY, G. J. (1971). *Mater. Res. Bull.* 6, 31–40.
MORRIS, D. F. C. & REED, G. L. (1965). *J. Inorg. Nucl. Chem.* 27, 1715–1717.
MULLER, O. & ROY, R. (1974). *Crystal Chemistry of Non-Metallic Materials*. 4. *The Major Ternary Structural Families*. New York: Springer-Verlag.
PAULING, L. (1927). *J. Amer. Chem. Soc.* 49, 765–794.
PAULING, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.
PETERSON, J. R. & CUNNINGHAM, B. B. (1967). *Inorg. Nucl. Chem. Lett.* 3, 327–336.
PETERSON, J. R. & CUNNINGHAM, B. B. (1968). *J. Inorg. Nucl. Chem.* 30, 1775–1781.
RIBBE, P. & GIBBS, G. V. (1971). *Amer. Min.* 56, 1155–1173.
SHANNON, R. D. (1975). Proc. NATO Conf. on Petrophysics, Newcastle-upon-Tyne, April 22–26.
SHANNON, R. D. & CALVO, C. (1973a). *Acta Cryst.* B29, 1338–1345.
SHANNON, R. D. & CALVO, C. (1973b). *J. Solid State Chem.* 6, 538–549.
SHANNON, R. D. & GUMERMAN, P. S. (1975). *J. Inorg. Nucl. Chem.* 38, 699–703.
SHANNON, R. D., GUMERMAN, P. S. & CHENAVAS, J. (1975). *Amer. Min.* 60, 714–716.
SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* B25, 925–945.
SHANNON, R. D. & VINCENT, H. (1974). *Struct. Bond. (Berlin)*, 19, 1–43.
SILVA, R. J., McDOWELL, W. J., KELLER, O. L. & TARRANT, J. R. (1974). *Inorg. Chem.* 13, 2233–2237.
SLEIGHT, A. W. (1975). Private communication.
SLEIGHT, A. W. & JONES, G. (1975). *Acta Cryst.* B31, 2748–2749.
STEWART, D., KNOP, O., MEADS, R. & PARKER, W. (1973). *Canad. J. Chem.* 51, 1041–1049.
STEWNER, F. & HOPPE, R. (1971). *Acta Cryst.* B27, 616–621.
TILLMANNS, E. & BAUR, W. H. (1970). *Acta Cryst.* B26, 1645–1654.
TILLMANNS, E., GEBERT, W. & BAUR, W. H. (1973). *J. Solid State Chem.* 7, 69–84.
TSCHERRY, V., SCHULZ, H., & LAVES, F. (1972). *Z. Kristallogr.* 135, 175–198.
VRIES, A. B. DE & HAAS, C. (1973). *J. Phys. Chem. Solids*, 34, 651–659.
VRIES, A. B. DE & JELLINEK, F. (1974). *Rev. Chim. Miner.* 11, 624–636.
WEIGERS, G., VAN DER MEER, R., VAN HEININGEN, H., KLOOSTERBOER, H. & ALBERINK, A. (1974). *Mater. Res. Bull.* 9, 1261–1266.
WILHELMI, K., LAGERVALL, E. & MULLER, O. (1970). *Acta Chem. Scand.* 24, 3406–3408.
WOLFE, R. W. & NEWNHAM, R. E. (1969). *J. Electrochem. Soc.* 116, 832–835.