

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

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The effective ionic radii of Shannon & Prewitt [Acta Cryst. (1969), B25, 925–945] are revised to include more unusual oxidation states and coordinations. Revisions are based on new structural data, empirical bond strength–bond length relationships, and plots of (1) radii *vs* volume, (2) radii *vs* coordination number, and (3) radii *vs* oxidation state. Factors which affect radii additivity are polyhedral distortion, partial occupancy of cation sites, covalence, and metallic character. Mean Nb<sup>5+</sup>–O and Mo<sup>6+</sup>–O octahedral distances are linearly dependent on distortion. A decrease in cation occupancy increases mean Li<sup>+</sup>–O, Na<sup>+</sup>–O, and Ag<sup>+</sup>–O distances in a predictable manner. Covalence strongly shortens Fe<sup>2+</sup>–X, Co<sup>2+</sup>–X, Ni<sup>2+</sup>–X, Mn<sup>2+</sup>–X, Cu<sup>+</sup>–X, Ag<sup>+</sup>–X, and M–H<sup>–</sup> bonds as the electronegativity of X or M decreases. Smaller effects are seen for Zn<sup>2+</sup>–X, Cd<sup>2+</sup>–X, In<sup>3+</sup>–X, Pb<sup>2+</sup>–X, and Tl<sup>+</sup>–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<sub>4</sub><sup>+</sup>; Ribbe & Gibbs (1971): OH<sup>–</sup>; Wolfe & Newnham (1969): Bi<sup>3+</sup>–La<sup>3+</sup>; McCarthy (1971): Eu<sup>2+</sup>–Sr<sup>2+</sup>; Silva, McDowell, Keller & Tarrant (1974): No<sup>2+</sup>. 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*<sup>3</sup> *vs* *V*) plots, as in

\* Polyhedral distortion was not considered in SP 69.

SP 69. Although such  $r^3$  vs  $V$  plots are not always linear (Shannon, 1975), their regular curvilinear nature still allows prediction of radii. This system is particularly accurate for radii in the middle of a series, and least reliable for large polarizable cations like Cs<sup>+</sup>, Ba<sup>2+</sup>, and Tl<sup>3+</sup>. 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<sub>3</sub> and LaF<sub>3</sub>. These radii were used in Table 1 after applying small corrections (+0.030 Å to <sup>IX</sup>La<sup>3+</sup>, <sup>IX</sup>Ce<sup>3+</sup>, <sup>IX</sup>Pr<sup>3+</sup>, and <sup>IX</sup>Nd<sup>3+</sup>; +0.025 Å to all other Greis & Petzel <sup>IX</sup>RE<sup>3+</sup> radii, and 0.015 Å to all

<sup>VIII</sup>RE<sup>3+</sup> 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: <sup>VI</sup>Os<sup>3+</sup>, <sup>VI</sup>Os<sup>6+</sup>, <sup>VI</sup>Os<sup>7+</sup>, <sup>VI</sup>Re<sup>4+</sup>, <sup>VI</sup>Re<sup>5+</sup>, <sup>VI</sup>Re<sup>6+</sup>, <sup>VI</sup>Re<sup>7+</sup>, <sup>VI</sup>Rh<sup>4+</sup>, <sup>VII</sup>U<sup>4+</sup>, <sup>VII</sup>U<sup>5+</sup>, and <sup>VII</sup>U<sup>6+</sup>.

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 <sup>IV</sup>Cu<sup>+</sup>, <sup>VI</sup>Cu<sup>+</sup>, <sup>IX</sup>Rb<sup>+</sup>, <sup>V</sup>Ni<sup>2+</sup>, <sup>VII</sup>Er<sup>3+</sup>, <sup>VII</sup>Yb<sup>3+</sup>, <sup>VII</sup>Tb<sup>3+</sup>, <sup>XII</sup>Nd<sup>3+</sup>, <sup>IV</sup>Cr<sup>4+</sup>,

Table 1. *Effective ionic radii*

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

ION	EC	CN	SP	CR	'IR'	ION	EC	CN	SP	CR	'IR'	ION	EC	CN	SP	CR	'IR'
AC+3 6P 6 VI			1.26	1.12	R	CL-1 3P 6 VI			1.67	1.81	P	GD+3 4F 7 VII			1.14	1.00	
AG+1 4D10 II			.81	.67		CL+5 3S 2 IIIPY			.26	.12		GL+5 3S 2 IIIPY			1.193	1.053	R
IV			1.14	1.00	C	CL+7 2P 6 IV			.22	.08	*	GE+2 4S 2 VI			1.247	1.107	RC
IVSQ			1.16	1.02		VI			.41	.27	A	GE+4 3D10 IV			.87	.73	A
V			1.23	1.09	C	CM+3 5F 7 VI			1.11	.99	R	VI			.330	.390	*
VI			1.29	1.15	C	CM+4 5F 6 VI			.99	.85	R	VI			.670	.530	R*
VIII			1.36	1.22		VIII			1.09	.95	R	H +1 1S 0 I			-.24	-.38	
VIII			1.42	1.28		CD+2 3D 7 IV	HS		.72	.58		II			-.04	-.18	
AG+2 4D 9 IVSQ			.93	.79		V			.81	.67	C	HF+4 4F14 V			.72	.58	R
VI			1.08	.94		VI	LS		.79	.65	R	VI			.85	.71	R
AG+3 4D 8 IVSQ			.81	.67		HS			.885	.745	R*	VIII			.90	.76	
VI			.89	.75	R	CD+3 3D 6 VIII	LS		1.04	.90		VI			.97	.83	
VI			.53	.39	*	VI	LS		.685	.565	R*	HG+1 6S 1 IIII			1.11	.97	
AL+3 2P 6 IV			.62	.48		HS			.75	.61		VI			1.33	1.19	
V			.675	.535	R*	CD+4 3D 5 IV	HS		.54	.40		HG+2 5D10 II			.83	.69	
AM+2 5F 7 VII			1.35	1.21		HS			.67	.53	R	IV			1.10	.96	
VIII			1.40	1.26		CR+2 3D 4 VI	LS		.87	.73	E	VI			1.16	1.02	
IX			1.45	1.31		HS			.94	.80	R	VIII			1.28	1.14	R
AM+3 5F 6 VI			1.115	.975	R	CR+3 3D 3 VI			.755	.615	R*	HO+3 4F10 VI			1.041	.901	R
VIII			1.23	1.09		CR+4 3D 2 IV			.53	.41	R	VIII			1.155	1.015	R
AM+4 5F 5 VI			.99	.85	R	VI			.69	.55	R	IX			1.212	1.072	R
VIII			1.09	.95		CR+5 3D 1 IV			.485	.345	R	X			1.26	1.12	A
AS+3 4S 2 VI			.72	.58	A	VI			.63	.49	EA	I -1 5P 6 VI			2.06	2.20	A
AS+5 3D10 IV			.875	.735	R*	VIII			.71	.57		I +5 5S 2 IIIPY			.58	.44	*
VI			.60	.46	C*	CR+6 3P 6 IV			.40	.26		VI			1.09	.95	
AT+7 5D10 VI			.76	.62	A	VI			.58	.44	C	I +7 4D10 IV			.56	.42	
AU+1 5D10 VI			1.51	1.37	A	CS+1 5P 6 VI			1.81	1.67		VI			.67	.53	
AU+3 5D 8 IVSQ			.82	.68		VIII			.88	.74		IN+3 4D10 IV			.76	.62	
VI			.99	.85	A	IX			1.92	1.78		VI			.940	.800	R*
AU+5 5D 6 VI			.71	.57	X	X			1.95	1.81		VIII			1.06	.92	RC
B +3 1S 2 III			.15	.01	*	XI			1.99	1.85		IR+3 5D 6 IV			.82	.68	E
IV			.25	.11	*	XII			2.02	1.88		IR+4 5D 5 VI			.765	.625	R
VI			.41	.27	C	CU+1 3D10 II			.60	.46		IR+5 5D 4 VI			.71	.57	EM
BA+2 5P 6 VI			1.49	1.35		IV			.74	.60	E	K +1 3P 6 IV			1.51	1.37	
VIII			1.52	1.38	C	VI			.91	.77	E	XII			1.52	1.36	C
VIII			1.56	1.42		CU+2 3D 9 IV			.71	.57	*	VII			1.60	1.46	
IX			1.61	1.47		IVSQ			.71	.57	*	VIII			1.65	1.51	
X			1.66	1.52		V			.79	.65	*	IX			1.69	1.55	
XI			1.71	1.57		VI			.87	.73		X			1.73	1.59	
XII			1.75	1.61	C	CU+3 3D 8 VI	LS		.68	.54		XII			1.78	1.64	
BE+2 1S 2 III			.30	.16		D +1 1S 0 II			.04	-.10		LA+3 4D10 VI			1.172	1.032	R
IV			.41	.27	*	DY+2 4F10 VI			1.21	1.07		VII			1.24	1.10	
VI			.59	.45	C	VIII			1.27	1.13		VIII			1.300	1.160	R
BI+3 6S 2 V			1.10	.96	C	VI			1.33	1.19		IX			1.356	1.216	R
VI			1.17	1.03	R*	UY+3 4F 9 VI			1.052	.912	R	X			1.41	1.27	X
VIII			1.31	1.17	R	VII			.11	.97		XII			1.50	1.36	C
BI+5 5D10 VI			.90	.76	E	VIII			1.167	1.027	R	LI+1 1S 2 IV			.730	.590	*
BK+3 5F 8 VI			1.10	.96	R	IX			1.223	1.083	R	VI			.90	.76	*
BK+4 5F 7 VI			.97	.83	R	ER+3 4F11 VI			1.030	.890	R	VIII			1.06	.92	C
VIII			1.07	.93	R	VII			1.085	.945		LU+3 4F14 VI			1.001	.861	R
BR-1 4P 6 VIII			1.82	1.66	P	VIII			1.144	1.004	R	VIII			1.117	.977	R
BR+3 4P 2 IVSQ			.73	.59		IX			1.202	1.062	R	IX			1.172	1.032	R
BR+5 4S 2 IIIPY			.45	.31		EU+2 4F 7 VI			1.31	1.17		VI			.71	.57	
BR+7 3D10 IV			.39	.25		VIII			1.34	1.20	V	VI			.80	.66	
C +4 1S 2 III			.06	-.08	A	IX			1.39	1.25		VIII			1.03	.89	C
IV			.29	.15	P	X			1.44	1.30		HS			.80	.66	
VI			.16	.02	A	EU+3 4F 6 VI			1.087	.947	R	HS			.89	.75	C
CA+2 3P 6 VI			1.14	1.00		VII			1.15	1.01		LS			.81	.67	E
VIII			1.20	1.06	*	VIII			1.206	1.066	R	HS			.970	.830	R*
VIII			1.26	1.12	*	IX			1.260	1.120	R	VII			1.04	.90	C
IX			1.32	1.18		F -1 2P 6 II			1.145	1.005	R	VIII			1.10	.96	R
X			1.37	1.23	C	III			1.16	1.30		MN+3 3D 4 V			.72	.58	
XII			1.48	1.34	C	IV			1.17	1.31		LS			.72	.58	R
CD+2 4D10 IV			.92	.78		VI			1.19	1.33		HS			.785	.645	R*
V			1.01	.87		F +7 1S 2 II			.22	.08	A	VI			.53	.39	R
VI			1.09	.95		HS			.77	.63		VI			.670	.530	R*
VIII			1.17	1.03	C	IVSQ			.78	.64		MN+5 3D 2 IV			.47	.33	R
VIII			1.24	1.10	C	VI			1.25	.61	E	MN+6 3D 1 V			.395	.255	
XII			1.45	1.31		HS			.920	.780	R*	MN+7 3P 6 V			.39	.25	
CE+3 6S 1 VI			1.15	1.01	R	VIII			1.06	.92	C	VI			.60	.46	A
VII			1.21	1.07	E	FE+3 3D 5 IV	HS		.63	.49	*	VI			.83	.69	E
VIII			1.283	1.143	R	VI			.72	.58		MO+4 4D 2 VI			.700	.560	RM
IX			1.336	1.196	R	VI	LS		.69	.55	R	MO+5 4D 1 IV			.60	.46	R
X			1.39	1.25	C	HS			.785	.645	R*	VI			.75	.61	R
XII			1.48	1.34	C	FE+4 3D 4 VI			.92	.78	C	VI			.64	.50	
CE+4 5P 6 VI			1.11	.97	R	FE+6 3D 2 IV			.39	.25	R	VI			.73	.59	R*
VIII			1.21	1.07		FR+1 6P 6 VI			1.94	1.80	A	VII			.87	.73	
X			1.28	1.14		GA+3 3D10 IV			.61	.47	*	VI			1.32	1.16	
XII			1.09	.95	R	VI			.69	.55		N -3 2P 6 IV			1.30	.16	A
CF+3 6D 1 VI			.961	.821	R	VI			.760	.620	R*	N +3 2S 2 VI			.04	-.10	A
CF+4 5F 8 VI			1.06	.92	VIII	GD+3 4F 7 VI			1.078	.938	R*	VII			.27	-.13	A

Table 1 (cont.)

ION	EC	CN	SP	CR	'IR'	ION	EC	CN	SP	CR	'IR'	ION	EC	CN	SP	CR	'IR'	
NA+1 2P 6 IV					.99	PR+3 4F 2 VI				1.13	.99 R	TC+4 4D 3 VI				.785	.645 RM	
V					1.14	VIII				1.266	1.126 R	TC+5 4D 2 VI				.74	.60 ER	
VII					1.16	IX				1.317	1.179 R	TC+7 4P 6 IV				.51	.37	
VIII					1.24	PR+4 4F 1 VI				.99	.85 R	TE-2 5P 6 VI				2.07	2.21 P	
VIII					1.32	VIII				1.10	.96 R	TE+4 5S 2 III				.86	.52	
IX					1.38	PT+2 5D 8 IVSQ				.74	.60	IV				.80	.66	
XII					1.53	IX				.94	.80 A	VI				1.11	.97	
NB+3 4D 2 VI					.86	PT+5 5D 5 VI				.765	.625 R	TE+6 4D10 IV				.57	.43 C	
NB+4 4D 1 VI					.82	PU+3 5F 5 VI				.71	.57 ER	VI				.70	.56 *	
VIII					.93	PU+4 5F 4 VI				1.14	1.00 R	TH+4 6P 6 VI				1.08	.94 C	
NB+5 4P 6 VI					.62	VIII				1.00	.86 R	IX				1.23	1.09 *	
VII					.78	PU+5 5F 3 VI				.88	.74 E	X				1.27	1.13 E	
VIII					.83	PU+6 5F 2 VI				.85	.71 R	XI				1.32	1.18 C	
VIII					.88	RA+2 6P 6 VIII				1.62	1.48 R	XII				1.35	1.21 C	
IX					1.43	XII				1.84	1.70 R	TI+2 3D 2 VI				1.00	.86 E	
IX					1.49	RB+1 4P 6 VI				1.66	1.52	TI+3 3D 1 VI				.810	.670 RM	
NB+3 4F 3 VI					1.123	VIII				1.70	1.56 E	TI+4 3P 6 IV				.56	.42 C	
VIII					1.249	VIII				1.75	1.61	V				.65	.51 C	
IX					1.303	IX				1.77	1.63 E	VI				.745	.605 RM	
XII					1.41	X				1.80	1.66	VIII				.88	.74 C	
NI+2 3D 8 IV					.69	XI				1.63	1.49	IX				1.64	1.50 R	
IVSQ					.63	XII				1.86	1.72	VIII				1.73	1.59 R	
V					.77	XIV				1.97	1.83	XII				1.84	1.70 RE	
VI					.830	RE+4 5D 3 VI				.77	.63 RM	IX				.89	.75 R	
NI+3 3D 7 VI	LS				.70	RE+5 5D 2 VI				.72	.58 E	VI				1.025	.885 R	
LS					.74	RE+6 5D 1 VI				.69	.55 E	VIII				1.12	.98 C	
NI+4 3D 6 VI	LS				.62	RE+7 5P 6 IV				.52	.38	IX				1.17	1.03 R	
NI+2 5F14 VI					1.24	RM+3 4D 6 VI				.67	.53	VI				1.23	1.09	
NP+2 5F 5 VI					1.24	RM+4 4D 5 VI				.67	.53	VIII				1.23	1.09	
NP+3 5F 4 VI					1.15	RM+5 4D 4 VI				.65	.51	VIII				1.134	.994 R	
NP+4 5F 3 VI					1.01	RU+3 4D 4 VI				.83	.69	IX				1.192	1.05 R	
VIII					1.12	RU+4 4D 3 VI				.74	.60 RM	U +3 5F 3 VI				1.165	1.025 R	
NP+5 5F 2 VI					.89	RU+5 4D 3 VI				.69	.55	U +4 5F 2 VI				1.03	.89	
NP+6 5F 1 VI					.84	RU+6 4P 6 IV				.83	.69	VII				1.09	.95 E	
NP+7 6P 6 VI					.85	RU+7 4D 1 IV				.52	.38	IX				1.19	1.05	
O -2 2P 6 II					1.21	RU+8 4P 6 IV				1.70	1.56	XII				1.31	1.17 E	
II					1.22	S -2 3P 6 VI				.51	.37 A	U +5 5F 1 VI				.90	.76	
IV					1.24	S +4 3S 2 VI				.26	.12 *	VI				1.10	1.00 RM	
V					1.26	S +6 2P 6 IV				.26	.12 *	VII				.98	.86 E	
VIII					1.28	SB+3 5S 2 IVPY				.90	.76	IX				.59	.45	
III					1.18	V				.94	.80	IV				.66	.52	
IV					1.20	SB+5 4D10 VI				.90	.76 A	VI				.87	.73 *	
IV					1.21	SC+3 3P 6 VI				.885	.745 RM	VIII				.95	.81 E	
OS+4 5D 4 VI					1.23	SE-2 4P 6 VI				1.010	.870 RM	V +2 3D 3 VI				.93	.79	
OS+5 5D 3 VI					.715	SE+4 4S 2 VI				1.80	1.69 P	V +3 3D 2 VI				.780	.640 RM	
OS+6 5D 2 V					.63	SE+6 3O10 IV				.64	.50 A	V +4 3D 1 V				.67	.53	
OS+7 5D 1 VI					.885	SE+8 5P 6 IV				.42	.28 *	VI				.72	.58 RM	
OS+8 5P 6 IV					.53	SI+4 2P 6 VI				.56	.42 C	VIII				.86	.72 E	
P +3 3S 2 VI					.58	V				.60	.46 *	V +5 3P 6 IV				.60	.46 *	
P +5 2P 6 IV					.31	SM+2 4F 6 VIII				1.36	1.22	V				.60	.46 *	
V					.43	VIII				1.41	1.27	W +4 5D 2 VI				.80	.66 RM	
VI					.52	IX				1.66	1.32	W +5 5D 1 VI				.76	.62 *	
PA+3 5F 2 VI					1.18	SM+3 4F 5 VI				1.098	.958 R	W +6 5P 6 IV				.56	.42 *	
PA+4 6D 1 VI					1.04	VII				1.16	1.02 E	V				.65	.51	
VIII					1.15	VIII				1.219	1.079 R	VI				.74	.60 *	
VIII					.92	IX				1.272	1.132 R	XE+8 4D10 IV				.54	.40	
VIII					1.05	XI				1.38	1.24 C	VI				.62	.48	
IX					1.09	XII				.69	.55 R	Y +3 4P 6 VI				1.040	.900 RM	
PB+2 6S 2 IVPY					1.12	SN+4 4D10 V				.78	.66 C	VIII				1.159	1.019 R*	
VI					1.33	IX				.830	.690 RM	IX				1.215	1.075 R	
VII					1.37	V				.89	.75	IX				1.16	1.02	
VIII					1.43	SR+2 4P 6 VI				1.32	1.18	YB+2 4F14 VI				1.22	1.08 E	
IX					1.49	VIII				1.35	1.21	VIII				1.28	1.14	
X					1.54	IX				1.40	1.26	YB+3 4F13 VI				1.008	.868 RM	
XI					1.59	IX				1.45	1.31	VII				1.065	.925 E	
XII					1.63	X				1.50	1.36 C	XIII				1.125	.985 R	
IV					.79	XI				1.58	1.44 C	IX				1.182	1.042 R	
V					.87	XII				.86	.72 E	VI				.74	.60 *	
VIII					.915	TA+3 5D 2 VI				.82	.68 E	V				.82	.68 *	
VIII					1.08	TA+4 5D 1 VI				.78	.64	VI				.880	.740 RM	
IX					.73	TA+5 5P 6 VI				.83	.69	VIII				1.04	.90 C	
IX					.78	VIII				.88	.74	IX				.73	.59 R	
IX					.90	IX				1.063	.923 R	V				.80	.66 C	
IX					.755	X				1.12	.98 E	VI				.86	.72 RM	
IX					1.11	TA+3 5D 2 VI				1.180	1.040 R	VII				.92	.78 *	
IX					1.233	TA+4 5D 1 VI				1.235	1.095 R	VIII				.98	.84 *	
IX					1.284	TA+5 5P 6 VI				.90	.76 R	IX				1.03	.89	
IX					1.08	VIII				1.02	.88							
IX					1.22	IX												
IX					.81													
PO+4 6S 2 VI					.81													
PO+6 5D10 VI					.81													

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

Another method used to estimate radii was based on the empirical relationship between interatomic distances and bond strengths. Brown & Shannon (1973) derived these relationships for the cations in the first three rows of the periodic table from a large number of experimental interatomic distances. These curves can be used to calculate hypothetical distances for cations in any coordination (Brown & Shannon, 1973; Shannon, 1975; Brown, 1975). Examples of cations whose radii were calculated in this way are:  $\text{IV Mn}^{2+}$ ,  $\text{VI Be}^{2+}$ ,  $\text{VI B}^{3+}$ ,  $\text{VI P}^{5+}$ ,  $\text{VI S}^{6+}$ ,  $\text{VIII Mg}^{2+}$ , and  $\text{VIII Fe}^{2+}$ . 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  $\text{Yb}^{2+}$ ,  $\text{Tm}^{2+}$ ,  $\text{Dy}^{2+}$ ,  $\text{Sm}^{2+}$ ,  $\text{Nd}^{2+}$  and the ions  $\text{Am}^{2+}$ ,  $\text{Ac}^{3+}$ ,  $\text{Np}^{3+}$ , and  $\text{U}^{4+}$ .

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

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

Table 2. References for Table 1

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

AG*3 VI	68 JINCA	30	823	AC	CL3
AG*1 I1	71 INDOA	10	719	AG	FE 02
72 ZAACA	99	24	58	SA	AG 04
73 ZENBA	288	263	BA	AG 04	04
AG*1 IV	71 JSSCB	3	364	AG2	CR 04
AG*1 V	42 JACSA	64	354	AG3	AS 04
69 ACSAA	23	2261	AG2	S 03	
AG*1 V	70 JSSCB	1	484	AG6	MO10 033
AG*1 V	32 ZKXKA	82	161	AG2	SO4
47 JACSA	69	222	AG3	PO4	
71 JSSCB	3	364	AG2	CR 04	
69 ACACB	25	5116	AG2	CR 02	
70 JSSCB	1	484	AG2	MO 04	
AG*1 VII	70 JSSCB	1	484	AG6	MO10 033
69 ACACB	25	5116	AG2	CR 02	
AG*1 VIII	65 ACCRA	19	180	AG7	M 011
AG*2 IVS0	71 JPSCA	32	543	AG F2	
AG*2 VI	71 JPSCA	32	543	AG F2	
AG*3 IVS0	65 ACCRA	19	180	AG7	M 011
AL*3 V	67 ACACB	23	754	NA T12	AL5 012
68 NJHMA	1968	80	CA	AL	B 04
70 AGBCA	26	102	BA	T16	D13
70 SPHCA	1970	59	CA12	AL12	D33
71 SPHDA	15	905	CA4	AL6	D10 (OH)6
71 SPHMA	15	905	CA4	AL6	D10 (OH)6
71 ACBCA	27	1892	BE1A	AL2	D3
72 JSSCB	4	60	AG	AL11	D17
AL*3 V	68 ACBCA	24	1518	(MG,FE)	AL3 S1 B 09
69 AMNIA	53	1096	AL2	PD4	10H13
AL*3 VI	71 AMNIA	56	18	NA3	AL2 L13 F1Z
72 JSSCB	4	11	ND	AL 03	
72 JSSCB	4	100	AG	AL11	D17
58 ACACB	5	484	MG	AL2 04	
72 ACBCA	28	1899	AL2	BE3	S16 D18
68 JACSA	80	2051	AL2	BE3	S16 D18
73 ACBCA	29	2295	AL	P 04+2	H2 0
67 ZKXKA	125	1423	CS	BE1	B12-X1 AL4 O28 H2
74 ACBCA	30	1312	NA	AL 04	D412 10 H14
74 ZKXKA	130	125	AL	10 H13	
AM*2 VII	72 JINCA	34	3427	AM 12	
AM*2 VIII	73 JINCA	35	483	AM BR2	
AM*2 IX	73 JINCA	35	483	AM CL2	
AM*3 VIII	11	2233	AM2	(S O4)3	OH2 0
AM*4 VI	67 ADCSA	71	228	BA	AM 03
67 INUCA	3	327	R	(BK+)	
AS*5 IV	69 ZKXKA	130	231	ZH2	CU AS2 08
68 CJCHA	46	917	CU3	AS2 08	
63 BAPCA	11	361	MG	AS2 07	
69 ACBCA	25	1544	CA	M AS 04+2	H2 0
68 AMNIA	53	1861	MN2	H AS 04	
63 CARMA	7	561	CA	CU AS 04	O M
70 ACBCA	26	1574	NA2	H AS 04+2	H2 0
69 CHDCA	268	1694	BA	N12	AS2 08
70 AMNIA	55	2023	MN9	10 H19	(H2 O)2
70 ACBCA	26	1899	IN	HO11	AS 04+2
70 ACSAA	24	3711	LI	MO	AS 04
70 INDOA	9	2259	CA2	AS 04	CL
65 ACACB	18	777	CU3	AS 04	O H13
70 CJCHA	48	890	MG2	AS2 07	
70 CJCHA	48	891	CU3	AS2 08	
71 CJCHA	49	1036	CA3	AS2 08	
70 AMNIA	55	1409	MN7	58	AS 012
71 ACBCA	27	2124	NA3	AS 04+12	H2 0
73 ACBCA	29	2611	MG3	AS2 08	
61 AMNIA	46	1077	CA2	B AS 04	10H14
73 CJCHA	51	2082	NA4	AS2 07	
66 ZACCA	347	133	SR	H AS 04	H2 0
66 ZACCA	347	140	SR	H AS 04	H2 0
71 AMNIA	56	1167	ZNA	AS2 08	10H12,2H2 0
70 ACBCA	26	403	CA	H AS 04	H2 0
70 ZKXKA	132	332	CD3	AS2 08	
73 ACBCA	29	141	LU	AS 04	
73 ACBCA	29	2121	MN4	AS 04	
AS*5 VI	71 CJCHA	49	2530	CL F2	AS F6
73 JSSCB	6	80	MG8	S	AS3 016
70 CJCHA	48	3124	CD8	AS3 016	
73 ACACB	29	266	CALCULATED		
74 INDOA	13	780	XL	AS F11,AE2	AS F9
74 ACBCA	30	250	R	AS F6	
AU*3 IVS0	69 JCSIA	1969	1936	R	AU F4
70 ZACCA	375	43	LI3	AU O3,K AU O2,RB AU O2	
70 JCSIA	1970	3092	R	AU UNO314	
AU*5 VI	74 INUCA	13	775	RE2	AU F17
D *3 VIII	68 NJHMA	1968	80	CA	AL B 04
70 ACBCA	26	102	BA	T16	D13
71 SPHCA	15	905	CA4	AL6	D10 F2
71 ACBCA	27	1892	BE1A	AL2	B 07
70 ACBCA	26	1899	AL2	BE3	S16 D18
71 ACBCA	27	1892	BE1A	AL2	B 07
70 ZKXKA	132	241	CA	B3	O5 10M1
71 JACCA	4	284	CU	AS 04	
74 JPSCA	60	1899	NA	B 04	07
74 MRBUA	9	1061	ND	AL 1	(B 03)14
B *3 IV	68 ACBCA	24	1518	(MG,FE)	AL3 S1 B 09
68 ACBCA	24	1518	(MG,FE)	AL3 S1 B 09	
68 CJCHA	46	917	CU3	AS2 08	
63 BAPCA	11	361	MG	AS2 07	
69 ACBCA	25	1544	CA	M AS 04+2	H2 0
68 AMNIA	53	1861	MN2	H AS 04	
63 CARMA	7	561	CA	CU AS 04	O M
70 ACBCA	26	1574	NA2	H AS 04+2	H2 0
69 CHDCA	268	1694	BA	N12	AS2 08
70 AMNIA	55	2023	MN9	10 H19	(H2 O)2
70 ACBCA	26	1899	IN	HO11	AS 04+2
70 ACSAA	24	3711	LI	MO	AS 04
70 INDOA	9	2259	CA2	AS 04	CL
65 ACACB	18	777	CU3	AS 04	O H13
70 CJCHA	48	890	MG2	AS2 07	
70 CJCHA	48	891	CU3	AS2 08	
71 CJCHA	49	1036	CA3	AS2 08	
70 AMNIA	55	1409	MN7	58	AS 012
71 ACBCA	27	2124	NA3	AS 04+12	H2 0
73 ACBCA	29	2611	MG3	AS2 08	
61 AMNIA	46	1077	CA2	B AS 04	10H14
73 CJCHA	51	2082	NA4	AS2 07	
66 ZACCA	347	133	SR	H AS 04	H2 0
66 ZACCA	347	140	SR	H AS 04	H2 0
71 AMNIA	56	1167	ZNA	AS2 08	10H12,2H2 0
70 ACBCA	26	403	CA	H AS 04	H2 0
70 ZKXKA	132	332	CD3	AS2 08	
73 ACBCA	29	141	LU	AS 04	
73 ACBCA	29	2121	MN4	AS 04	
AS*5 VI	71 CJCHA	49	2530	CL F2	AS F6
73 JSSCB	6	80	MG8	S	AS3 016
70 CJCHA	48	3124	CD8	AS3 016	
73 ACACB	29	266	CALCULATED		
74 INDOA	13	780	XL	AS F11,AE2	AS F9
74 ACBCA	30	250	R	AS F6	
AU*3 IVS0	69 JCSIA	1969	1936	R	AU F4
70 ZACCA	375	43	LI3	AU O3,K AU O2,RB AU O2	
70 JCSIA	1970	3092	R	AU UNO314	
AU*5 VI	74 INUCA	13	775	RE2	AU F17
D *3 VIII	68 NJHMA	1968	80	CA	AL B 04
70 ACBCA	26	102	BA	T16	D13
71 SPHCA	15	905	CA4	AL6	D10 F2
71 ACBCA	27	1892	BE1A	AL2	B 07
70 ACBCA	26	1899	AL2	BE3	S16 D18
71 ACBCA	27	1892	BE1A	AL2	B 07
70 ZKXKA	132	241	CA	B3	O5 10M1
71 JACCA	4	284	CU	AS 04	
74 JPSCA	60	1899	NA	B 04	07
74 MRBUA	9	1061	ND	AL 1	(B 03)14
B *3 IV	68 ACBCA	24	1518	(MG,FE)	AL3 S1 B 09
68 ACBCA	24	1518	(MG,FE)	AL3 S1 B 09	
68 CJCHA	46	917	CU3	AS2 08	
63 BAPCA	11	361	MG	AS2 07	
69 ACBCA	25	1544	CA	M AS 04+2	H2 0
68 AMNIA	53	1861	MN2	H AS 04	
63 CARMA	7	561	CA	CU AS 04	O M
70 ACBCA	26	1574	NA2	H AS 04+2	H2 0
69 CHDCA	268	1694	BA	N12	AS2 08
70 AMNIA	55	2023	MN9	10 H19	(H2 O)2
70 ACBCA	26	1899	IN	HO11	AS 04+2
70 ACSAA	24	3711	LI	MO	AS 04
70 INDOA	9	2259	CA2	AS 04	CL
65 ACACB	18	777	CU3	AS 04	O H13
70 CJCHA	48	890	MG2	AS2 07	
70 CJCHA	48	891	CU3	AS2 08	
71 CJCHA	49	1036	CA3	AS2 08	
70 AMNIA	55	1409	MN7	58	AS 012
71 ACBCA	27	2124	NA3	AS 04+12	H2 0
73 ACBCA	29	2611	MG3	AS2 08	
61 AMNIA	46	1077	CA2	B AS 04	10H14
73 CJCHA	51	2082	NA4	AS2 07	
66 ZACCA	347	133	SR	H AS 04	H2 0
66 ZACCA	347	140	SR	H AS 04	H2 0
71 AMNIA	56	1167	ZNA	AS2 08	10H12,2H2 0
70 ACBCA	26	403	CA	H AS 04	H2 0
70 ZKXKA	132	332	CD3	AS2 08	
73 ACBCA	29	141	LU	AS 04	
73 ACBCA	29	2121	MN4	AS 04	
AS*5 VI	71 CJCHA	49	2530	CL F2	AS F6
73 JSSCB	6	80	MG8	S	AS3 016
70 CJCHA	48	3124	CD8	AS3 016	
73 ACACB	29	266	CALCULATED		
74 INDOA	13	780	XL	AS F11,AE2	AS F9
74 ACBCA	30	250	R	AS F6	
AU*3 IVS0	69 JCSIA	1969	1936	R	AU F4
70 ZACCA	375	43	LI3	AU O3,K AU O2,RB AU O2	
70 JCSIA	1970	3092	R	AU UNO314	
AU*5 VI	74 INUCA	13	775	RE2	AU F17
D *3 VIII	68 NJHMA	1968	80	CA	AL B 04
70 ACBCA	26	102	BA	T16	D13
71 SPHCA	15	905	CA4	AL6	D10 F2
71 ACBCA	27	1892	BE1A	AL2	B 07
70 ACBCA	26	1899	AL2	BE3	S16 D18
71 ACBCA	27	1892	BE1A	AL2	B 07
70 ZKXKA	132	241	CA	B3	O5 10M1
71 JACCA	4	284	CU	AS 04	
74 JPSCA	60	1899	NA	B 04	07
74 MRBUA	9	1061	ND	AL 1	(B 03)14
B *3 IV	68 ACBCA	24	1518	(MG,FE)	AL3 S1 B 09
68 ACBCA	24	1518	(MG,FE)	AL3 S1 B 09	
68 CJCHA	46	917	CU3	AS2 08	
63 BAPCA	11	361	MG	AS2 07	
69 ACBCA	25	1544	CA	M AS 04+2	H2 0
68 AMNIA	53	1861	MN2	H AS 04	
63 CARMA	7	561	CA	CU AS 04	O M
70 ACBCA	26	1574	NA2	H AS 04+2	H2 0
69 CHDCA	268	1694	BA	N12	AS2 08
70 AMNIA	55	2023	MN9	10 H19	(H2 O)2
70 ACBCA	26	1899	IN	HO11	AS 04+2
70 ACSAA	24	3711	LI	MO	AS 04
70 INDOA	9	2259	CA2	AS 04	CL
65 ACACB	18	777	CU3	AS 04	O H13
70 CJCHA	48	890	MG2	AS2 07	
70 CJCHA	48	891	CU3	AS2 08	
71 CJCHA	49	1036	CA3	AS2 08	
70 AMNIA	55	1409	MN7	58	AS 012
71 ACBCA	27	2124	NA3	AS 04+12	H2 0
73 ACBCA	29	2611	MG3	AS2 08	
61 AMNIA	46	1077	CA2	B AS 04	10H14
73 CJCHA	51	2082	NA4	AS2 07	
66 ZACCA	347	133	SR	H AS 04	H2 0
66 ZACCA	347	140	SR	H AS 04	H2 0
71 AMNIA	56	1167	ZNA	AS2 08	10H12,2H2 0
70 ACBCA	26	403	CA	H AS 04	H2 0
70 ZKXKA	132	332	CD3	AS2 08	
73 ACBCA	29	141	LU	AS 04	
73 ACBCA	29	2121	MN4	AS 04	
AS*5 VI	71 CJCHA	49	2530	CL F2	AS F6
73 JSSCB	6	80	MG8	S	AS3 016
70 CJCHA	48	3124	CD8	AS3 016	
73 ACACB	29	266	CALCULATED		
74 INDOA	13	780	XL	AS F11,AE2	AS F9
74 ACBCA	30	250	R	AS F6	
AU*3 IVS0	69 JCSIA	1969	1936	R	AU F4
70 ZACCA	375	43	LI3	AU O3,K AU O2,RB AU O2	

Table 2 (cont.)

74 ZAACA 403 1 R3 VS V (DY F3)  
ER+3 VI 26 484 ER2 S12 07  
ER+3 VII 15 36 ER2 GEZ 07  
70 SPHCA 2 197 ER 0 (THD)10 IO H12  
72 JCMCLB 2 47 ER P 04; ER V 04  
ER+3 VIII 9 2100 ER (C2 04) (M C2 04).3H2 0  
70 INOCA 8 1745 ER3 FE5 U12  
70 SSCGO 5 372 ER (M U C H2 C D 0)3.2H2 0  
74 ZAACA 403 1 R3 VS V (ER F3)  
72 JCMCLB 2 197 ER 0 (THD)10 IO H12  
ER+3 IX 112 362 ER (C2 M5 S 04)3.9H2 0  
74 ZAACA 403 1 R3 VS V (ER F3)  
EU+2 VI 374 201 LI EU3 04  
EU+2 VII 374 201 LI EU3 04  
69 ACBGA 25 1104 EU 12 V (ER F3)  
73 REF 3 L12 EU5 08  
EU+2 VIII 10 77 EU CL2 EU BR2  
UNPUI EU F2; EU BR2  
73 RVCHA 10 77 EU CL2 EU F2  
UNPUI EU F2  
EU+2 X 58 218 EU2 S1 04  
71 NATMA 58 218 EU2 S1 04  
EU+3 VI 4 EU4 AL2 09  
70 ZAACA 374 201 LI EU3 04  
73 REF 3 L12 EU5 08  
EU+3 VII 4 EU4 AL2 09  
73 REF 3 L12 EU5 08  
EU+3 VIII 48 1094 EU3 FE2 GA3 012  
74 ZAACA 403 1 R3 VS V (EU F3)  
73 ACSAA 27 2827 EU2 (C3 H2 04)3.8H2 0  
EU+3 IX 74 ZAACA 403 1 R3 VS V (EU F3)  
73 ACSAA 27 2827 EU2 (C3 H2 04)3.8H2 0  
71 ACSAA 25 3347 EU TRISGLYCOLATE  
FE+2 IV SQ HS 59 1166 BA FE S14 010  
FE+2 V HS 166 1399 (NA)K12 FE4 S112 030.H2 0  
69 ZAACA 369 306 FE V2 04  
71 JUPSA 31 452 FE2 T1 04  
72 JUPSA 33 1296 FE2 M1 04  
FE+2 VI LS 25 925 R VS A (FE S2)  
FE+2 VII HS 430 FE AL2 IP 0412 IO H12 IO H216  
69 NUNMA 1069 430 FE AL2 IP 0412 IO H12 IO H216  
70 BUFGA 93 190 FE S 04  
71 SPHCA 15 999 FE3 BE S13 09 (F,0 H12  
67 ACCRA 22 775 FE (NH4)215 0412.0H2 0  
68 CMFTA 68 290 FE 04  
74 AMMIA 59 486 FE2 S1 04  
FE+2 VIII 56 791 GARNETS  
71 ZKRKA 134 333 FE3 AL2 S13 012  
73 ACBGA 29 266 CALCULATED  
FE+3 IV HS 26 1469 CA2 FE2 05  
70 ACBGA 8 1745 ER3 FE5 012  
71 ACBGA 27 1263 BA FE2 04  
71 MRBUA 6 725 BA CA FE4 08  
71 ACSAA 25 3616 CA2 FE2 05  
73 ACBGA 29 832 BA FE2 04  
FE+3 V 4 1 FE V 04  
FE+3 VI HS 26 1469 CA2 FE2 05  
70 ACBGA 8 1745 ER3 FE5 012  
71 SSCGO 9 335 K FE F4  
71 JSSCB 4 1 FE V 04  
71 JPCSA 32 1315 FE 03  
71 ACSAA 25 3016 CA2 FE2 05  
69 ACCRA 23 239 FE (C5 M7 02)3  
69 CCJDA 1969 440 FE (C7 M5 02)3  
FE+3 VIII 8 331 ESTIMATED  
FE+3 IX 8 331 R3 VS V (PEROVSKITES)  
73 JSSCB 8 43 R2 FE 04  
FE+3 X 8 43 R3 VS V (K2 FE 04)  
GA+3 IV 27 616 L15 04 04  
75 ACBGA 31 948 SR GA S12 08  
GA+3 V 30 1364 C15 H21 06 GA  
GD+3 VII 26 484 GD2 S12 07  
72 ACBGA 28 60 GD2 M03 012  
72 SPHCA 16 790 GD2 GE2 07  
69 IVMMA 5 1823 GD0.33 S16 026  
72 JSSCB 5 286 GD0.33 S16 026  
GD+3 VIII 15 926 NA GD S1 04  
72 SPHCA 16 790 GD2 GE2 07  
74 ZAACA 403 1 R3 VS V (GD F3)  
GD+3 IX 16 790 GD2 GE2 07  
69 IVMMA 5 1823 GD0.33 S16 026  
74 ZAACA 403 1 R3 VS V (GD F3)  
GE+4 IV 126 299 GD GE 03  
69 SCIEA 165 586 M2 GE 04  
69 ZKRKA 129 427 M3 FE2 GE3 012  
70 JSSCB 2 612 HG28 GE10 048  
71 SPHCA 15 926 NA GE 04  
70 ACSAA 24 1287 NA4 S2 GE4 012 IO M14  
67 ACSAA 21 1281 NA8 S4 GE4 012 IO M14  
70 NDCMB 102 964 NA2 GE 03  
71 NDCMB 102 1245 R2 GE4 09  
72 SPHCA 17 246 GD GE 03  
72 NDCMB 103 1560 GE5 0 (P 04)16  
GE+4 V 1 557 CA2 GE 04  
70 JSSCB 2 612 HG28 GE10 048  
71 NDCMB 102 1245 R2 GE4 09  
71 ACBGA 27 2133 GE 02  
72 AMMIA 57 62 M2 GE 04 DELTA  
72 ZKRKA 136 387 GE (D M) P 04  
72 NDCMB 103 1560 GE5 0 (P 04)16  
M+1 I 1 43 T F  
56 JCPSA 45 275 M F  
M+1 IV 13 275 R3 VS V (M4 M 04)  
M+1 V 53 126 M F 02  
69 ACSAA 19 3541 M (D H12 S 04).H2 0  
74 ACSAA 27 3407 M4 IOH18 (C4 04).H2 0  
M+1 VIII 27 2455 M F IO H12 S 04  
M+1 VI 1971 466 HG2 F2  
M+2 II 29 869 HG MO 04

73 ACBGA 29 869 HG MO 04  
HDC+3 VIII 30 2049 K MO BE F6  
74 ACBGA 8 1745 M03 FE5 012  
72 BUFGA 95 437 MO P5 014  
74 ZAACA 403 1 R3 VS V (MO F3)  
MDC+3 IX 403 1 R3 VS V (MO F3)  
74 ZAACA 30 2613 M02C M5 S 04)3.9H2 0  
74 ACBGA 13 2535 M01H2 014 (M C 03)3.2H2 0  
73 CJCHA 53 831 (M IO2)10(M D)515  
MDC+4 IV 54 2556 N H4 I 03  
66 ACCRA 20 758 LI 1 03  
66 ACCRA 20 894 LI 1 03  
58 ACCRA 9 1015 CE (I 03)4  
58 ACCRA 11 796 CE (I 03)4.H2 0  
43 TICCPB 62 739 N M H 1 03  
I+5 VI 54 2556 N H4 I 03  
1+7 IV 26 1782 NA I 04  
28 ZEPFA 59 381 K I E 03  
71 JCSIA 1971 1857 I+7)1-0  
I+7 VI 20 765 M5 I 04  
65 ACCRA 19 629 K4 H2 I2 010.8H2 0  
37 JACSA 59 2036 (M H4)12 H3 I 06  
IN+3 IV 409 97 RB IN4 07  
74 ZAACA 395 280 SR2 IN2 05  
IN+3 VI 409 97 RB IN4 07  
61 ACSAA 15 1437 (M 0 H S 04).1H2 012  
68 ACCRA 24 388 CUE IN2 05  
70 ACSAA 24 1662 (M 0 D) H  
69 INOCA 8 1985 IN2 03  
74 ACBGA 30 1882 K H2 S12 06  
74 SPHDA 18 761 IN2 GE2 07  
IR+4 VI 3 174 SR IR 03  
71 JSSCB 9 1177 R3 VS V (C02 IR2 07)  
74 MRBUA 358 241 K AG 0  
K+1 IV K2 0  
68 ZAACA 264 144 K S8 F6  
51 ZAACA 12 1095 K V M02 08  
69 CCJDA 11 602 K H2 S12 05  
69 ACBGA 25 1919 K UZ F9  
K+1 VII 46 935 K2 CR2 07  
68 CJCHA 1969 849 K2 MO 04  
71 SSCGO 9 335 K FE F4  
K+1 VIII 74 306 K H2 P 04  
62 ZKRKA 117 411 K2 T16 013  
47 ZKRKA 98 286 K H2 (M3 01) 85 010  
71 INUGA 7 873 K H C2 04  
68 CJCHA 46 935 K2 CR2 07  
70 JCSIA 1970 3092 K (M 03)4  
65 ACCRA 19 629 K4 H2 I2 010.8H2 0  
K+1 IX 27 K1.4 NA5.5 GA0.3 AL7.5  
69 ACBGA 25 600 L16 S 032  
69 ACBGA 25 1919 K UZ F9  
K+1 X 51 2613 K AL P2 07  
73 CJCHA 13 420 K V M2 08  
71 INOCA 10 1264 K2 PB CU (M 02)16  
67 INOCA 5 514 K2 BA CU (M 02)16  
74 JACSA 96 6606 K2 GA CU (M 02)16  
75 ACBGA 31 594 K2 BA CU (M 02)16  
57 PISAA 50 143 K CL 04  
LA+3 V 129 259 CU LA 02  
69 ZKRKA 8 1269 R3 VS V (REZ M3 012)  
73 MRBUA 59 1277 LA5 MG2 T13 S14 022  
LA+3 VIII 29 2074 LA2 M03 012  
68 INOCA 7 2295 LA (C5 M7 02)3 (H2 012  
74 ZAACA 403 1 R3 VS V (LA F3)  
74 SPHCA 18 675 LA2 SR3 (B 03)4  
LA+3 IX 6 23 LA FE 03  
74 ZAACA 403 1 R3 VS V (LA F3)  
74 AMMIA 59 1277 LA4 MG2 T13 S14 022  
L1+1 IV 102 119 LI 0 H+H2 0  
70 ZAACA 379 157 C 02  
70 INOCA 9 1096 YB LI F6  
71 AMMIA 56 18 NA3 AL2 L13 F12  
71 ACBGA 27 618 L15 04 04  
73 JSSCB 6 538 L13 V 04  
73 ACBGA 29 2625 LI (M2 M5) BE F4  
73 ACBGA 29 2628 LI M3 D M S 04  
64 ACCRA 17 793 L12 C2 04  
74 ACBGA 30 2434 L12 BE S1 04  
L1+1 VI 24 225 L13 AL F6  
69 ZAACA 371 306 L12 ZR 03  
70 ZKRKA 132 118 L12 L12 S13 010  
71 MRBUA 6 555 L12 MO F6  
65 ACCRA 19 561 LI C6 07 H7  
74 ACTEA 86 819 LI NB 02  
68 CMFTA 68 290 LI FE P 04  
71 ACSAA 25 3337 LI M03 08  
73 CJCHA 51 265 LI V 03  
73 ACBGA 29 2294 L12 ZR F6  
LU+3 VI 377 70 CA LUG 04  
71 JACCA 4 284 LU B 03  
LU+3 VIII 403 1 R3 VS V (LU F3)  
LU+3 IX 403 1 R3 VS V (LU F3)  
MG+2 IV 28 267 K2 MG5 S112 030  
22 ACCRA 5 684 MG AL2 04  
72 ACBGA 28 3583 M2 H1 S16 015  
74 ACBGA 30 2467 K6 MG P2 08  
MG+2 V 22 1966 MG3 P2 08  
66 UNPUI 1966 142 MG P2 08  
UNPUI MG3 P2 08  
MG+2 VI 43 1139 MG2 P2 07  
65 BAPCA 11 361 MG2 AS2 07  
70 ACBGA 26 1429 MG N H4 P 04  
71 CJCHA 49 1030 MG N H4 P 04  
69 INOLA 8 1665 C54 MG3 F10  
69 ZKRKA 129 65 MG S1 03  
65 SPHCA 13 933 M 04  
70 JSSCB 2 612 HG28 M10 048  
65 MRLMD 1965 1960 MG AL B 04  
70 SCIEA 1970 M243 S 04.H2 0  
71 ACBGA 27 815 M3 T 06  
68 ACSAA 22 1466 MG3 P2 08  
70 RLF 1 CA MG S1 04

74 ACBGA 30 2491 MG2 V2 07  
71 AMMIA 56 1553 MG (86 07 IO M16).2H2 0  
73 AMMIA 58 1029 MG C 03  
74 CJCHA 52 1185 GA18 MG2 H2 IP 04)14  
70 INOCA 9 151 MG (MPPA)3 (CL 04)12  
72 CJCHA 50 3619 MG V2 04  
74 ACBGA 29 2613 M03 AS2 08  
MG+2 VIII 29 266 CALCULATED  
73 ACBGA 29 266 CALCULATED  
MNA+2 IV 53 1489 MNT S8 AS 012  
69 ZKRKA 369 306 MN V2 04  
71 ACBGA 27 1044 MN CO CR 04  
69 PHSSA 32 891 MN CR2 04  
73 ACBGA 29 266 CALCULATED  
MNA+2 V HS 53 1841 M2 0 M 45 04  
74 MPRTA 21 246 M2 AS 04 04  
MNA+2 VI LS 29 925 A VS 0 ELECTRONS  
MNA+2 VII HS 165 586 M2 GE 04  
69 JCPSA 51 4928 BA MN F4  
70 ZKRKA 132 1 MMS IO M12 S12 08  
69 AMMIA 54 1312 MN FE2 IP 04)12 (M12).2H2 0  
70 NMJIA 113 1 MNT NA12 (S 04)11.15H2 0  
65 ACCRA 19 854 MN S 04  
72 AMMIA 57 621 M2 GE 04  
67 PRLLA 92 125 MN C 03  
67 HCAGA 50 2023 MNS 08  
MNA+2 VIII 57 621 M2 GE 04  
MNA+2 IX 129 427 M3 FE2 GE 012  
71 AMMIA 56 791 GARNETS  
71 JSSCB 12 109 M3 AL2 GE3 012  
74 JCPSA 49 1875 MN B4 07  
MNA+3 VI HS 21 2871 M2 03  
67 ACBGA 124 428 M2 03  
68 ACBGA 24 1233 M4 0 D H  
69 JCPSA 50 1068 (M H4)2 MN F5  
69 PHSSA 5 K444 M2 03  
68 BUFGA 91 339 TB MN 03; PR MN 03; ND MN 03  
71 JSSCB 3 238 LA MN 03; M3 04  
LA+5 CA05 M3 03  
73 JSSCB 6 16 NA MNT 012  
74 AMMIA 59 985 M2 MN B 05  
68 ACBGA 24 1114 M4 MNA T15 018  
74 INOCA 13 1854 MN (C7 M5 02)3.1/4 C6 M5 CH3  
74 INOCA 13 1864 MN (C6ACT)3  
MNA+4 IV 13 275 R3 VS V (M4 MN 04)  
MNA+4 V 8 234 BA MN 03  
69 INOCA 8 335 NA12 MN NB12 038.50M2 0  
65 CEFPA 13 308 NA4 MN M1 03)3.12H2 0  
67 HCAGA 50 2023 MNS 08; C02 M3 08  
MNA+4 VI 28 2845 K2 MN 04  
MNA+4 VII 24 1053 AG MN 04  
MNA+4 VIII 25 400 K3 MO CL6  
69 INOCA 8 2694 K3 MO F6  
MNA+4 IX 6 555 L12 MO F6  
MNA+5 I 13 2715 R3 VS V (RE MO 04)  
MNA+5 VI 10 922 BA2 ND MO 06  
MNA+5 VII 48 2619 CU MO 04  
68 SPHDA 12 1095 K V M02 08  
69 JCSIA 1969 849 K2 MO 04  
72 ACBGA 28 60 GU2 M03 012  
69 JCPSA 50 86 M02 M03 012  
71 SPHCA 15 811 L13 FE M03 012  
71 SPHCA 15 829 K AL M02 08; K FE M02 08  
71 JCPSA 55 1093 CA MO 04; SR MO 04  
73 ACBGA 29 2074 LA2 M03 012  
71 JCSIA 1971 1857 M0+6) -0  
MNA+5 VIII 1967 374 K2 M03 010  
68 JCSIA 1968 1398 K2 M03 010  
MNA+5 IX 1968 1398 K2 M03 010  
68 JCSIA 1968 1398 K2 M03 010  
70 JSSCB 1 486 AG6 M10 033  
70 INOCA 4 2228 NA3 (C4 MO 06 024 H6)1.8H2 0  
70 ACSAA 24 3711 LI M02 U2 AS 04  
66 ACCRA 20 2698 MO F6 (GA5)  
70 CCJDA 1970 50 M0 C H2 012  
72 ACBGA 28 2222 M03.2H2 0  
67 INOCA 3 1803 K2 (M02 02 (C2 04) H2 012 0  
73 ACBGA 29 869 MG 04 04  
74 ACBGA 30 1795 M0 03)9H2 0  
N+3 IV REF 6 M3 N2.S13 N4.B N.TI N  
N+5 III REF 6 N4.N 03.NA N 03.K N 03.  
BAIN 03)12.TIIN 03)14  
NA+1 IV 409 69 NA6 ZN 04  
REF 2 NA2 0  
NA+1 V 24 1077 NA2 S12 05  
68 SPHDA 12 987 NA2 ZN2 S12 07  
64 JACSA 329 110 NA2 MG 02  
NA+1 VI 24 1287 NA4 S2 GE4 012 IO M14  
65 ACCRA 19 561 NA C6 07 M7  
63 ACCRA 15 1233 NA B (DM)4.2H2 0  
60 ZKRKA 113 430 NA2 AL2 S13 010.2H2 0  
58 ZKRKA 111 241 NA CL 03  
56 ACCRA 9 811 (NA AS 03)1X  
53 ARKCA 8 77 NA S8 F4  
59 ACCRA 12 526 NA U ACETATE  
74 ACBGA 30 1872 NA2 M 04  
75 ACBGA 31 890 NA2 C 03.H2 0  
NA+1 VII 15 926 NA GO S1 04  
70 NMJIA 113 1 MNT NA12 (S 04)11.15H2 0  
73 ACBGA 29 890 NA2 CR2 07 ALPHA  
NA+1 VIII 24 1703 NA B F4  
68 SPHDA 12 987 NA2 ZN2 S12 07  
71 AMMIA 56 1843 AL2 L13 F12  
NA+1 X11 3 89 NA13 NB35 094  
12 ZKRKA 81 135 NA AL S1 04  
NB+3 IV 86 819 LI NB 02  
NB+3 V 97 2713 NB(DPM)4  
NB+3 VI 48 5048 BA27 SRT.5 M2 05.78  
70 JSSCB 1 459 M+M2 05  
70 JSSCB 1 459 M+M2 05  
70 AMMIA 55 90 CA M2 06  
55 PRVAA 98 903 C02 M2 07  
71 JSSCB 3 89 NA13 NB35 094  
71 ZAACA 380 119 MN M2 04  
74 JINCA 36 1965 CA2 NB2 07  
71 JCSIA 1971 1280 B13 NB07 047

Table 2 (cont.)

70 ACBCA	26	105 BA3 S14 N86 D26
71 ACSAA	25	3347 L1 NB3 08
59 SPSCA	4	796 1Y 7B3 NB 04
73 JSSCA	4	150 B1 NB 04
66 ACSAA	20	72 NB P 05
74 BUCFA	97	3 NA3 NB D4
NB+5 VII		
70 JSSCB	1	454 NA2 NB 011
71 JSSCB	1	89 NA1 NB 094
71 ACBCA	27	1610 (NM4)3 N8 0 (C2 O4)3, H2 O
75 ACBCA	31	673 NB2 05
ND+2 VIII		
UNPUL		ND 12
ND+2 IX		
UNPUL		ND CL2+ ND BR2
ND+3 VI		
71 INDOA	10	922 BA2 ND MD 06
74 MRBUA	9	1661 ND AL B4 012
ND+3 VIII		
69 JCPFA	50	86 ND2 MD3 012
71 JSSCB	3	458 ND V 04
70 SPHCA	14	518 K ND M2 08
70 ACBCA	26	1484 ND2 T12 07
70 ACSAA	25	3408 ND4 REZ 011
71 SPHDA	15	636 ND2 M 06
71 SPHCA	15	991 ND4 M5 015
74 MRBUA	9	129 ND 05 014
74 ZAACA	403	1 R3 VS V (ND F3)
74 ACBCA	30	468 ND P3 02
ND+3 IX		
70 ACSAA	24	2969 ND2 (C2 O4)3, 10, 5H2 O
71 SPHCA	15	991 ND4 M5 015
73 ACSAA	27	2441 ND2 (C3 H2 O4)3, H2 O
74 ZAACA	403	1 R3 VS V (ND F3)
73 ACSAA	27	2815 ND2 (C3 H2 O4)3, H2 O
73 ACSAA	27	2973 ND 04 03
74 AMHIA	59	1277 ND4 MG2 T13 S14 022
ND+3 XII		
72 JSSCB	4	11 ND AL 03
NI+2 IV		
61 JAPFA	32	685 NI CR2 04
65 BSCFA	1965	1085 SPINELS
NI+2 V		
66 INDOA	5	1200 NI (DPM)2
NI+2 V		
67 BAPCA	15	47 NI2 P2 07
NI+2 VI		
74 AMHIA	59	486 NI2 S1 04
74 ACBCA	30	1086 NI (PY N D16 1B F4)2
68 ZAACA	358	125 NI SE 04
67 BAPCA	15	47 NI2 P2 07
70 ACBCA	26	1464 RB NI F3
70 ZAACA	378	129 SR2 NI TE 06
70 JSSCB	2	416 RB NI F3
71 PHSSA	438	125 NI (D H)2
70 REF	1	NIZ S1 01
64 ACBCA	17	1481 NI (C5 H7 O2)2, H2 O
73 ACBCA	29	2742 NI S1 F6, H2 O
63 ZKKA	118	291 NI (H O)2, H2 O
74 JCPFA	61	852 NI CA 04, H2 O
73 JGRLB	3	181 NI (C5 O2)2, (C2 H5 O)2 H2 O
73 ACBCA	29	2304 NI3 V2 08
NI+3 VI		
74 ZAACA	405	167 M2 N1 F6
71 CHDOA	272	2163 HO NI 03
NI+3 VI		
54 JACSA	76	1499 NA NI 02
NI+4 VI		
67 STBGA	3	1 R3 VS V (FLUORIDES)
74 JINCA	36	1561 R2 NI 04
ND+2 VI		
74 INDOA	13	2233 ESTIMATED
NP+4 VI		
68 JINCA	30	823 NP CL3
NP+4 VI		
67 INUCA	3	327 ESTIMATED
74 CJCHA	52	2175 R3 VS V
NP+6 VI		
R3 VS V (BA2 SR NP 06)		
OH-1 III		
71 AMHIA	56	1155 MG6, 6 FE, 4 S13 O12 F O H, R10H-11=RF-11+, 04
OH-1 III		
71 AMHIA	56	1155 MG6, 6 FE, 4 S13 O12 F O H, R10H-11=RF-11+, 04
OH-1 IV		
R10H-11=RF-11+, 04		
OH-1 VI		
R10H-11=RF-11+, 04		
OS+4 VI		
69 JCDMA	17	459 OS 02
70 ACSAA	24	123 OS 02
OS+5 VI		
71 JCSIA	1971	2789 OS F5
74 SSCDA	14	357 R4 VS V (C02 OS2 07)
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 04
73 ACBCA	29	1983 OS 04
65 ACCRA	19	157 OS 04
71 JCSIA	1971	1857 OS(8+) -0
P+5 IV		
72 ACBCA	28	2883 C02 P2 07
68 CJCHA	46	605 C02 P2 07
65 CUCHA	43	1139 M02 P2 07
68 INDOA	7	1345 CA2 P2 07
71 BSCFA	1971	426 ZR P2 07
70 ACBCA	26	1826 M3 P 04, 1/2 H2 O
71 ACBCA	27	291 NA2 H2 P2 07, H2 O
71 NMMA	1971	241 SR AL3 IP 0412 (O H)5, H2 O
69 ZKKA	130	148 R ZR2 IP 0413
71 ACBCA	27	2128 NA3 P 04, 1/2 H2 O
68 ACSAA	22	1822 NA CR2 P2 012
68 ZKKA	127	21 AL3 P2 08, 5H2 O
68 CIMFA	68	291 L1 FE 04
70 ACBCA	26	1826 M3 P 04
72 AMHIA	57	45 MN, 45 FE, 35 P 04
72 ACBCA	28	2045 (M H4)2 M P 04
73 ACBCA	29	141 LU P 04
71 ACBCA	27	2247 CA 1M2 P 04, 1/2 H2 O
73 ACBCA	29	2292 AL P 04, 1/2 H2 O
71 ACSAA	25	512 K H5 IP 0412
70 JSSCB	1	120 ZH2 P2 07
P+5 V		
67 JACSA	89	2268 C23 H29 OS P
67 JACSA	89	2270 C23 H29 OS P
P+5 VI		
71 ZAACA	380	51 P CL5
72 CCJDA	1972	676 ET3 M H (C6 H4 O2)3 P
74 ACBCA	29	246 CALCULATED
PA+4 VI		
67 INUCA	3	327 R (PU+4)
74 CJCHA	52	2175 R3 VS V
PA+5 VI		
71 ACBCA	27	731 K PA 03
PA+5 IX		
67 JCSIA	1967	1429 K2 PA F7
PB+2 IV		
68 ZKKA	126	98 PB S1 03
PB+2 VI		
70 ACACB	26	501 PB2 03
PB+2 VIII		
69 ZKKA	128	213 PB CA2 S13 09
64 ACCRA	17	1539 PB P2 06
PB+2 VIII		
71 SPHCA	15	928 PB M 04
64 ACCRA	17	1539 PB P2 06
73 CJCHA	51	70 PB2 V2 07
72 MRBUA	7	1025 B1 TITANATES
PB+2 IX		
67 ACCRA	22	744 PB F2
73 CJCHA	51	70 PB2 V2 07
74 ZKKA	139	215 PB C 03
74 CJCHA	52	2701 PB V2 06
PB+2 X		
70 ZKKA	132	228 PB3 P2 08
PB+2 XII		
57 ACCRA	10	103 PB (N O)312
70 ZKKA	132	228 PB3 P2 08
71 INDOA	10	1264 X2 PB CU (N O2)6
PB+4 IV		
72 JCSIA	1972	2448 R3 VS V (NA4 PB 04)
PB+4 V		
70 ZAACA	375	255 RB2 PB 03
PB+4 VI		
70 ACACB	26	501 PB2 03
65 JINCA	27	1509 PB3 04
74 CJCHA	52	2175 R3 VS V
PD+4 VIII		
68 MRBUA	3	153 PB 02
PD+2 IV		
67 INDOA	6	730 PD (C6 H5 CH3 CH1C O2)2
68 JSTCA	9	166 PD (C6 H5 CH3 CH2 C O2)2
PD+4 VI		
68 MRBUA	3	699 R3 VS V (M2 PD2 07)
73 INDOA	12	1726 KE PD F11
61 JCSIA	1961	3728 K2 PD F6
PM+3 VI		
74 ZAACA	403	1 R3 VS V (PM F3)
PM+3 IX		
74 ZAACA	403	1 R3 VS V (PM F3)
PO+4 VI		
74 CJCHA	52	2175 R3 VS V
PO+4 VIII		
R3 VS V (FLUORITE)		
PR+3 VI		
71 MRBUA	6	545 R3 VS V (PR2 MD3 012)
PR+3 VIII		
70 SPHCA	15	28 PR2 M2 09
74 ZAACA	403	1 R3 VS V (PR F3)
PR+3 IX		
70 SPHCA	15	28 PR2 M2 09
59 ZKKA	112	362 PR (C2 H5 S O4)3, H2 O
74 ZAACA	403	1 R3 VS V (PR F3)
PR+4 VI		
72 ACBCA	28	956 BA PR 03
75 ACBCA	31	971 RB 012
73 JSSCB	8	331 R (PR+4)
74 CJCHA	52	2175 R3 VS V
PT+2 IV		
72 REF 5		PT3 CO 06
PT+4 VI		
69 JINCA	31	3803 PT 02
74 CJCHA	52	2175 R3 VS V
PT+5 VI		
67 STBGA	3	1 R3 VS V (FLUORIDES)
67 JCSIA	1967	478 KE PT F11
PU+3 VI		
67 INUCA	3	327 R (PU+3)
75 JINCA	37	743 R (PU+3)
PU+4 VI		
67 INUCA	3	327 R (PU+4)
73 JSSCB	8	331 R (PU+4)
74 CJCHA	52	2175 R3 VS V
PU+6 VI		
R3 VS V (BA2 SR PU 04)		
RB1 VI		
70 ZAACA	375	255 RB2 PB 03
RB1 IX		
74 ACBCA	30	1640 RB2 S 04
RB1 XI		
74 ACBCA	30	1640 RB2 S 04
RB1 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 02 (N O)312
RE+4 VI		
68 INDOA	7	108 LA4 RE6 019
74 CJCHA	52	2175 R3 VS V
RE+5 VI		
70 ACSAA	24	3406 ND4 RE2 011
UNPUL		CD2 RE2 07
68 ACBCA	24	874 RE CL3
RE+6 VI		
75 JSSCB	13	77 BA2 MN RE 06
R3 VS V (PEROVSKITES)		
RE+7 IV		
68 ACIEA	7	295 RE2 07 (O H)212
71 JCSIA	1971	1857 RE1+7) -0
70 CJCHA	48	219 (RE2 (M-C4 H7 O2)2) (RE 04)2
RE+7 VI		
68 ACIEA	7	295 RE2 07 (H2 O)2
RH+3 VI		
70 ACBCA	26	1876 RH2 03
RH+5 VI		
73 INDOA	12	2640 RH F5
RU+3 VI		
R3 VS V (LA RU 03)		
RU+4 VI		
70 ACSAA	24	116 RU 02
74 ACBCA	30	1459 NA1=K1 RU 09
74 CJCHA	52	2175 R3 VS V
RU+5 VI		
71 JCSIA	1971	2789 RU F5
REF 7		K3 VS V (C02 RU2 07)
73 INDOA	12	1717 RE RU F11
RU+7 IV		
54 JACSA	76	3317 K RU 04
RU+8 IV		
67 ACSAA	21	737 RU 04
S+6 IV		
68 ACBCA	24	508 CU S 04, 3 H2 O
70 ZKKA	132	90 PR2 S 05
70 BUCFA	93	190 FE S 04 ALPHA
70 BUCFA	93	185 FE S 04 O H
70 BSCFA	1970	4263 MO S 04 H2 O
71 ACBCA	27	272 N H4 M S 04
70 NMMA	11	11 M7 NA12 S 04, 1/2 H2 O
69 ACCRA	19	854 MN S 04
71 ACSAA	25	3213 NA H S 04 H2 O
72 ACBCA	21	864 MN S 04
72 NATUA	238	95 CA S 04, 2H2 O
72 ACBCA	28	2865 K2 S 04
74 JSTCA	14	409 T12 S 04
74 ACBCA	30	921 CA S 04, 2H2 O
74 NMMA	121	208 FE2 S 04, 3
S+6 VI		
73 ACACB	29	266 CALCULATED
SB+3 IV		
70 ACSAA	24	320 SB P 04
SB+3 VI		
70 AMHIA	55	1489 M7 SB AS 012
71 JCSIA	1971	942 AS SB F8
71 JCSIA	1971	2318 HR2 SB F16
74 JCSIA	345	NA SB 03
SL+3 VI		
68 CJCHA	46	1448 SC2 03
68 ARKEA	29	343 SC2 03
UNPUL		SC2 S12 07
73 SPHCA	17	749 SC2 S12 07
73 INDOA	12	927 SC (C5 H7 O2)3
73 ACBCA	29	2615 NA SC S12 06
74 INDOA	13	1886 M SC (C7 H5 O2)3
73 ACSAA	27	2841 SC U M (C3 H2 O4)2, H2 O
69 SPMDA	14	9 NA3 SC S12 07
SC+3 VIII		
74 INUCA	10	137 SC M (C7 H5 O2)3
72 ACSAA	26	1337 SC2 (C2 O4)3, H2 O
74 INDOA	13	1886 M SC (C7 H5 O2)3
74 INDOA	13	1886 M SC (C7 H5 O2)3
SE+6 IV		
68 ZAACA	358	125 M4 SE 04, CO SE 04, NI SE 04
51 JCSIA	217	948 M2 SE 04
70 ACBCA	26	436 NA2 SE 04
70 ACBCA	26	1451 K2 SE 04
70 ZAACA	379	204 NI SE 04, H2 O
72 ACBCA	28	2845 K2 SE 04
69 ACBCA	25	19 CU (N H3)4 SE 04
71 JCSIA	1971	1857 SE(4+) -0
SI+4 IV		
61 NATWA	50	91 FE2 S1 04
73 ZKKA	137	86 M2 S1 04
61 ACCRA	14	835 M3 AL2 S13 012
61 ACCRA	132	1 M45 M2 S12 012
58 ACCRA	11	437 CA3 AL2 S13 012 (GROSSULARITE)
71 AMHIA	56	193 G02 CA2 S13 010, 2H2 O
71 SPHCA	15	926 NA CU S1 04
71 SPHCA	15	806 Y2 S1 04
71 NATWA	58	218 EU2 S1 04
70 REF 14	3	161 G02 S1 04
70 ACBCA	26	105 BA3 S14 N86 026
71 ACBCA	27	747 CAZ S1 04, CA CL2
71 ACBCA	27	648 CA2 S1 04
71 AMHIA	56	1222 NA, 16 K, 84 CA, 1518 O2O1F, H2 O
58	1155	MG5, 6 FE, 4 S13 O12, M2 F O H
69 NSAPA	2	31 LI M S12 D6, NA M S12 06
CA MG S12 06		
69 NSAPA	2	95 FE, 6 NA, 108 R, CA, 1 S18 O22, 1 (OH)1, 4 F, 5
69 NSAPA	2	101 LI, 2 NA, 1 MG12, 9 S11, 7
AL, 1 D, 1 F, 4, 3 (OH)1, 3		
70 ZKKA	132	288 CA5 S12 07 (C O)312
71 ACBCA	27	2269 NA2 S1 03, H2 O
71 SPHCA	16	1021 BE2 SM (S O4)2, H2 O
72 ACBCA	28	1899 AL2 BE3 S16 018
74 ACBCA	30	2434 LI2 BE S1 04
SI+4 VI		
62 NATWA	49	345 S1 02
69 CJCHA	47	3859 CU S1 F6, H2 O
70 ACBCA	26	233 S1 07
71 ACBCA	27	2133 S1 02
71 ACBCA	27	594 CA3 S1 01 H16, 12H2 O, 504, CO3
73 ACBCA	29	2741 M S1 F6, H2 O
73 ACBCA	29	2748 CU S1 F6, H2 O
70 CJCHA	52	2175 R3 VS V
SM+2 VII		
UNPUL		SM 12
SM+2 VIII		
UNPUL		SM BR2, SM F2
SM+2 IX		
UNPUL		SM CL2, SM BR2
SM+3 VI		
71 SPHCA	15	924 NA SM GE 04
SM+3 VIII		
70 SPHCA	15	214 SM2 S12 07
74 SPHCA	18	575 K2 SM F5
SM+3 IX		
74 ZAACA	403	1 R3 VS V (SM F3)
74 ACBCA	30	1751 SM P5 014
SM+3 XI		
69 ACACB	25	62

Table 2 (cont.)

72 ACBCA	28	956 BA TB 03
TC+5 VI		
67 STBGA	3	1 R3 VS V (FLUORIDES)
TC+7 IV		
69 ACIEA	8	381 T2 07
71 ZAACA	380	146 T2 07
TE+4 IV		
69 ACCHA	25	1551 H3 FE2 TE4 O12 CL
71 ACBCA	27	602 TI TE3 O8, 3M TE3 O8, TE O2, HF TE3 O8, ZR TE3 O8
71 ACBCA	27	608 U TE3 O9
TE+4 VI		
61 ZKXKA	116	345 TE 02
71 ACBCA	27	602 M TE3 O8
71 ACBCA	27	608 U TE3 O9
TE+0 IV		
71 JCSIA	1971	1857 TE(+6)+0
TE+6 VI		
69 ZENBA	24	647 L16 TE 06
70 NRUBA	5	109 M03 TE 06
69 ACSAA	23	3062 NA2 KA TE2 O8 IO H12 IH2 O114
64 INDOCA	3	634 K TE IO H15,H2 O
64 NATMA	51	552 K TE O H
66 ACSAA	20	2138 K4 TE2 O6 IO H14,H2 O
70 NATMA	57	393 M03 TE 06
70 ZAACA	378	129 SR2 NI TE 06
70 ACSAA	24	3178 TE IO H16
66 ACSAA	20	1535 TE F6
66 ACBCA	27	615 M03 TE 06
65 ZAACA	334	225 K TE O2 IO H13
68 CHODA	267	1435 O02 TE 06
69 HOCMB	100	1809 AG2 TE O2 IO H14
71 BUFGA	94	172 TE IO H16
73 ACBCA	29	647 TE O8
73 ACBCA	29	656 H2 TE 06
73 ACSAA	27	85 TE IO H16
74 ACBCA	30	813 H2 TE 06
74 ACBCA	30	2095 IN H416 (TE M06 O24) TE (OH)16 H2 O
TH+4 VI		
74 CJCHA	52	2175 R3 VS V
TH+4 VIII		
71 ACBCA	27	629 K5 TH F9
71 ACBCA	27	2290 K7 TH F31
74 ICHAA	8	273 K TH P3 O10
TH+4 IX		
68 CCJDA	1968	990 IN H414 TH F8
69 ACBCA	25	1958 IN H414 TH F8
68 CCACA	40	147 K TH P3 O12
70 ICHAA	4	571 NA TH2 (P O4)3
71 ACBCA	27	1823 RB TH F13
71 ACBCA	29	2976 NA BE TH10 P45
70 ACBCA	26	1185 K NA TH F6
71 ACBCA	27	2279 IN H413 TH F7
TH+4 X		
73 ACBCA	29	2687 TH IN O314 (IC6 H5)3 P O12
TH+4 XI		
66 ACCRA	20	842 TH IN O314,SH2 O
66 ACCRA	20	836 TH IN O314,SH2 O
TH+4 XII		
65 ACCRA	18	698 MG TH IN O316,SH2 O
TI+3 VI		
73 JSSCB	6	213 TI 07
63 PRVBA	130	2230 TI2 O3
74 JSSCB	9	255 TI2 O3
74 ACBCA	30	662 CS TI 15 O4)2,12H2 O
TI+4 IV		
67 STBGA	3	1 R3 VS V (FLUORIDES)
TI+4 V		
70 ACBCA	29	2009 BA2 TI 04
61 ACCRA	14	875 BA2 TI 04
71 JCSIA	1971	1857 TI(+4)+0
74 ZAACA	408	60 RB2 TI 03
TI+4 V		
68 ACBCA	24	1327 V2 TI 05
TI+4 VI		
70 ZKXKA	131	278 V2 TI2 O7
71 ACBCA	27	635 M6 H6 TI F6
71 JSSCB	3	340 TI 07
70 ACACB	40	337 BA TI 03
64 ACCRA	17	240 CO TI 03
71 JCPSSA	55	3266 TI 02
1	72	CSCMC BA TI6 O13
72 ZKXKA	136	273 TI 02
74 ZKXKA	139	103 K TI P O5
72 INDOCA	11	2989 (TI O1CS H7 O2)212
74 ICHAA	11	243 (NH4)2 TI O1C2 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 R3 VS V (AF)
TI+4 VI		
75 ACBCA	31	365 TL N O3
TI+3 IV		
71 ZAACA	381	129 L15 TL O4
73 ZAACA	396	113 SR4 TL2 O7
74 ZAACA	405	197 BA2 TL2 O5
TI+3 V		
68 ZKXKA	126	143 TL2 O3
74 ZAACA	405	197 BA2 TL2 O5
75 ZAACA	412	37 RB TL F4
TI+3 VIII		
72 ZAACA	393	223 TL F3
TM+2 VI		
UNPUI		TM 12
TM+2 VII		
UNPUI		TM CL2,TH BRZ
TM+2 V		
63 PHSSA	3	K446 TR2 O3
TM+3 VIII		
70 SSCDA	8	1745 TH3 FE5 O12
74 ZAACA	403	1 K3 VS V (TM F3)
TM+3 IX		
74 ZAACA	403	1 K3 VS V (TM F3)
UN+3 VI		
68 JINCA	30	823 R (U+3)
UN+4 VI		
73 JSSCB	8	331 R3 VS V
67 INDOCA	3	327 R (U+4)
74 CJCHA	52	2175 R3 VS V
UN+4 VIII		
70 ACBCA	26	38 IN H414 U F8
73 ACBCA	29	1442 U CL4
UN+4 IX		
69 ACBCA	25	1910 R U2 F9
69 ACBCA	25	2103 K2 U F6
73 ACBCA	27	245 CU U6 F25
73 ACBCA	27	245 CU U6 F25
74 ACBCA	30	1906 B - NHA U F5
UN+5 VI		
67 ACCRA	23	805 CS U F6
70 JINGCA	32	3701 NA U O3
65 BUFGA	86	214 U CR O4
67 BUFGA	90	251 U FE U O4
UN+5 VII		
73 SPHCA	18	323 U2 MD O8
UN+6 VI		
68 ACBCA	24	987 CU U O4
69 ACBCA	25	787 S U O4, BA U O4, CAZ U O5, SR2 U O5, CA3 U O6,SR4 U O5
UN+6 VII		
66 JOPDA	27	726 M8 U O4
62 JOPDA	23	677 CO U O8
65 ACSAA	19	1955 U FA (GAS)
71 INDOCA	7	455 U O3
71 JINCA	33	2867 CR2 U O8
72 ACBCA	28	3609 U O2 IO H12
73 ACBCA	29	7 U F6
UN+6 VIII		
72 ACBCA	28	3609 U O3
UN+6 IX		
69 ACBCA	25	787 CA U O4
69 ACCRA	19	205 RB U OZ IN O313
V+2 VI		
UNPUS		V F2
V+3 VI		
70 PRVBA	2	3771 V2 O3
73 JSSCB	6	419 V4 O7
69 ACBCA	25	1354 V (CS H7 O2)13
69 ZAACA	369	306 M V2 O4
74 HROBA	9	1091 (VO,99 CRD,O)112 O3
70 JPCSA	31	2569 V2 O3
V+4 V		
65 ACCRA	19	432 LI V2 O5
61 JCPSSA	55	55 V O (CS H7 O2)12
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	2844 V3 O7
71 ACSAA	25	2075 M6 O13
70 ACSAA	24	420 VO2
74 PRVBA	10	490 VO2
V+4 VII		
68 ACBCA	24	292 V U O4
68 CHPLB	2	47 ER V O4
67 ACCRA	25	280 M2 V O7
70 ZKXKA	131	161 BA3 (V O4)2
71 JSSCB	3	458 ND V O4
71 ACBCA	27	612 ND V O4
70 INDOCA	9	2259 CAZ V O4 CL
71 CJCHA	49	1629 M03 V2 O8
73 ACBCA	29	2364 CO1 V2 O8, N13 V2 O8
72 JSSCB	4	29 FE V O4
73 CJCHA	51	1004 V2 V2 O7
73 JSSCB	6	538 LI3 V O4
72 CJCHA	50	3944 CO3 V2 O8
71 CJCHA	51	70 CHAMA
73 ACBCA	29	141 V U O4
73 ACBCA	29	1338 CU5 V O10
73 CJCHA	51	265 LI3 V O3
74 ACBCA	30	1678 NA V O3
74 NIMMA	5	210 CA5 (V O4)3 O H
V+5 V		
50 ACSAA	4	1119 V2 O5
71 RVBCA	8	300 ND O2 O5
74 ACBCA	30	2644 V2 O7
74 ACBCA	30	2491 M2 V2 O7
73 ACBCA	29	2612 V2 O7
70 CHODA	270	952 CA V2 O8
V+5 VI		
71 JSSCB	5	432 V P O5
71 ACSAA	25	2675 M6 O13
72 CJCHA	50	3619 M2 V O6
71 CJCHA	51	265 LI3 V O3
74 CJCHA	52	2184 K3 V O2 C2 O4,3H2 O
73 ACBCA	29	1743 CU V2 O6
V+5 VII		
67 STBGA	3	1 R3 VS V (FLUORIDES)
M+6 IV		
69 ACBCA	25	1704 K2 M O4
71 SPHDA	15	636 ND2 M O6
71 SPHDA	15	928 PB M O4
72 ACBCA	28	3174 SN O4
71 JCPSSA	55	1093 SR M O4,BA M O4
71 JCSIA	1971	1857
74 ACBCA	30	1872 NA2 M O4
74 ACBCA	30	1878 AL2 IN O4)3
M+6 V		
74 ACBCA	30	2587 CA3 M O5 CL2
M+6 VI		
69 SPHCA	13	933 MG M O4
69 SSCDA	7	1797 B12 M O6
70 SPHCA	14	518 R ND IN O4)2
70 SPHCA	14	515 LI2 FE M O4
70 SPHCA	15	28 PR2 M O9
70 ACBCA	26	1020 CU M O4
70 JSSCB	2	278 LI FE (M O4)2
66 ACSAA	20	2698 M F6 (GAS)
72 ZENBA	27	203 SN M O4
71 SPHCA	15	991 NMO M3 O15
74 JSSCB	10	5 FE2 M O4
74 ACBCA	30	2069 BA M O4
XE+0 IV		
71 JCPSSA	52	812 XE O4
71 JCSIA	1971	1857 XE(+8)+0
XE+0 V		
64 INDOCA	3	1412 NA4 XE O6,SH2 O
64 INDOCA	3	1417 NA4 XE O6,SH2 O
Y+3 VI		
68 INDOCA	22	354 Y2 BE O4
68 ZAACA	358	138 SR Y2 O4
67 SPHCA	11	583 NA Y S1 O4
69 ACBCA	25	2140 Y2 O3
71 SPHCA	15	806 Y2 S1 O5
71 JCSIA	1971	229 C66 H72 I3 N12 O6 Y
Y+3 VII		
68 INDOCA	7	1777 Y(C66COCH3)3,H2O
Y+3 VIII		
68 ACBCA	24	292 Y U O4
57 ACCRA	10	239 Y3 FE5 O12
68 SPHDA	12	1095 K Y NDZ O8
69 SPHCA	13	420 K Y W2 U8
70 ZKXKA	131	278 Y2 TI2 O7
67 ACCRA	23	939 Y TA O4
74 ZAACA	403	1 R3 VS V (Y F3)
Y+3 IX		
69 ZKXKA	112	362 Y (C2 H5 S O4)3,SH2 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+2 VI		
70 SPHCA	14	854 YB2 S1 O5
70 ACBCA	24	984 YB2 S1 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 S1 O5
69 INDOCA	8	22 Y2 YB2 H7 O2)13 (H2 O)
69 INDOCA	8	29 YB IC5 H7 O2)13 (H2 O) 1/2 C6 H6
YB+3 VIII		
70 INDOCA	9	1094 YB LI F4
70 SSCDA	8	1745 YB FE5 O12
74 HROBA	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)
ZM+4 IV		
68 SPHDA	12	987 NA2 ZM2 S12 O7
69 ACBCA	25	1233 ZM O4
69 PHSSA	32	K91 ZM FE2 O4
73 ACSAA	27	1541 ZM S O3,2 1/2H2 O
64 INDOCA	3	245 ZM (OPN)2
ZM+2 V		
70 JSSCB	1	120 ZM2 P2 O7
73 CJCHA	51	1004 ZM2 V2 O7
71 AMNIA	56	1147 ZM4 AS2 O8 IO H12,2H2 O
ZM+2 VI		
65 CJCHA	43	1147 ZM2 P2 O7
68 SPHCA	13	127 ZM V O4
70 JSSCB	1	120 ZM2 P2 O7
71 CJCHA	49	3056 ZM3 V2 O8
71 AMNIA	56	1147 ZM4 AS2 O8 IO H12,2H2 O
73 ACBCA	29	2741 ZM S1 F6,4H2 O
73 ACSAA	27	1541 ZM S O3,2 1/2H2 O
ZR+4 I		
75 JSSCB	13	275 R3 VS V (M4 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	2658 ZR IH AS O4)2,H2 O
69 ZAACA	371	306 LI2 ZR O3
70 JSSCB	1	478 K2 ZR O5
68 ACSAA	22	1822 NA ZR P3 O12
73 ACBCA	29	2294 LI2 ZR F6
71 ACBCA	27	1944 RB5 ZR F21
74 CJCHA	52	2175 R3 VS V
ZR+4 VII		
69 ACBCA	25	2104 NA2 ZR F6
70 ACBCA	24	617 IN H413 R F7
70 JACTA	53	126 ZR O2
73 ACSAA	27	177 ZR4 IO H16 (CR O4)5,H2 O
73 ACBCA	27	2414 ZR IO H12 S O4,H2 O
71 ACBCA	27	1944 RB5 ZR F21
ZR+4 VIII		
69 ACBCA	25	1558 ZR2 IS O4)4 (H2 O)8,H2 O
69 ACBCA	25	1566 ZR2 IS O4)4 (H2 O)8,H2 O
69 ACBCA	25	1572 ZR2 IS O4)4,5H2 O
71 ACBCA	27	638 M6 H6 ZR F6
71 AMNIA	56	782 ZR S1 O4
63 INDOCA	2	243 ZR (KAC)4
71 ACBCA	27	1944 RB5 ZR F21
63 INDOCA	2	250 NA4 ZR (C2 O4)4,3H2 O
REF 1	G. E. BROWN, PH.D. THESIS, VIRGINIA POLYTECH. INST., UNIV. MICROFILMS, 78-998	
REF 2		
REF 3		
REF 4		
REF 5		
REF 6		
REF 7		
UNPUI		
UNPUI2		
UNPUI3		
UNPUI4		
UNPUI5		
ACACB		
ACBCA		
ACCA		
ACIEA		
ACSAA		
ACRCA		
AMNIA		
ANCPA		
ARKEA		
BAPCA		
BCCSA		
BSCA		
BUFGA		
CANCA		
CCACA		
CCJDA		
CHODA		
CHUDA		
CHPLB		
CHPCA		
CHPCA		
CHPCA		
CSCMC		
CZCHA		
DANKA		
HCACA		
ICHAA		
INDCA		
INDMA		

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

Wolfe & Newnham (1969) studied  $\text{Bi}_{4-x}\text{RE}_x\text{Ti}_3\text{O}_{12}$  and concluded that  $\text{Bi}^{3+}$  and  $\text{La}^{3+}$  have nearly equal radii. From a study of  $\text{BiTaO}_4$  Sleight & Jones (1975) have concluded that although  $\text{Bi}^{3+}$  and  $\text{La}^{3+}$  have essentially equal radii, the size of  $\text{Bi}^{3+}$  depends on the degree of the  $6s^2$  lone-pair character. When  $\text{BiTaO}_4$  transforms from a structure where the lone-pair character is dominant to the  $\text{LaTaO}_4$  structure, it undergoes a volume reduction. Table 3 shows a comparison of isotopic  $\text{Bi}^{3+}$  and  $\text{La}^{3+}$  compounds where the lone-pair character of  $\text{Bi}^{3+}$  is (1) constrained and (2) dominant. Bi pyrochlores such as  $\text{Bi}_2\text{Ru}_2\text{O}_7$ ,  $\text{Bi}_2\text{Ir}_2\text{O}_7$  and  $\text{Bi}_2\text{Pt}_2\text{O}_7$  were omitted from the table because no corresponding La pyrochlore exists, but they have unit-cell volumes close to those of the Sm or Nd pyrochlores and thus have smaller volumes than those of La. When  $\text{Bi}^{3+}$  is forced into high symmetry, a  $\text{Bi}^{3+}$  compound has a smaller volume than that of  $\text{La}^{3+}$ , but when the lone-pair character is dominant, the  $\text{Bi}^{3+}$  compound is distorted and  $\text{Bi}^{3+}$  and  $\text{La}^{3+}$  compounds have approximately equal volumes. This behavior was also noted in the highly symmetric garnet structure where the hypothetical  $\text{Bi}_3\text{Fe}_3\text{O}_{12}$  was estimated to have cell dimensions between those of the hypothetical  $\text{Nd}_3\text{Fe}_3\text{O}_{12}$  and  $\text{Pr}_3\text{Fe}_3\text{O}_{12}$  (Geller, Williams, Espinosa, Sherwood & Gilleo, 1963). For practical purposes,  $\text{Bi}^{3+}$  is listed as slightly smaller than  $\text{La}^{3+}$  but this dependence on lone-pair character must be kept in mind when comparing the volumes of  $\text{Bi}^{3+}$  and  $\text{La}^{3+}$  compounds. Similar behavior may also exist for  $\text{Pb}^{2+}$  and  $\text{Sr}^{2+}$ , but this relationship was not investigated.

Table 3. Cell volumes of isotopic  $\text{Bi}^{3+}$  and  $\text{La}^{3+}$  compounds

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

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

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

$\text{Bi}_2\text{MoO}_6$	268.5 ( $\times 8$ )	1.00
$\text{La}_2\text{MoO}_6$	267.3	
$\text{BiFeO}_3$	62.49 ( $\times 6$ )	1.03
$\text{LaFeO}_3$	60.77 ( $\times 4$ )	
$\text{Bi}_2\text{Sn}_2\text{O}_7$	1219.9 ( $\times 8$ )	1.00
$\text{La}_2\text{Sn}_2\text{O}_7$	1225.3	

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

The nature of  $\text{Sn}^{2+}$ ,  $\text{NH}_4^+$ , and  $\text{H}^-$  made it impossible to define their ionic radii. The coordination of  $\text{Sn}^{2+}$  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  $\text{NH}_4^+$  ion by analyzing the N-O distances in a large number of ammonium salts. They concluded that  $\text{NH}_4^+$  has an octahedral radius of 1.61 Å, between that of  $\text{Rb}^+$  (1.52 Å) and  $\text{Cs}^+$  (1.67 Å). Alternatively, cell volumes of  $\text{NH}_4^+$  and  $\text{Rb}^+$  fluorides, chlorides, bromides, iodides and oxides may be compared. This leads to the conclusion that  $\text{NH}_4^+$  is not significantly different in size from  $\text{Rb}^+$ . No explanation is offered for this inconsistency and therefore the radius of  $\text{NH}_4^+$  is not included.

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

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

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

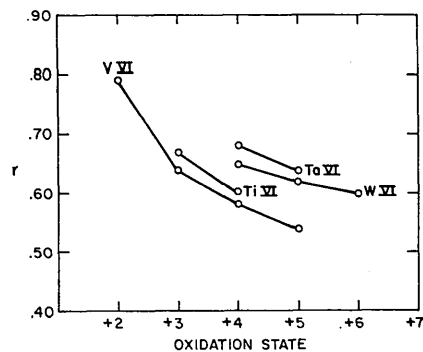


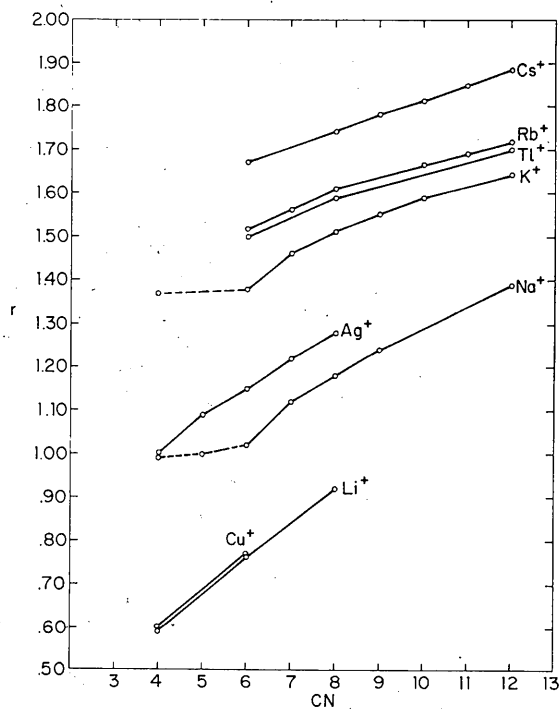
Fig. 1. Effective ionic radius (Å) vs oxidation state.



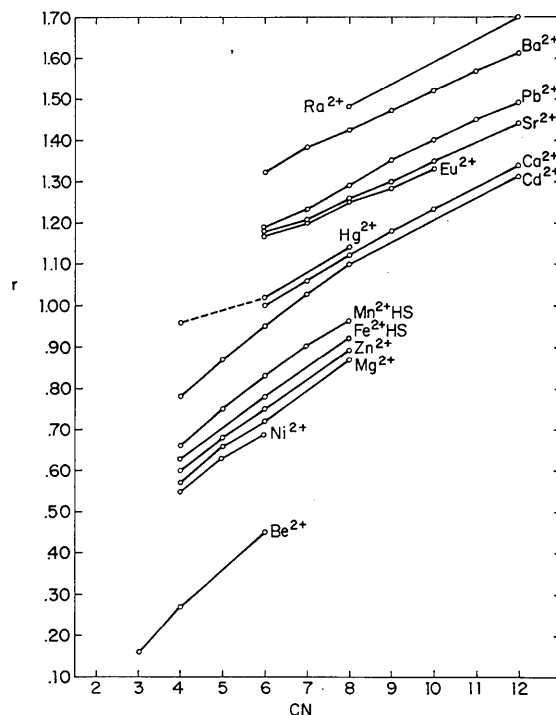
## Results and discussion

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

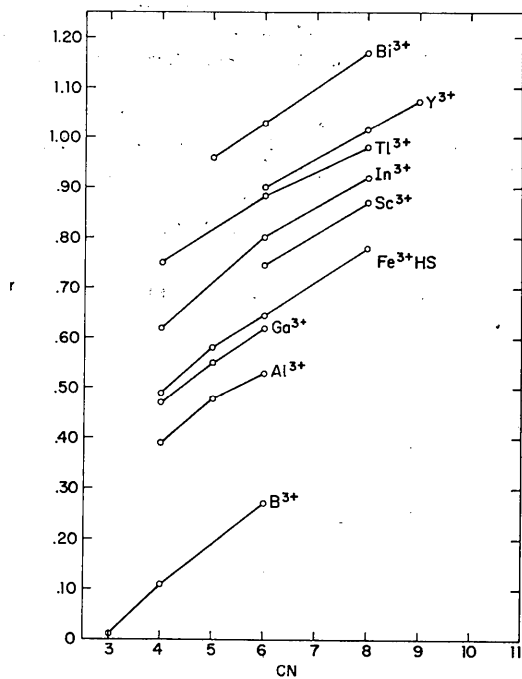
other set is based on  $r(\text{VI}\text{O}^{2-}) = 1.26$  and  $r(\text{VI}\text{F}^-) = 1.19 \text{ \AA}$ , and corresponds to crystal radii as defined by Fumi & Tosi (1964). As pointed out in SP 69, crystal radii differ from traditional radii only by a constant factor



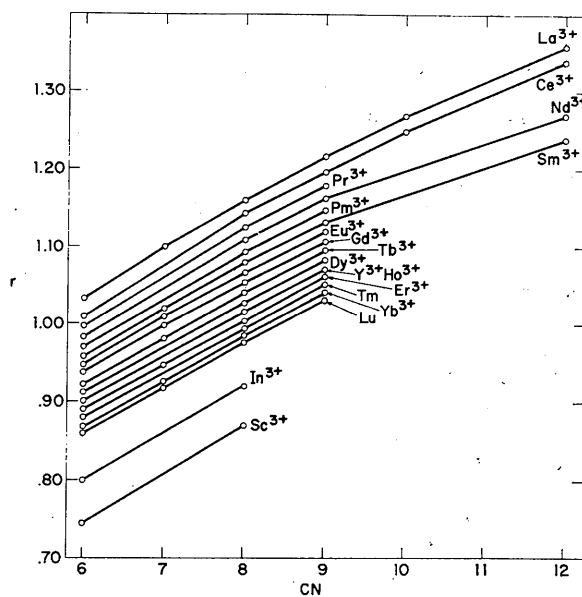
(a)



(b)

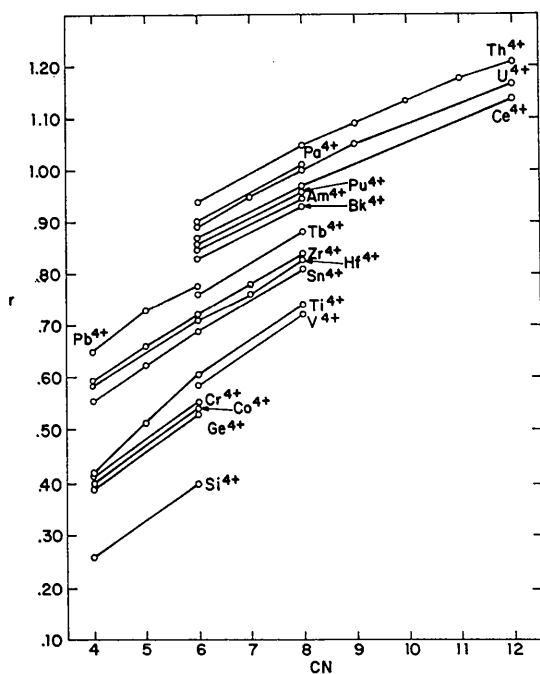


(c)



(d)

Fig. 2. (a)–(e) Effective ionic radius (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  $\pm 0.01$  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  ${}^{\text{VI}}\text{Fe}^{2+}\text{LS}$ ,  ${}^{\text{VI}}\text{Mn}^{2+}\text{LS}$ ,  ${}^{\text{VI}}\text{Cr}^{2+}\text{LS}$ ,  ${}^{\text{VI}}\text{V}^{2+}$ ,  ${}^{\text{VI}}\text{Ni}^{3+}\text{HS}$ ,  ${}^{\text{VI}}\text{Ir}^{3+}$ ,  ${}^{\text{VI}}\text{Mo}^{3+}$ ,  ${}^{\text{VI}}\text{Ta}^{3+}$ ,  ${}^{\text{VI}}\text{Pa}^{3+}$ ,  ${}^{\text{VI}}\text{Ta}^{4+}$ ,  ${}^{\text{IV}}\text{Pb}^{4+}$ ,  ${}^{\text{VI}}\text{Ir}^{5+}$ ,  ${}^{\text{VI}}\text{Os}^{5+}$ ,  ${}^{\text{VI}}\text{Re}^{5+}$ ,  ${}^{\text{VI}}\text{Pu}^{5+}$ ,  ${}^{\text{VI}}\text{Bi}^{5+}$ ,

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

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

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

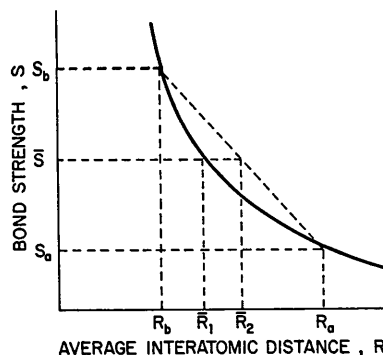
$$\frac{R_{\text{CsCl}}}{R_{\text{NaCl}}} = \left[ \frac{A_{\text{NaCl}}}{A_{\text{CsCl}}} \frac{B_{\text{CsCl}}}{B_{\text{NaCl}}} \right]^{1/(n-1)}$$

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

There are a few small irregularities in *r*–CN plots probably caused by poor or insufficient data, *e.g.* curves for  $\text{Ti}^{3+}$  *vs*  $\text{Y}^{3+}$ . The differences in slopes of  $\text{Ti}^{4+}$  *vs*  $\text{Cr}^{4+}$  and  $\text{V}^{5+}$  *vs*  $\text{As}^{5+}$  are probably caused by  $\text{Ti}^{4+}$ –O and  $\text{V}^{5+}$ –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  $\text{Cu}^{2+}$  and  $\text{Ag}^+$  are equal to or slightly greater than corresponding tetrahedral radii, consistent with the trend anticipated from anion

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

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

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

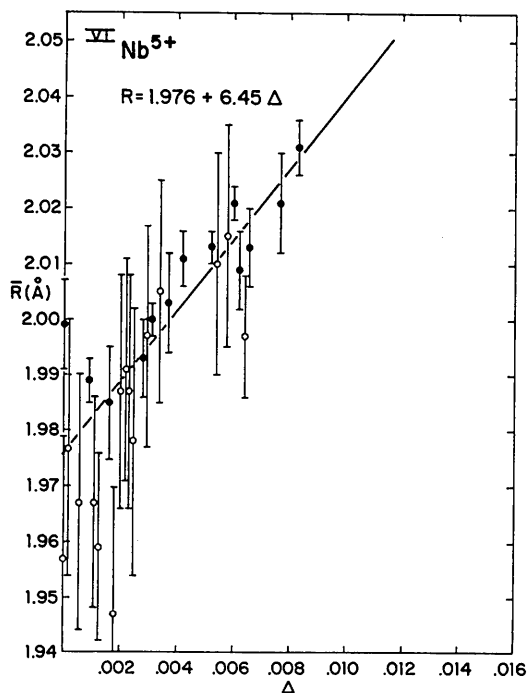


Fig. 4. Mean  $\text{Nb}^{5+}$ -O bond length *vs* distortion. Vertical bars represent average e.s.d.'s quoted by the authors. Solid circles represent more accurate data.

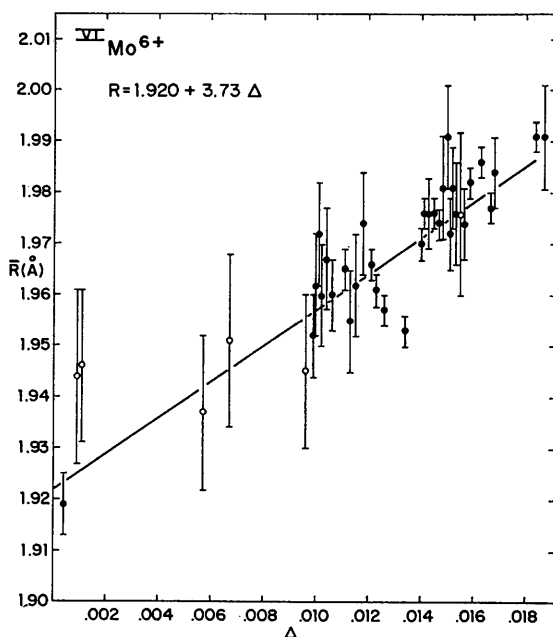


Fig. 5. Mean  $\text{Mo}^{6+}$ -O bond length *vs* distortion.

Table 4. *Interatomic distances in some compounds containing tetrahedral and octahedral  $\text{Na}^+$*

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

### Factors affecting mean interatomic distances

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

#### 1. Polyhedral distortion

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

The effects of distortion on mean bond lengths in numerous polyhedra have been determined. Although distortions in tetrahedra are not as important as in octahedra, they can contribute to variations in mean tetrahedral distances (Baur, 1974; Hawthorne, 1973). Strongly distorted octahedra like those containing  $V^{5+}$ ,  $Cu^{2+}$ , and  $Mn^{3+}$  show a significant variation in mean distance with distortion,  $\Delta^*$  (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-

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-

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

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

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

Compound	$\bar{R}$ (Å)	Distortion		Reference	
		$\Delta = \langle (\Delta R/R)^2 \rangle \times 10^4$			
Hg <sub>2</sub> Nb <sub>2</sub> O <sub>7</sub>	1.999	0	68 INOCA	7	1704
Cd <sub>2</sub> Nb <sub>2</sub> O <sub>7</sub>	1.957	0	72 CJCHA	50	3648
Na <sub>2</sub> Nb <sub>4</sub> O <sub>11</sub>	1.977	1	70 JSSCB	1	454
Ba <sub>0.27</sub> Sr <sub>0.75</sub> Nb <sub>2</sub> O <sub>5.78</sub>	1.967	6	61 JCPSA	48	5048
Na <sub>13</sub> Nb <sub>35</sub> O <sub>94</sub>	1.965	7	71 JSSCB	3	89
Ba <sub>3</sub> Si <sub>4</sub> Nb <sub>6</sub> O <sub>26</sub>	1.989	9	70 ACBCA	26	102
Na <sub>13</sub> Nb <sub>35</sub> O <sub>94</sub>	1.967	11	71 JSSCB	3	89
Na <sub>13</sub> Nb <sub>35</sub> O <sub>94</sub>	1.959	12	71 JSSCB	3	89
Na <sub>13</sub> Nb <sub>35</sub> O <sub>94</sub>	1.964	12	71 JSSCB	3	89
NaNbO <sub>3</sub>	1.985	16	69 ACBCA	25	851
Na <sub>13</sub> Nb <sub>35</sub> O <sub>94</sub>	1.947	18	71 JSSCB	3	89
Na <sub>13</sub> Nb <sub>35</sub> O <sub>94</sub>	1.991	22	71 JSSCB	3	89
Na <sub>13</sub> Nb <sub>35</sub> O <sub>94</sub>	1.987	22	71 JSSCB	3	89
Na <sub>13</sub> Nb <sub>35</sub> O <sub>94</sub>	1.978	24	71 JSSCB	3	89
LiNb <sub>5</sub> O <sub>8</sub>	1.993	28	71 ACSAA	25	3337
LiNbO <sub>3</sub>	2.000	31	66 JPCSA	27	997
Ca <sub>2</sub> Nb <sub>2</sub> O <sub>7</sub>	1.997	31	74 JINCA	36	1965
Ca <sub>2</sub> Nb <sub>2</sub> O <sub>7</sub>	2.005	34	74 JINCA	36	1965
SbNbO <sub>4</sub>	2.003	37	65 CCJDA	1965	611
KNbO <sub>3</sub>	2.011	42	67 ACACA	22	639
Na <sub>3</sub> NbO <sub>4</sub>	2.013	52	74 BUFGA	97	3
Ca <sub>2</sub> Nb <sub>2</sub> O <sub>7</sub>	2.010	53	74 JINCA	36	1965
Ca <sub>2</sub> Nb <sub>2</sub> O <sub>7</sub>	2.015	58	74 JINCA	36	1965
Na <sub>3</sub> NbO <sub>4</sub>	2.021	60	74 BUFGA	97	3
CaNb <sub>2</sub> O <sub>6</sub>	2.021	76	70 AMMIA	55	90
GaNbO <sub>4</sub>	2.031	83	65 ACACA	18	874

Table 6. Comparison of mean octahedral Mo<sup>6+</sup>-O distances with distortion

Only structures with e.s.d.'s for Mo-O distances of &lt;0.025 Å were used.

Compound	$\bar{R}$ (Å)	Distortion		Reference	
		$\Delta = \langle (\Delta R/R)^2 \rangle \times 10^4$			
Mo <sub>2</sub> (O <sub>2</sub> C <sub>6</sub> Cl <sub>4</sub> ) <sub>6</sub>	1.919	5	75 JACSA	97	2123
Mo <sub>4</sub> O <sub>11</sub> orthorhombic	1.944	9	63 ARKEA	21	365
Mo <sub>4</sub> O <sub>11</sub> monoclinic	1.946	10	63 ARKEA	21	365
Mo <sub>4</sub> O <sub>11</sub> monoclinic	1.937	56	63 ARKEA	21	365
Mo <sub>4</sub> O <sub>11</sub> orthorhombic	1.951	67	63 ARKEA	21	365
Mo <sub>4</sub> O <sub>11</sub> orthorhombic	1.911	96	63 ARKEA	21	365
Mo <sub>4</sub> O <sub>11</sub> monoclinic	1.945	96	63 ARKEA	21	365
(C <sub>15</sub> H <sub>11</sub> O <sub>2</sub> ) <sub>2</sub> MoO <sub>2</sub>	1.952	99	74 ACBCA	30	300
(NH <sub>4</sub> ) <sub>6</sub> [Mo <sub>7</sub> O <sub>24</sub> ].4H <sub>2</sub> O	1.962	99	75 JCSIA	1975	505
(NH <sub>4</sub> ) <sub>6</sub> [Mo <sub>7</sub> O <sub>24</sub> ].4H <sub>2</sub> O	1.972	101	75 JCSIA	1975	505
(NH <sub>4</sub> ) <sub>6</sub> [Mo <sub>7</sub> O <sub>24</sub> ].4H <sub>2</sub> O	1.960	104	75 JCSIA	1975	505
LiMoO <sub>2</sub> AsO <sub>4</sub>	1.967	104	70 ACSAA	24	3711
(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>8</sub> O <sub>27</sub> .4H <sub>2</sub> O	1.960	106	74 ACBCA	30	48
HgMoO <sub>4</sub>	1.965	111	73 ACBCA	29	869
(NH <sub>4</sub> ) <sub>6</sub> [Mo <sub>7</sub> O <sub>24</sub> ].4H <sub>2</sub> O	1.955	113	75 JCSIA	1975	505
(NH <sub>4</sub> ) <sub>6</sub> [Mo <sub>7</sub> O <sub>24</sub> ].4H <sub>2</sub> O	1.962	115	75 JCSIA	1975	505
(NH <sub>4</sub> ) <sub>6</sub> [Mo <sub>7</sub> O <sub>24</sub> ].4H <sub>2</sub> O	1.974	118	68 JACSA	90	3275
MoO <sub>3</sub> .2H <sub>2</sub> O	1.966	121	72 ACBCA	28	2222
MoO <sub>3</sub> .2H <sub>2</sub> O	1.961	123	72 ACBCA	28	2222
MoO <sub>3</sub> .2H <sub>2</sub> O	1.957	126	72 ACBCA	28	2222
MoO <sub>3</sub> .2H <sub>2</sub> O	1.953	134	72 ACBCA	28	2222
(NH <sub>4</sub> ) <sub>5</sub> [MoO <sub>3</sub> ] <sub>5</sub> (PO <sub>4</sub> )(HPO <sub>4</sub> )].3H <sub>2</sub> O	1.970	140	74 JCSIA	1974	941
Na <sub>3</sub> (CrMo <sub>6</sub> O <sub>24</sub> H <sub>6</sub> ).8H <sub>2</sub> O	1.976	141	70 INOCA	9	2228
(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>8</sub> O <sub>27</sub> .4H <sub>2</sub> O	1.976	141	74 ACBCA	30	48
Na <sub>3</sub> CrMo <sub>6</sub> O <sub>24</sub> H <sub>6</sub> .8H <sub>2</sub> O	1.976	143	70 INOCA	9	2228
(NH <sub>4</sub> ) <sub>5</sub> [(MoO <sub>3</sub> ) <sub>5</sub> (PO <sub>4</sub> )(HPO <sub>4</sub> )].3H <sub>2</sub> O	1.974	145	74 JCSIA	1974	941
(NH <sub>4</sub> ) <sub>6</sub> [TeMo <sub>6</sub> O <sub>24</sub> ].Te(OH) <sub>6</sub> .7H <sub>2</sub> O	1.981	147	74 ACBCA	30	2095
CoMoO <sub>4</sub>	1.991	150	65 ACACA	19	269
(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>8</sub> O <sub>27</sub> .4H <sub>2</sub> O	1.972	151	74 ACBCA	30	48
MoO <sub>3</sub>	1.981	151	63 ARKEA	21	357
(NH <sub>4</sub> ) <sub>6</sub> [Mo <sub>7</sub> O <sub>24</sub> ].4H <sub>2</sub> O	1.976	152	68 JACSA	90	3275
K <sub>2</sub> {[MoO <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> )(H <sub>2</sub> O)] <sub>2</sub> O}	1.976	152	64 INOCA	3	1603
(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>8</sub> O <sub>27</sub> .4H <sub>2</sub> O	1.974	152	74 ACBCA	30	48
(NH <sub>4</sub> ) <sub>5</sub> [(MoO <sub>3</sub> ) <sub>5</sub> (PO <sub>4</sub> )(HPO <sub>4</sub> )].3H <sub>2</sub> O	1.982	159	74 JCSIA	1974	941
Na <sub>3</sub> CrMo <sub>6</sub> O <sub>24</sub> H <sub>6</sub> .8H <sub>2</sub> O	1.986	163	70 INOCA	9	2228
(NH <sub>4</sub> ) <sub>5</sub> [(MoO <sub>3</sub> ) <sub>5</sub> (PO <sub>4</sub> )(HPO <sub>4</sub> )].3H <sub>2</sub> O	1.977	167	74 JCSIA	1974	941
MoO <sub>3</sub> .H <sub>2</sub> O	1.984	167	74 ACBCA	30	1795
(NH <sub>4</sub> ) <sub>5</sub> [(MoO <sub>3</sub> ) <sub>5</sub> (PO <sub>4</sub> )(HPO <sub>4</sub> )].3H <sub>2</sub> O	1.991	186	74 JCSIA	1974	941
(NH <sub>4</sub> ) <sub>6</sub> [Mo <sub>7</sub> O <sub>24</sub> ].4H <sub>2</sub> O	1.991	189	75 JCSIA	1975	505
(NH <sub>4</sub> ) <sub>6</sub> [Mo <sub>7</sub> O <sub>24</sub> ].4H <sub>2</sub> O	2.008	197	75 JCSIA	1975	505

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

Ion	Maximum $\Delta \times 10^4$	N*	R <sub>0</sub> †	r <sub>0</sub> ‡	m	Correlation coefficient	Goodness of fit (× 10 <sup>3</sup> )
Mo <sup>6+</sup>	212	38	1.920		3.73	0.74	67
				0.572	3.01	0.63	70
W <sup>6+</sup>	122	7	1.925		3.30	0.75	19
				0.565	3.28	0.66	24
V <sup>5+</sup>	576	16	1.887		2.62	0.98	8
Nb <sup>5+</sup>	83	29	1.976		6.45	0.69	71
				0.599	6.83	0.44	99
Ta <sup>5+</sup>	79	6	1.984		6.70	0.81	18
				0.617	3.79	0.15	46
Mn <sup>3+</sup>	71	15	1.994		7.08	0.82	30
				0.624	6.15	0.54	50
Cu <sup>2+</sup>	316	26	2.085		3.99	0.82	77
Mg <sup>2+</sup>	156	28	2.094		8.31	0.72	21
				0.728	8.86	0.77	18
Co <sup>2+</sup>	46	15	2.106		7.38	0.42	19
				0.734	11.70	0.70	16
Zn <sup>2+</sup>	71	16	2.099		7.70	0.64	21
				0.736	8.20	0.74	16
Li <sup>+</sup>	148	11	2.159		8.42	0.81	30
				0.784	9.02	0.79	35

\* N = number of independent octahedra

† R = R<sub>0</sub> + mΔ.‡ r = r<sub>0</sub> + mΔ.

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

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

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

### 3. Effects of covalence

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

ides, bromides, sulfides, selenides, *etc.* and (2) tetrahedral oxyanions such as the  $\text{VO}_4^{3-}$  and  $\text{AsO}_4^{3-}$  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.*  $\text{Fe}^{2+}$  in  $\text{Fe}_2\text{GeO}_4$  and  $\text{Fe}_2\text{GeS}_4$  vs  $\text{Mg}^{2+}$  in  $\text{Mg}_2\text{GeO}_4$  and  $\text{Mg}_2\text{GeS}_4$ . Covalence shortens both Fe-S and Mg-S bonds relative to Fe-O and Mg-O bonds, but because of the greater electronegativity of  $\text{Fe}^{2+}$  (1.8) compared to  $\text{Mg}^{2+}$  (1.2), the Fe-S bonds are shortened to a greater extent. Thus a 'covalency contraction' parameter (Shannon & Vincent, 1974) can be defined:

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

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

A similar parameter

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

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

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

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

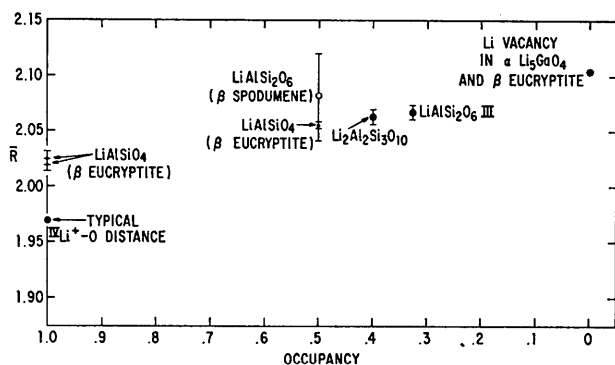


Fig. 6. Mean  $\text{Li}^+\text{-O}$  bond length vs partial occupancy.

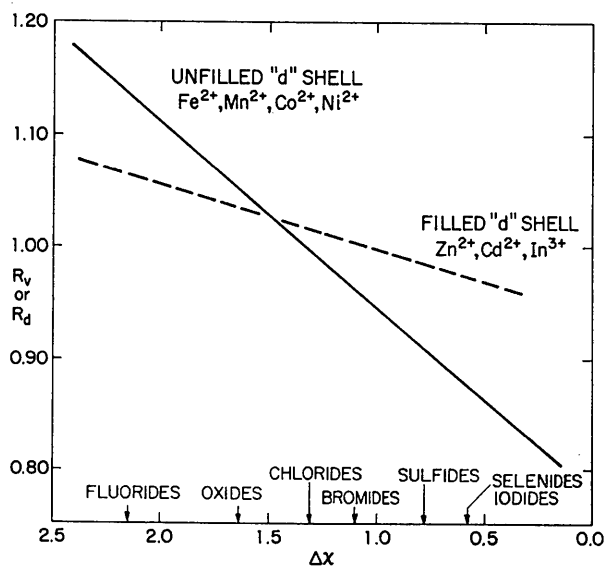


Fig. 7. Covalency contraction parameter,  $R_v$  or  $R_d$ , vs  $\Delta\chi$  for filled and unfilled  $d$  shell cations.

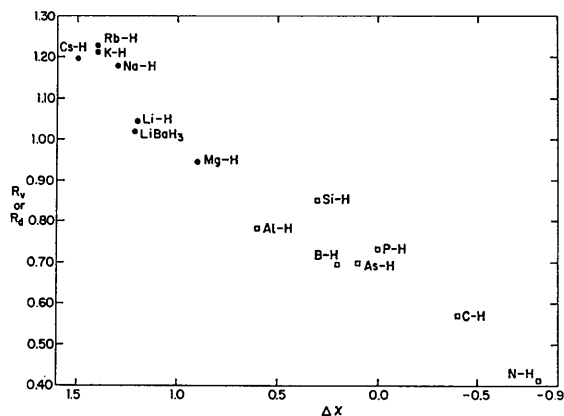


Fig. 8. Covalency contraction parameter,  $R_v$  or  $R_d$ , vs  $\Delta\chi$  for hydrides. Solid circles represent ratios of cell volumes of isotopic compounds. Squares represent ratios of the cubed  $\text{M-H}$  distances to the cubed  $\text{M-F}$  distances.

dependence of  $R_v$  on  $\Delta\chi$ . For  $\text{Fe}^{2+}\text{-Mg}^{2+}$  the  $\text{Fe}^{2+}$  fluoride volumes are  $\sim 110\%$  of the corresponding  $\text{Mg}^{2+}$  fluoride volumes whereas the  $\text{Fe}^{2+}$  sulfide volumes are  $\sim 96\%$  of the corresponding  $\text{Mg}^{2+}$  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  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Mn}^{2+}$  from fluorides to oxides. This effect is particularly noticeable in  $R_v\text{-}\Delta\chi$  plots for the pairs  $\text{Cu}^+\text{-Li}^+$  and  $\text{Ag}^+\text{-Na}^+$  (Shannon & Gummerman, 1975). The  $\text{Cu}^+\text{-Li}^+$  and  $\text{Ag}^+\text{-Na}^+$  plots are very steep, e.g. the volume of  $\text{AgF}$  is 120% of the volume of  $\text{NaF}$ , whereas the volume of  $\text{Ag}_2\text{Se}$  is only 72% of the volume of  $\text{Na}_2\text{Se}$ . 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  $\text{Cu}^+$  (0.96 Å) and  $\text{Ag}^+$  (1.26 Å) are considerably larger than those in Table 1 (0.77 and 1.15 Å respectively). Since these radii were derived from comparison of alkali halide distances, using an equation relating effective nuclear charge and screening constants (Pauling, 1927), they are valid in primarily ionic crystals. The smaller radii in Table 1 are applicable in the more covalent oxides. Extrapolation of  $R$  vs  $\Delta\chi$  curves such as in Fig. 7 leads to values of 0.91 Å and 1.23 Å for fluorides, which are close to Pauling's ionic values.

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

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

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

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

#### 4. Effects of electron delocalization

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

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

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

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

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

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

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



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