CONTRIBUTION FROM THE MATERIALS SCIENCE LABORATORIES,
DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF TEXAS AT AUSTIN, AUSTIN, TEXAS 78712

The Influence of Crystal Radii and Electronegativities on the Crystallization of AB_2X_4 Stoichiometries[1]

BY K. KUGIMIYA AND H. STEINFINK

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The quantitative relationships between compounds having AB_2O_4 stoichiometries and their crystal structures were investigated. Diagrams relating the ratio of the radius of atom A to that of oxygen, the ratio of the radius of atom B to that of oxygen, and an artificial parameter described as a force constant between A and B atoms and derived from their electronegativities and the equilibrium distance between them show distinct areas for different structure types. In particular, a plot of r_a/r_b *vs.* the force constant provides good resolution among structures. A three-dimensional illustration in which the axes are ratios of radii of A and B atoms to that of oxygen and the force constant resolves the frequently occurring structures into separate volumes. A similar plot was constructed for compounds with AB_2X_4 stoichiometries where X is S, Se, and Te. Although fewer known compounds are available for mapping, it was, nevertheless, possible to separate different structures into different regions. A mathematical relationship between oxygen and cation occupancy of tetrahedral and octahedral voids is derived which describes possible crystal structures.

Introduction

The ability to predict the type of crystallization in which a given stoichiometry of cations and anions will crystallize is a goal which has been pursued by crystal chemists for a considerable number of years. Many attempts have been made to systematize a large amount of information by plotting or correlating suitable physical and chemical parameters so that a scheme becomes evident which will permit such predictions. Evans[2] discussed the relationship between chemical compositions and the crystal structures of metal alloys and ionic compounds. Mooser and Pearson[3] have reported that in compounds of the type A_mB_n a correlation exists among the electronegativity differences, average principle quantum number, and the crystal structure. Later Pearson[4] reported finding a better correlation by taking account of the effect of the radius ratio for the two atoms. Roth[5] studied a large number of perovskite- and ABO_3-type compounds and reported observing a relationship among crystal structure, radius ratio, and polarizibility of the A and B atoms. Keith and Roy[6] related the radius ratio and the tolerance factor of perovskite-type compounds to their crystal structures. Recently Kjekshus and Pearson[7] surveyed the stoichiometry AB and discussed the compounds which form the nickel arsenide structure.

The mineral spinel, $MgAl_2O_4$, has a crystal structure which occurs in a large number of compounds having the general formula AB_2O_4. Spinel-type compounds have received much attention because of the discovery that the magnetic properties which can be incorporated into this structure permit their use in various electronic devices of considerable technological importance. The substitution of various cations into the tetrahedral and octahedral positions in the close-packed oxygen framework gives rise to hundreds of compounds in which physical properties can be tailored to fit requirements for a particular application. However, other structures are also found for compounds of this stoichiometry. The olivine, $CaFe_2O_4$, K_2SO_4, $BaAl_2O_4$, and phenacite structures constitute major types in which many compounds crystallize. In addition to the major structure types, a few of the compounds have structures which are related to two major types.

The crystallization of spinels in the normal or inverse structure was successfully explained in terms of the stability energy of ions in tetrahedral or octahedral configuraton. Glasser and Glasser[8] investigated the relation of ionic radii and resultant crystal structure for some AB_2O_4 stoichiometries where A was Ba, Pb, Sr, Ca, or Cd, and B was Al, Ga, Cr, Fe, or V. Because of the interests in this type of structure, an attempt is made here to relate the type of crystallization to the intrinsic properties of the ions so that one can predict with a certain amount of assurance the crystal structure of an unknown compound with this stoichiometry.

Crystal Parameters

A comparison of the normal spinel and olivine illustrates the principles which need to be considered in the formation of such structures. Both types have a basic unit, A–B–O, consisting of four cations surrounding one oxygen ion: three B cations in octahedral voids and one A ion in a tetrahedral void. The structures are formed by the close packing of the large oxygen ions, cubic close packing in spinel and hexagonal close packing in olivine. In the spinel structure the three B ions in octahedral voids and the A ion in a tetrahedral void around oxygen are situated so as to maximize the A–B distances while at the same time maximizing the B–B distances which are less than A–B. The A ion sees every B ion at an equivalent distance. In the olivine structure there are two basic A–B–O units. One is the

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[1] Research sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force.

[2] R. C. Evans, "An Introduction to Crystal Chemistry," Cambridge University Press, London, 1939.

[3] E. Mooser and W. B. Pearson, *Acta Cryst.*, **12**, 1015 (1959).

[4] W. B. Pearson, *J. Phys. Chem. Solids*, **23**, 103 (1962).

[5] R. S. Roth, *J. Res. Natl. Bur. Std.*, **58**, 75 (1957).

[6] M. L. Keith and R. Roy, *Am. Mineralogist*, **39**, 1 (1954).

[7] A. Kjekshus and W. B. Pearson, "Progress in Solid State Chemistry," H. Reiss, Ed., Pergamon Press Inc., New York, N. Y., 1965.

[8] F. P. Glasser and L. S. D. Glasser, *J. Am. Ceram. Soc.*, **46**, 377 (1963).

unit described above for the spinel structure and the other consists again of three B ions in octahedral voids and one A ion in a tetrahedral void, but the B–B distances are first maximized and then A is placed into a tetrahedral void so as to maximize the A–B distances.

The spinel cation arrangement will occur if the repulsion between A and B ions is greater than among the B ions, and, if the repulsion between A and B is smaller than that between the B ions, the olivine-type arrangement will occur. At the same time the repulsive forces among the cations must not be so large as to prevent their contact with the oxygen ions or else the structure becomes unstable.

The assumption is made in this development that the ions are hard spheres although it is recognized that the overlap of bonding electrons, bond angles, and the polarizability influence the ion arrangement. However, the inclusion of these additional factors complicates the problem to an extent that it becomes intractable by the procedure adopted here. The bond stretching force constant, K, is considered to represent this interplay of forces and is given by

$$K = aN\left(\frac{\chi_a\chi_b}{r_e^2}\right)^{3/4} + b$$

where a and b are constants, N is the bond order, r_e is the equilibrium distance, and χ_a and χ_b are the electronegativities of the A and B ions, respectively.[9,10] If the assumption is made that a and N are constants and that b is small and constant so that it can be neglected, then K can be written as

$$K_{ab} = \frac{\chi_a\chi_b}{r_e^2}$$

where $r_e^2 = (r_a + r_o)^2 + (r_b + r_o)^2 + 1.155(r_a + r_o)\cdot(r_b + r_o)$, r_a, r_b, and r_o are the radii of the A, B, and O ions. A further simplification can be introduced by considering r_e to be approximately constant and then $K_{ab} = \chi_a\chi_b$. The ratio K_{ab}/K_{bb} can be considered as a measure of the respective repulsive forces between A–B and B–B and from the known arrangements it can be postulated that the spinel structure will be preferred when this ratio is small, and the olivine structure will be preferred when this ratio becomes larger. In addition to these electrostatic interactions, the radius ratios of the various cations and anions greatly influence the crystallization.

The correlation between electronegativity differences and average quantum number has successfully grouped crystal structures in binary compounds. The choice of the type of difference function, whether simply $\chi_a - \chi_b$ or a more complicated expression, will strongly influence the resultant map when this method is applied to compounds containing three different atoms. We found that maps based on $\chi_a - \chi_b$, or other simple difference expressions, were not as effective in separating crystal structures as the expression adopted in this investigation. It is quite possible, however, that the choice of a correctly formulated difference function could yield results as good as or better than those shown here.

We have defined a tolerance factor for the spinel structure as the ratio $[110]/\sqrt{2}[100]$. On the assumption that all ions are ideally spherical and rigid and that they contact each other along each direction as they build up the ideal spinel structure, the length of the face diagonal is

$$4(r_a + r_o)\frac{\sqrt{2}}{\sqrt{3}} + 4r_o$$

and the lattice constant is $4(r_b + r_o)$. Thus the tolerance factor is

$$T = \frac{1}{\sqrt{3}}\,\frac{r_a + r_o}{r_b + r_o} + \frac{1}{\sqrt{2}}\,\frac{r_o}{r_b + r_o}$$

and becomes unity if the ideal spinel structure is assumed. In order to compare the calculated lattice constant of the spinel structure as obtained from the ionic radii with the experimentally measured value, L_{exptl} is taken as the average of $1/\sqrt{2}[110]$ and $[100]$ and the calculated lattice constant is

$$L_{\text{calcd}} = \frac{2\sqrt{3}}{3}(r_a + r_o) + 2(r_b + r_o) + \sqrt{2}r_o$$

No attempt was made to calculate the lattice constants of other structures.

Computations of Parameters

Tables I and II list the electronegativities and ionic radii of the cations and anions used in the calculations of K_{ab}, K_{ab}/K_{bb}, the tolerance factor, the various radius ratios, and the products of electronegativities. The radii shown are for octahedral coordination and were multiplied by 0.94 to obtain the value for tetrahedral coordination. If the cationic radii in the interstices did not contact the anions, then they were adjusted as follows. (1) If the cationic radii were too small, they were assigned values of $0.414r_o$ and $0.225r_o$ for the octahedral and tetrahedral sites, respectively. (2) If the tetrahedral ion was too large to fit the interstice, then the length of the tetrahedral oxygen edge was calculated. If the octahedral ion radius was now too small, it was expanded to touch the six oxygen ions. The conditions expressing this are: if

$$\frac{0.94r_a + r_o}{1.225} \geq \frac{r_b + r_o}{1.414}$$

then $r_b = 1.154r_a + 0.154r_o$ and r_a has the value shown in Table I. (3) If the octahedral ion was too large for the interstice, then the length of the octahedral oxygen edge was calculated and the tetrahedral cationic radius was enlarged to fit the void. The conditions expressing this are: if

$$\frac{0.94r_a + r_o}{1.225} < \frac{r_b + r_o}{1.414}$$

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(9) W. Gordy, *J. Chem. Phys.*, **14**, 305 (1946).

(10) A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, London, 1962.

then $r_a = 0.866r_b - 0.134r_o$ and r_b has the value shown in Table I. The above modifications in the ionic radii were used only in the calculation of K_{ab} and K_{ab}/K_{bb}.

Table I

Electronegativities, χ, and Ionic Radii,[a] r, of Cations

Valence 1		
Element	r, Å	χ
Li	0.68	0.97
Na	0.97	1.01
K	1.33	0.91
Cu	0.96	1.75
Rb	1.47	0.89
Ag	1.26	1.42
Cs	1.67	0.86
Au	1.37	1.42
Tl	1.47	1.44

Valence 2		
Element	r, Å	χ
Be	0.35	1.47
Mg	0.66	1.23
Ca	0.99	1.04
V	0.88	1.45
Mn	0.80	1.60
Fe	0.74	1.64
Co	0.72	1.70
Ni	0.69	1.75
Cu	0.72	1.75
Zn	0.74	1.66
Ge	0.73	2.02
Sr	1.12	0.99
Pd	0.80	1.35
Ag	0.89	1.42
Cd	0.97	1.46
Sn	0.93	1.72
Ba	1.34	0.97
Pt	0.80	1.44
Hg	1.10	1.44
Pb	1.20	1.55
Ra	1.43	0.97

Valence 3		
Element	r, Å	χ
Al	0.51	1.47
Sc	0.81	1.20
Ti	0.76	1.32
V	0.74	1.45
Cr	0.63	1.56
Mn	0.66	1.60
Fe	0.64	1.64
Co	0.63	1.70
Ga	0.62	1.82
Y	0.92	1.11
Rh	0.68	1.45
In	0.81	1.49
Sb	0.76	1.82
La	1.14	1.08
Ce	1.07	1.06
Pr	1.06	1.07
Nd	1.04	1.07
Sm	1.00	1.07
Eu	0.98	1.01
Gd	0.97	1.11
Tb	0.93	1.10
Dy	0.92	1.10
Ho	0.91	1.10
Er	0.89	1.11
Tm	0.87	1.11
Yb	0.86	1.06
Lu	0.85	1.14
Au	0.85	1.42
Tl	0.95	1.44
Bi	0.96	1.67

Valence 4		
Element	r, Å	χ
Si	0.42	1.74
S	0.37	2.50
Ti	0.68	1.32
V	0.63	1.45
Mn	0.60	1.60
Ge	0.53	2.02
Se	0.50	2.48
Zr	0.79	1.22
Mo	0.70	1.30
Ru	0.67	1.42
Pd	0.65	1.35
Sn	0.71	1.72
Te	0.70	2.01
Ce	0.94	1.06
Pr	0.92	1.07
Tb	0.81	1.10
Hf	0.78	1.23
W	0.70	1.40
Re	0.72	1.46
Ir	0.68	1.55
Pt	0.65	1.44
Pb	0.84	1.55
Th	1.02	1.11
Pa	0.98	1.14
U	0.97	1.22

Valence 5		
Element	r, Å	χ
V	0.59	1.45
Nb	0.69	1.23
Mo	0.66	1.30
Sb	0.62	1.82
I	0.62	2.21
Ta	0.68	1.33
W	0.66	1.40
Re	0.66	1.46
Bi	0.74	1.67
Pa	0.89	1.14
U	0.88	1.22

Valence 6		
Element	r, Å	χ
S	0.30	2.44
Cr	0.52	1.56
Se	0.42	2.48
Mo	0.62	1.30
Te	0.56	2.01
W	0.62	1.40
Re	0.61	1.46
Os	0.69	1.52
U	0.80	1.22

[a] L. H. Ahrens, *Geochem. Cosmochim. Acta*, **2**, 155 (1952).

Table II

Electronegativities, χ, and Ionic Radii, r, of Anions

Element	r, Å	χ
O	1.40	3.50
S	1.84	2.44
Se	1.98	2.48
Te	2.21	2.01

Results and Discussion

Information regarding compounds listed in Table III without asterisks was obtained from Wyckoff;[11] structures of compounds with a single asterisk were obtained from the ASTM card file.[12] The degree of inversion of the spinel structures marked with the double asterisk was taken from Wells[10] and the numbers next to the compounds indicate the particular reference from which the information was obtained.[13-16]

Several ambiguities exist about structures for the same materials. The compound $CuFe_2O_4$ is reported to be a spinel and also to have the Mn_3O_4 structure. It is therefore listed under both structures in Table III. The inverse spinel structure and the Mn_3O_4 structure are reported for $CdIn_2O_4$, and $CuRh_2O_4$ is said to have the spinel structure.[11] Both the spinel and olivine structures are reported for $GeMg_2O_4$,[11] and $SrCr_2O_4$ is said to have the stuffed silica structure although it is not definite.[8] The compound $CaAl_2O_4$ has a distorted stuffed silica structure;[8] $SrFe_2O_4$ has an $CaFe_2O_4$ structure[8] although it was previously reported to have hexagonal symetry.[11] Cruickshank[17] reported that $CaIn_2O_4$, $CdIn_2O_4$, $SrIn_2O_4$, and $BaIn_2O_4$ have the distorted spinel structure and that their structures are related to that of $CaFe_2O_4$. For AB_2O_4 compounds, in which A is Sr or Ba and B is Er, Tm, or Lu, the $CaFe_2O_4$ structure is reported by Bhargava, *et al.*,[13] though Schwarz[14] reported that those compounds have other structures. Queyroux[15] studied the compounds $CaYb_2O_4$ and $CaDy_2O_4$ and reported that they are similar to $CaFe_2O_4$. For comparison with compounds having the formula AB_2O_4, several compounds with compositions AB_2X_4, where X is sulfur, selenium, or tellurium, are also listed in Table III.

The equation for L_{calcd}, derived with the assumption stated previously, provided agreement between observed and calculated lattice constants with an average deviation of 1.5% except for $PbFe_2O_4$. The same equation, but using modified ionic radii according to the models previously discussed, gave calculated values which were 10–15% larger than observed values. It would have been reasonable to expect that these modified radii should give closer agreement and the failure to do so can be ascribed to distortion which the cations apparently undergo, giving rise to deviations from sphericity which permit them to fill the available space in the close-packed oxygen layers. The two calculated lattice constants of $PbFe_2O_4$, for the different valences for the cations, are 8.8 Å, which is significantly larger than the experimental value, 7.81 Å. It must be assumed that either the reported value or the reported structure is wrong.

Figure 1 is a plot of K_{ab} *vs.* r_a/r_b for known structures. It is seen that the different structures cluster into certain areas of the diagram, although some compounds actually lie on the boundaries as shown. The phenacite structure, Be_2SiO_4, provides an exception and is found scattered throughout the diagram. Compounds with the Mn_3O_4 structure and those with a closely related distorted spinel structure are almost all contained in the normal and inverse spinel areas. It is interesting to observe that structures formed by slight deviations from type structures are found on the boundary lines between the two major structure areas. The large intermediate

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(11) R. W. G. Wyckoff, "Crystal Structures," Vol. 3, 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1965.

(12) Powder Diffraction File, American Society for Testing Materials, Philadelphia, Pa., 1963.

(13) H. D. Bhargava, L. M. Kovba, L. I. Martynenko, and V. I. Spitsyn, *Dokl. Akad. Nauk SSSR*, **161**, 594 (1965).

(14) H. Schwarz, *Z. Naturforsch.*, **19b**, 955 (1964).

(15) F. Queyroux, *Compt. Rend.*, **261**, 4430 (1965).

(16) J. Flahaut, M. Guittard, M. Patrie, M. P. Pardo, S. M. Golabi, and L. Domange, *Acta Cryst.*, **19**, 14 (1965).

(17) F. R. Cruickshank, *J. Inorg. Nucl. Chem.*, **26**, 937 (1964).

TABLE III

CRYSTAL DATA FOR KNOWN STRUCTURES HAVING THE AB_2X_4 COMPOSITION

SPINEL

MO	AG	O		6	1	.42	.90	.46	1.85	.09	.67	.80	9.590	9.260	
MO	AG	O		4	2	.47	.64	.74	1.85	.12	.67	.95	8.937	9.260	
MG	AL	O		2	3	.44	.36	1.22	1.81	.12	.81	1.13	8.133	8.030	0.0
FE	AL	O		2	3	.50	.36	1.36	2.41	.15	.81	1.15	8.220	8.119	0.0
CU	AL	O		2	3	.48	.36	1.33	2.57	.16	.87	1.15	8.198	8.064	0.0**
CO	AL	O		2	3	.48	.36	1.33	2.50	.16	.84	1.15	8.198	8.017	0.0**
CD	AL	O		2	3	.65	.36	1.79	2.15	.11	.72	1.22	8.470	8.078	
ZN	AL	O		2	3	.50	.36	1.36	2.44	.15	.82	1.15	8.220	8.088	0.0**
NI	AL	O		2	3	.46	.36	1.27	2.57	.17	.87	1.14	8.166	8.048	0.0**
SN	AL	O		2	3	.62	.36	1.71	2.53	.13	.85	1.21	8.426	8.120	
MN	AL	O		2	3	.54	.36	1.47	2.35	.14	.79	1.17	8.285	8.258	0.0**
CU	CO	O		2	3	.48	.45	1.07	2.97	.19	.75	1.08	8.438	8.039	
GE	CO	O		4	2	.36	.51	.69	3.43	.26	.86	.98	8.412	8.319	0.0
GE	CO	O		2	3	.49	.45	1.09	3.43	.22	.86	1.08	8.449	8.319	0.0
MG	CO	O		2	3	.44	.45	.98	2.09	.14	.53	1.06	8.373	8.107	
MN	CO	O	*	4	2	.40	.51	.78	2.72	.19	.68	1.00	8.488	8.268	
MN	CO	O	*	2	3	.54	.45	1.19	2.72	.16	.68	1.10	8.525	8.268	
NI	CO	O	*	2	3	.46	.45	1.03	2.97	.19	.75	1.07	8.406	8.112	
SN	CO	O		4	2	.48	.51	.93	2.92	.19	.74	1.03	8.607	8.644	0.5
SN	CO	O		2	3	.62	.45	1.39	2.92	.15	.74	1.13	8.666	8.644	0.5
TI	CO	O		4	2	.46	.51	.89	2.24	.15	.56	1.02	8.575	8.420	
ZN	CO	O		2	3	.50	.45	1.10	2.82	.18	.71	1.08	8.460	8.108	0.0**
CD	CR	O		2	3	.65	.45	1.45	2.28	.12	.68	1.15	8.710	8.596	
CO	CR	O		2	3	.48	.45	1.07	2.65	.17	.79	1.08	8.438	8.354	0.0
FE	CR	O		2	3	.50	.45	1.10	2.56	.16	.76	1.08	8.460	8.376	
MG	CR	O		2	3	.44	.45	.98	1.92	.13	.57	1.06	8.373	8.333	0.0**
MN	CR	O		2	3	.54	.45	1.19	2.50	.15	.75	1.10	8.525	8.436	0.0**
NI	CR	O		2	3	.46	.45	1.03	2.73	.18	.82	1.07	8.406	8.320	
ZN	CR	O		2	3	.50	.45	1.10	2.59	.16	.77	1.08	8.460	8.335	0.0**
CD	FE	O		2	3	.65	.46	1.42	2.39	.12	.65	1.14	8.730	8.705	
CU	FE	O		2	3	.48	.46	1.06	2.79	.18	.75	1.07	8.458	8.390	0.5
CU	FE	O		2	3	.48	.46	1.06	2.87	.18	.78	1.07	8.458	8.445	0.5
GE	FE	O		4	2	.36	.53	.67	3.31	.25	.90	.97	8.452	8.411	0.0
GE	FE	O		2	3	.49	.46	1.07	3.31	.21	.90	1.08	8.469	8.411	0.0
MG	FE	O		2	3	.44	.46	.97	2.02	.13	.55	1.06	8.393	8.389	0.5
MN	FE	O		4	2	.40	.53	.76	2.62	.19	.71	.99	8.528	8.511	0.1
MN	FE	O		2	3	.54	.46	1.17	2.62	.15	.71	1.09	8.545	8.511	0.1
MO	FE	O		4	2	.47	.53	.89	2.13	.14	.58	1.02	8.637	8.501	0.25
NI	FE	O		2	3	.46	.46	1.01	2.87	.19	.78	1.07	8.426	8.353	0.5
PB	FE	O		4	2	.56	.53	1.07	2.54	.14	.69	1.05	8.789	7.810	
PB	FE	O		2	3	.81	.46	1.76	2.54	.11	.69	1.20	8.979	7.810	
TI	FE	O		4	2	.46	.53	.86	2.16	.14	.58	1.01	8.615	8.500	0.5
ZN	FE	O		2	3	.50	.46	1.09	2.72	.17	.74	1.08	8.480	8.443	0.0**
CD	GA	O		2	3	.65	.44	1.47	2.66	.14	.58	1.15	8.690	8.570	0.25
CO	GA	O		2	3	.48	.44	1.09	3.09	.20	.68	1.08	8.418	8.325	
CU	GA	O		2	3	.48	.44	1.09	3.18	.20	.70	1.08	8.418	8.390	
MG	GA	O		2	3	.44	.44	1.00	2.24	.15	.49	1.07	8.353	8.280	0.5
NI	GA	O		2	3	.46	.44	1.05	3.18	.21	.70	1.08	8.386	8.262	0.5
ZN	GA	O		2	3	.50	.44	1.12	3.02	.19	.66	1.09	8.440	8.323	
CD	IN	O		2	3	.65	.58	1.13	2.18	.11	.71	1.05	9.070	9.115	0.5
MG	IN	O		2	3	.44	.58	.77	1.83	.12	.60	.98	8.733	8.810	0.5
GE	MG	O		4	2	.36	.47	.75	2.48	.19	1.19	1.01	8.292	8.246	
SN	MG	O		4	2	.48	.47	1.01	2.12	.14	1.02	1.06	8.487	8.639	
TI	MG	O		4	2	.46	.47	.97	1.62	.11	.78	1.05	8.455	8.440	0.5
V	MG	O		4	2	.42	.47	.90	1.78	.12	.86	1.04	8.401	8.386	
CU	MN	O		2	3	.48	.47	1.03	2.80	.18	.79	1.06	8.498	8.330	
NI	MN	O		2	3	.46	.47	.98	2.80	.18	.79	1.05	8.466	8.403	
TI	MN	O		4	2	.46	.57	.80	2.11	.16	.60	.99	8.735	8.670	0.5
MO	NA	O		6	1	.42	.69	.60	1.31	.08	.94	.90	9.010	9.108	
W	NA	O		6	1	.42	.69	.60	1.41	.09	1.01	.90	9.010	9.130	
GE	NI	O		4	2	.36	.49	.72	3.53	.27	.84	1.00	8.352	8.221	
SI	NI	O		4	2	.28	.49	.57	3.05	.25	.72	.97	8.233	8.044	
CD	RH	O		2	3	.65	.49	1.34	2.12	.11	.73	1.12	8.810	8.781	
CO	RH	O		2	3	.48	.49	1.00	2.47	.16	.85	1.05	8.538	8.495	
CU	RH	O		2	3	.48	.49	1.00	2.54	.16	.88	1.05	8.538	8.290	
MG	RH	O		2	3	.44	.49	.91	1.78	.12	.62	1.04	8.473	8.530	
MN	RH	O		2	3	.54	.49	1.11	2.32	.14	.80	1.07	8.625	8.613	
ZN	RH	O		2	3	.50	.49	1.02	2.41	.15	.83	1.06	8.560	8.540	
MG	TI	O		2	3	.44	.54	.82	1.62	.11	.68	1.00	8.633	8.474	0.0
MN	TI	O		2	3	.54	.54	.99	2.11	.12	.88	1.03	8.785	8.600	0.0
SN	ZN	O		4	2	.48	.53	.90	2.86	.18	.75	1.02	8.647	8.700	0.5
TI	ZN	O		4	2	.46	.53	.86	2.19	.14	.58	1.01	8.615	8.467	0.5
CD	V	O		2	3	.65	.53	1.23	2.12	.11	.73	1.09	8.930	8.680	
FE	V	O		2	3	.50	.53	.94	2.38	.15	.82	1.03	8.680	8.468	
MG	V	O		2	3	.44	.53	.84	1.78	.12	.62	1.01	8.593	8.394	
MN	V	O		4	2	.40	.63	.64	2.32	.16	.80	.93	8.808	8.520	0.0
MN	V	O		2	3	.54	.53	1.02	2.32	.14	.80	1.04	8.745	8.520	
ZN	V	O		2	3	.50	.53	.94	2.41	.15	.83	1.03	8.680	8.393	
ZN	AL	S		2	3	.38	.28	1.36	2.44	.10	.82	1.18	10.230	9.968	
SN	CU	S		4	2	.36	.39	.93	3.01	.13	.71	1.07	10.618	0.870	
HG	IN	S		2	3	.56	.44	1.28	2.15	.07	.70	1.12	11.221	10.833	
FE	IN	S		2	3	.38	.44	.86	2.44	.10	.80	1.04	10.830	10.619	
CO	IN	S		2	3	.37	.44	.84	2.53	.11	.83	1.04	10.809	10.580	
CD	IN	S		2	3	.50	.44	1.13	2.18	.08	.71	1.09	11.080	10.818	
CA	IN	S		2	3	.51	.44	1.15	1.55	.06	.51	1.09	11.102	10.795	
CU	CO	S		2	3	.37	.34	1.07	2.97	.13	.75	1.12	10.449	9.458	
CD	CR	S		2	3	.50	.34	1.45	2.28	.08	.68	1.17	10.720	10.207	
CO	CR	S		2	3	.37	.34	1.07	2.65	.11	.79	1.12	10.449	9.910	
CU	CR	S		2	3	.37	.34	1.07	2.73	.12	.82	1.12	10.449	9.629	
FE	CR	S		2	3	.38	.34	1.10	2.56	.11	.76	1.12	10.470	9.970	
HG	CR	S		2	3	.56	.34	1.64	2.25	.07	.67	1.20	10.861	0.201	
MN	CR	S		2	3	.41	.34	1.19	2.50	.10	.75	1.13	10.536	10.045	
ZN	CR	S		2	3	.38	.34	1.10	2.59	.11	.77	1.12	10.470	9.974	
HG	CR	SE		2	3	.52	.32	1.64	2.25	.07	.67	1.20	11.501	10.753	
CD	CR	SE		2	3	.46	.32	1.45	2.28	.07	.68	1.18	11.360	10.721	
CU	CR	SE		2	3	.34	.32	1.07	2.73	.11	.82	1.12	11.088	10.357	
ZN	CR	SE		2	3	.35	.32	1.10	2.59	.10	.77	1.13	11.110	10.443	
CU	CR	TE		2	3	.31	.29	1.07	2.73	.09	.82	1.14	12.139	11.051	
HG	GA	TE	*	2	3	.47	.28	1.67	2.62	.07	.58	1.21	12.532	6.017	
MG	IN	S		2	3	.34	.44	.77	1.83	.08	.60	1.03	10.744	10.708	
MN	IN	S		2	3	.41	.44	.93	2.38	.10	.78	1.06	10.896	10.715	
NI	IN	S		2	3	.35	.44	.80	2.61	.11	.85	1.03	10.776	10.485	
CU	TI	S		2	3	.37	.41	.89	2.31	.10	.96	1.06	10.709	9.880	
CU	V	S		2	3	.37	.40	.91	2.54	.11	.88	1.07	10.669	9.824	

Mn_3O_4

BA	IN	O		2	3	.90	.58	1.56	1.45	.06	.47	1.14
CA	IN	O		2	3	.66	.58	1.15	1.55	.08	.51	1.06
CD	IN	O		2	3	.65	.58	1.13	2.18	.11	.71	1.05
SR	IN	O		2	3	.75	.58	1.30	1.48	.07	.48	1.09
CU	FE	O		2	3	.48	.46	1.06	2.87	.18	.78	1.07
FE	FE	O		2	3	.50	.46	1.09	2.69	.17	.73	1.08
CD	MN	O		2	3	.65	.47	1.38	2.34	.12	.66	1.13
MG	MN	O		2	3	.44	.47	.94	1.97	.13	.56	1.05
MN	MN	O		4	2	.40	.57	.70	2.56	.18	.73	.97
MN	MN	O		2	3	.54	.47	1.14	2.56	.15	.73	1.08
ZN	MN	O		2	3	.50	.47	1.05	2.66	.17	.75	1.07
CU	RH	O		2	3	.48	.49	1.00	2.54	.16	.88	1.05

DIST. SPINEL

CU	CR	O		2	3	.48	.45	1.07	2.73	.17	.82	1.08
CU	RH	O		2	3	.48	.49	1.00	2.54	.16	.88	1.05
NI	RH	O		2	3	.46	.49	.95	2.54	.16	.88	1.04

PHENACITE

GE	BE	O		4	2	.36	.25	1.42	2.97	.22	1.00	1.19
SI	BE	O		4	2	.28	.25	1.13	2.56	.22	.86	1.16
MO	LI	O		6	1	.42	.49	.86	1.26	.09	.97	1.03
W	LI	O		6	1	.42	.49	.86	1.36	.09	1.05	1.03
GE	ZN	O		4	2	.36	.53	.67	3.35	.25	.88	.97
SI	ZN	O		4	2	.28	.53	.53	2.89	.23	.76	.95

OLIVINE

BE	AL	O		2	3	.23	.36	.65	2.16	.20	.73	1.04
GE	BA	O		4	2	.36	.96	.37	1.96	.09	1.51	.76
GE	CA	O		4	2	.36	.71	.50	2.10	.13	1.41	.87
BE	CR	O		2	3	.23	.45	.52	2.29	.20	.69	.98
GE	MG	O		4	2	.36	.47	.75	2.48	.19	1.19	1.01
SI	MG	O		4	2	.28	.47	.60	2.14	.18	1.03	.98
GE	MN	O		4	2	.36	.57	.62	3.23	.24	.92	.95
GE	MN	O		2	3	.49	.47	1.04	3.23	.20	.92	1.07
GE	SR	O		4	2	.36	.80	.44	2.00	.11	1.48	.83

$CaFe_2O_4$

BA	LA	O	13	2	3	.90	.81	1.10	1.05	.04	.65	.99
BA	CE	O	13	2	3	.90	.76	1.18	1.03	.04	.67	1.02
BA	PR	O	13	2	3	.90	.76	1.19	1.04	.04	.66	1.03
BA	ND	O	13	2	3	.90	.74	1.21	1.04	.04	.66	1.04
BA	SM	O	13	2	3	.90	.71	1.26	1.04	.04	.66	1.05
BA	EU	O	13	2	3	.90	.70	1.29	.98	.04	.78	1.06
BA	GD	O	13	2	3	.90	.69	1.30	1.08	.04	.64	1.07
BA	TB	O	13	2	3	.90	.68	1.35	1.07	.04	.64	1.08
BA	DY	O	13	2	3	.90	.66	1.37	1.07	.04	.64	1.09
BA	HO	O	13	2	3	.90	.65	1.38	1.07	.04	.64	1.09
BA	Y	O	13	2	3	.90	.66	1.37	1.08	.04	.64	1.09
BA	ER	O	18	2	3	.90	.64	1.42	1.08	.04	.64	1.10
BA	TM	O	18	2	3	.90	.62	1.45	1.08	.04	.64	1.11
BA	LU	O	18	2	3	.90	.61	1.48	1.11	.04	.62	1.12
CA	CR	O		2	3	.66	.45	1.48	1.62	.08	.48	1.15
CA	FE	O		2	3	.66	.46	1.45	1.71	.09	.46	1.14
CA	V	O	16	2	3	.66	.53	1.26	1.51	.08	.52	1.09
SR	FE	O	16	2	3	.75	.46	1.64	1.62	.07	.44	1.18
SR	LA	O	13	2	3	.75	.81	.92	1.07	.05	.67	.95
SR	CE	O	13	2	3	.75	.76	.98	1.05	.05	.68	.97
SR	PR	O	13	2	3	.75	.76	.99	1.06	.05	.67	.98
SR	ND	O	13	2	3	.75	.74	1.01	1.06	.05	.67	.99
SR	SM	O	13	2	3	.75	.71	1.05	1.08	.05	.67	1.00
SR	EU	O	13	2	3	.75	.70	1.07	1.00	.05	.71	1.01
SR	GD	O	13	2	3	.75	.69	1.09	1.10	.05	.65	1.02
SR	TB	O	13	2	3	.75	.66	1.13	1.09	.05	.65	1.03
SR	DY	O	13	2	3	.75	.66	1.14	1.09	.05	.65	1.04
SR	HO	O	13	2	3	.75	.65	1.16	1.09	.05	.65	1.04
SR	Y	O	13	2	3	.75	.66	1.14	1.10	.05	.65	1.04
SR	ER	O	18	2	3	.75	.64	1.18	1.10	.05	.65	1.05
SR	TM	O	18	2	3	.75	.62	1.21	1.10	.05	.65	1.06
SR	YB	O	18	2	3	.75	.61	1.22	1.05	.05	.68	1.06
SR	LU	O		2	3	.75	.61	1.24	1.13	.05	.63	1.07

K_2SO_4

CR	CS	O		6	1	.35	1.19	.29	1.34	.05	1.32	.68
S	CS	O		6	1	.20	1.19	.17	2.18	.08	2.06	.64
CR	K	O		6	1	.35	.95	.37	1.42	.07	1.85	.76
S	K	O		6	1	.20	.95	.21	2.22	.11	1.95	.72
SE	K	O		6	1	.28	.95	.30	2.26	.11	1.98	.74
TE	K	O		6	1	.38	.95	.40	1.83	.09	1.61	.77
CR	TL	O		6	1	.35	1.05	.33	2.25	.10	.79	.72
S	TL	O		6	1	.20	1.05	.19	3.51	.18	1.63	.68
SE	TL	O		6	1	.28	1.05	.27	3.57	.18	1.25	.71

K_2MgF_4

PB	BA	O		4	2	.56	.96	.59	1.58	.07	1.16	.88
SN	BA	O		4	2	.48	.96	.50	1.47	.08	1.29	.88
MN	CA	O		4	2	.40	.71	.57	1.66	.11	1.12	.89
U	CS	O		6	1	.54	1.19	.45	1.05	.04	1.03	.73
CU	GD	O		2	3	.48	.69	.70	1.94	.12	1.15	.92
U	K	O		6	1	.54	.95	.57	1.11	.05	.97	.82
NI	LA	O		2	3	.46	.81	.57	1.89	.11	1.18	.86
CU	ND	O		2	3	.48	.74	.65	1.87	.11	1.19	.90
NI	ND	O		2	3	.46	.74	.62	1.87	.11	1.19	.89
U	RB	O		6	1	.54	1.05	.51	1.09	.05	1.00	.78
CU	SM	O		2	3	.48	.71	.68	1.87	.12	1.19	.91
IR	SR	O		4	2	.46	.80	.57	1.53	.09	1.14	.86
MN	SR	O		4	2	.40	.80	.50	1.58	.09	1.18	.84
MO	SR	O		4	2	.47	.80	.59	1.29	.07	.95	.86
RU	SR	O		4	2	.45	.80	.56	1.41	.08	1.04	.86
SN	SR	O		4	2	.48	.80	.60	1.70	.10	1.26	.87
TI	SR	O		4	2	.46	.80	.57	1.31	.07	.97	.86

$BeAl_2O_4$

BA	AL	O		2	3	.90	.36	2.47	1.43	.06	.48	1.32
CA	AL	O	16	2	3	.66	.36	1.82	1.53	.08	.51	1.22
PB	AL	O	16	2	3	.81	.36	2.21	2.28	.10	.77	1.28
SR	AL	O		2	3	.75	.36	2.06	1.48	.07	.49	1.26
SR	CR	O	16	2	3	.75	.45	1.67	1.54	.07	.46	1.19
BA	FE	O	16	2	3	.90	.46	1.97	1.59	.06	.43	1.24
BA	GA	O		2	3	.90	.44	2.03	1.77	.07	.39	1.25
PB	GA	O		2	3	.81	.44	1.82	2.82	.12	.62	1.21
SR	GA	O		2	3	.75	.44	1.70	1.80	.08	.40	1.19
BA	YB	O	13	2	3	.90	.61	1.46	1.03	.04	.67	1.12

OTHER STRUCTURES

BA	V	O	16	2	3	.90	.53	1.70	1.41	.05	.49	1.18
SR	V	O	16	2	3	.75	.53	1.42	1.46	.07	.50	1.12
ZN	SB	O	*	2	3	.50	.54	.92	3.02	.19	.86	1.02
SN	PB	O	*	4	2	.48	.86	.56	2.67	.14	.81	.84
U	CA	O	*	4	2	.65	.71	.92	1.27	.06	.85	.97
BA	CR	O	16	2	3	.90	.45	2.00	1.51	.06	.45	1.24
S	NA	O	*	6	1	.20	.69	.29	2.46	.16	1.76	.83
SE	NA	O	*	6	1	.28	.69	.41	2.50	.16	1.79	.86
CR	NA	O	*	6	1	.35	.69	.50	1.58	.10	1.12	.88
S	RB	O	*	6	1	.20	1.05	.19	2.17	.10	1.99	.68
SI	FE	O	*	4	2	.28	.53	.53	2.85	.23	.77	.95
SI	MN	O	*	4	2	.28	.57	.49	2.78	.21	.79	.92
CA	GA	O	16	2	3	.66	.44	1.50	1.89	.10	.42	1.16
CA	TI	O		2	3	.66	.54	1.22	1.37	.07	.57	1.08
CA	YB	O		2	3	.66	.61	1.08	1.10	.06	.71	1.03
CA	DY	O		2	3	.66	.66	1.01	1.14	.06	.69	1.01
SI	SR	O		4	2	.28	.80	.35	1.72	.10	1.28	.88
CR	AG	O	*	6	1	.35	.90	.39	2.22	.11	.80	.78
TI	BA	O		4	2	.46	.96	.48	1.28	.06	.99	.79
SI	CA	O		4	2	.28	.71	.40	1.81	.12	1.22	.85
S	LI	O		6	1	.20	.49	.41	2.37	.20	1.03	.94
BA	BI	S	*	2	3	.68	.52	1.31	1.62	.05	.42	1.18
CU	BI	S	*	2	3	.37	.52	.70	2.92	.13	.76	.98
PB	BI	S	*	2	3	.61	.52	1.17	2.59	.08	.67	1.08
NI	CR	S	*	2	3	.35	.34	1.03	2.73	.12	.82	1.11
PB	LA	S	*	2	3	.61	.62	.99	1.67	.05	1.04	1.01
FE	SB	S	*	2	3	.38	.41	.92	2.98	.13	.85	1.06
CD	IN	SE	*	2	3	.46	.41	1.13	2.18	.07	.71	1.10

Ag_2HgI_4

CD	AL	S		2	3	.50	.28	1.79	2.15	.08	.72	1.23
HG	AL	S		2	3	.56	.28	2.03	2.12	.07	.71	1.26
CD	AL	SE		2	3	.46	.26	1.79	2.15	.07	.72	1.23
HG	AL	SE		2	3	.52	.26	2.03	2.12	.06	.71	1.26
ZN	AL	SE		2	3	.35	.26	1.36	2.44	.09	.82	1.18
CD	AL	TE		2	3	.41	.23	1.79	2.15	.06	.72	1.24
HG	AL	TE		2	3	.47	.23	2.03	2.12	.05	.71	1.26
ZN	AL	TE		2	3	.31	.23	1.36	2.44	.08	.82	1.19
CD	GA	S		2	3	.50	.34	1.47	2.66	.10	.58	1.17
HG	GA	S		2	3	.56	.34	1.67	2.62	.09	.58	1.20
ZN	GA	S		2	3	.38	.34	1.12	3.02	.13	.66	1.12
CD	GA	SE		2	3	.46	.31	1.47	2.66	.09	.58	1.18
HG	GA	SE		2	3	.52	.31	1.67	2.62	.08	.58	1.21
ZN	GA	SE		2	3	.35	.31	1.12	3.02	.12	.66	1.13
CD	GA	TE		2	3	.41	.28	1.47	2.66	.07	.58	1.19
HG	GA	TE		2	3	.47	.28	1.67	2.62	.07	.58	1.21
ZN	GA	TE		2	3	.31	.28	1.12	3.02	.10	.66	1.15
CA	IN	SE		2	3	.47	.41	1.15	1.55	.05	.51	1.10
HG	IN	SE		2	3	.52	.41	1.28	2.15	.06	.70	1.13
ZN	IN	SE		2	3	.35	.41	.86	2.47	.09	.81	1.06
CD	IN	TE		2	3	.41	.37	1.13	2.18	.06	.71	1.11
HG	IN	TE		2	3	.47	.37	1.28	2.15	.06	.70	1.14
ZN	IN	TE		2	3	.31	.37	.86	2.47	.08	.81	1.07

[a] The first three columns correspond to A, B, and X. The single and double asterisks and numbers in the columns immediately following the anions are references. The succeeding columns are: valence states of A and B cations; three radius ratios r_a/r_x, r_b/r_x, and r_a/r_b; product of electronegativities $\chi_a\chi_b$; force constant K_{ab}; ratio of force constants K_{ab}/K_{bb}; tolerance factor; calculated unit cell constants; experimentally observed unit cell constant; degree of spinel inversion.

area between the spinel region and the $CaFe_2O_4$ region contains $CaDy_2O_4$ and $CaYb_2O_4$ which are monoclinic with a cation arrangement similar to $CaFe_2O_4$; UCa_2O_4 which has a tetragonal symmetry; $CaIn_2O_4$, $SrIn_2O_4$, and $BaIn_2O_4$ which are distorted spinels and have a structure related to that of $CaFe_2O_4$; BaV_2O_4 and SrV_2O_4 which are defect perovskite structures; $CaTi_2O_4$ which is body-centered orthorhombic; and CaV_2O_4 and $CaGa_2O_4$ which are reported to have structures depending on the conditions of the formation of the crystals. The compound $GeMg_2O_4$ which can have both the spinel and olivine structures lies on the boundary between the spinel and olivine regions. Some monoclinic crystal structures which deviate from major structure types are also observed on boundaries.

There are a few known compounds which do not fall into the proper regions in Figure 1. Those are $MoAg_2O_4$, $GeMn_2O_4$, MnV_2O_4, $GeFe_2O_4$, $GeCo_2O_4$, $MnFe_2O_4$, $SnCo_2O_4$, $NiAl_2O_4$, $CdIn_2O_4$, $MgTi_2O_4$, $CdGa_2O_4$, $BaCr_2O_4$, $BaYb_2O_4$, and phenacites. All of these except for $NiAl_2O_4$, $CdIn_2O_4$, $MgTi_2O_4$, $CdGa_2O_4$, $BaIn_2O_4$, and phenacite have two possible valence states, mainly 4–2 and 2–3. One assumption of valence distribution places it into an incorrect area while the other assumption assigns it to the correct structure region. Thus the compound $Mo^{VI}Ag^{I}{}_2O_4$ lies almost on the boundary between the K_2AgI_4 and the olivine structure areas, while $Mo^{IV}Ag^{II}{}_2O_4$ falls properly into the inverse spinel region. Similarly $Ge^{II}Mn^{III}{}_2O_4$ is contained in the spinel region while $Ge^{IV}Mn^{II}{}_2O_4$ lies properly in the olivine region. The compounds $NiAl_2O_4$ and $CdGa_2O_4$ which fall into the normal spinel area are reported to be partially inverted spinels with $\lambda = 0.38$ and 0.25, respectively, and the reported inverse spinel structure for $CdIn_2O_4$, which lies in the normal spinel region, is stated to be doubtful.[11] The compound Fe_3O_4 which lies in the normal spinel region near the boundary line with the inverse spinel region is known to have an inverted structure. Consequently the notable exceptions are phenacites, $MgTi_2O_4$, $BaYb_2O_4$, and $BaCr_2O_4$. Phenacites are scattered throughout the diagram of Figure 1, $MgTi_2O_4$ lies in the inverse spinel region although its structure is reported to be normal, $BaYb_2O_4$ lies in the $CaFe_2O_4$ structure area although it

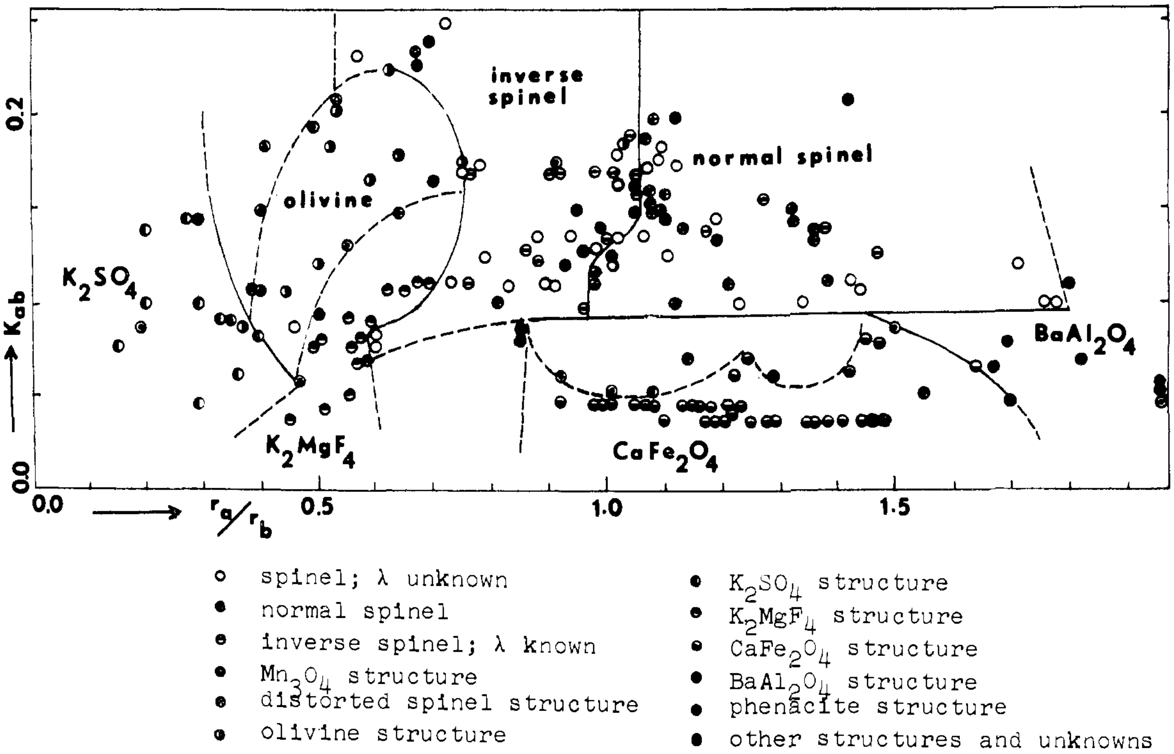

Figure 1.—Plot of K_{ab} *vs.* radius ratio of cations of known crystal structures for compounds having the formula AB_2O_4.

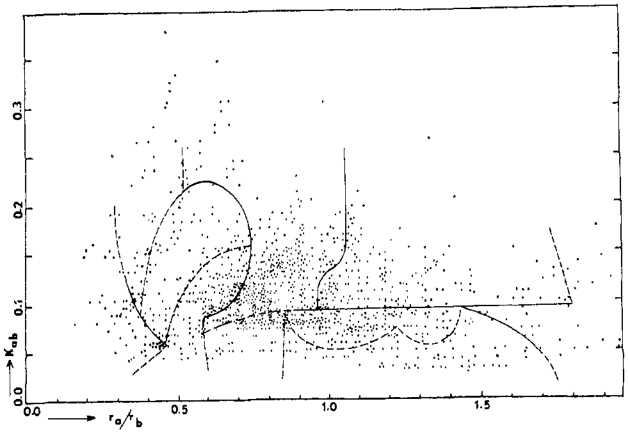

Figure 2.—Plot of K_{ab} *vs.* r_a/r_b for computer-generated compounds. Each dot represents a compound AB_2O_4. The boundaries are transferred onto this diagram from Figure 1

has hexagonal symmetry, and $BaCr_2O_4$ falls in the stuffed silica structure region although it has a monoclinic crystal structure.

Among the areas of the various structures, the spinel region covers the largest area in the diagram and contains almost half of the compounds whose structures were known. This may imply that the spinel structure is one of low potential energy and is therefore a preferred structure type.

The ions listed in Table I were used to generate 1236 compounds of the type AB_2O_4 and they are plotted in Figure 2. The boundaries shown in this figure are the same as those of Figure 1. The positions of some boundaries are subject to error since there are very few known structures close to the boundaries themselves and thus the structures to be predicted for unknown compounds, generated by the elements listed in Table I, which fall onto the boundaries can be the distorted structure or some other structures related to two adjacent major structure types. Uncertainty also exists for unknown structures which fall into the part of the inverse spinel area which is mapped on the basis of only two known compounds, $MoNa_2O_4$ and WNa_2O_4.

There are several regions which contain no or only a very few known compounds. Those regions are left blank in Figure 1 and none of the boundary lines in Figure 2 is extended past $K_{ab} = 0.25$. The known compounds lie within relatively small values of K_{ab} at the fixed r_a/r_b values. The generated compounds which have large K_{ab} values are presumably difficult to prepare and may form multiphase material containing compounds such as $ABO_3 + BO$ or $AO + B_2O_3$ which satisfy the stoichiometry AB_2O_4. Perhaps an additional thermodynamic variable, such as pressure, is required to prepare these compounds.

The correlations among K_{ab}, r_a/r_b, and r_b/r_o are schematically illustrated in three dimensions in Figure 3. The regions of the spinel structure and of the olivine structure are shown by solid lines, and the regions of the K_2SO_4 structure, the K_2MgF_4 structure, and others are omitted except for their base lines on the zero level in order to keep the diagram simple. In the volume of high K_{ab} or low K_{ab} values only a few compounds exist. The surfaces which define the spinel and olivine volumes are simply continued to separate those spaces.

Again fairly good separations of compounds are observed in Figure 3. The exceptions are $MoMg_2O_4$,

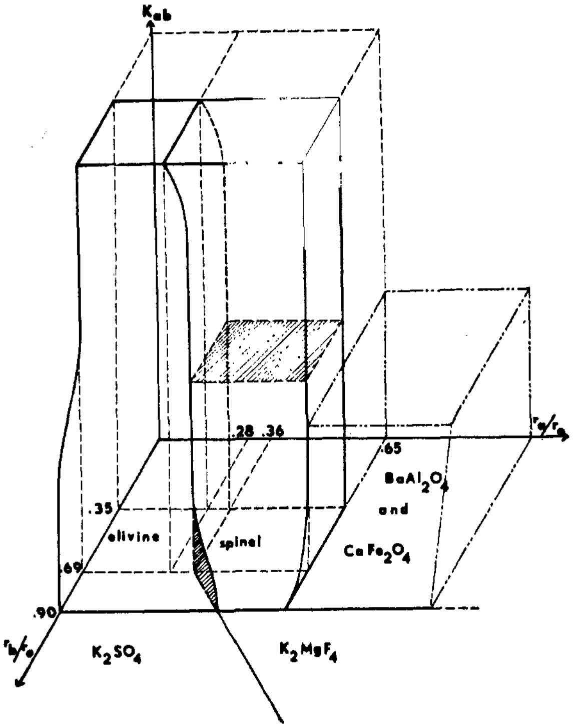

Figure 3.—Three-dimensional surface resulting from a plot of K_{ab} *vs.* r_b/r_o *vs.* r_a/r_o for known crystal structures of compounds having the AB_2O_4 composition.

$GeMg_2O_4$, $PbFe_2O_4$, $SiNi_2O_4$, $BaIn_2O_4$, $SrIn_2O_4$, and phenacites. The compound $CaIn_2O_4$ lies on a separating surface. Among these compounds the structure of $GeMg_2O_4$ is not certain;[11] the compound $PbFe_2O_4$ is a spinel but a valence distribution 2–3 places it out of the spinel structure region, while a 4–2 valence distribution properly places it in the spinel region. It is reasonable to assume therefore, that in $PbFe_2O_4$ the valences are 4–2 or perhaps mixed 4–2 and 2–3 and in $MoAg_2O_4$ a similar valence distribution occurs as previously stated.

The spinel structure region in Figure 3 is almost a rectangular parallelepiped, except for the areas of large and small values of the force constant. This feature is also observed for regions of other structures and implies that the radius ratio is a dominant factor in the determination of the structure. The radius ratios of all spinels except $SiNi_2O_4$ are within the limits

$$r_a/r_o = 0.36\text{–}0.65$$

$$r_b/r_o = 0.35\text{–}0.69$$

where r_a is the tetrahedral radius. Phenacites and a few compounds of other structures are also found within these limits.

In addition to $SiNi_2O_4$, $BaIn_2O_4$, and $SrIn_2O_4$, as previously discussed, $MoNa_2O_4$ and WNa_2O_4, which have low values of K_{ab}, are also exceptions from this relation. $CaTi_2O_4$, $CaFe_2O_4$, CaV_2O_4, and $CaCr_2O_4$ fall nearly on the face of the spinel region. The radius ratios for them are $r_a/r_o = 0.66$. It is also observed that the known compounds having the olivine structure have larger K_{ab} values than the compounds with the spinel structure.

Crystal Chemistry of AB_2X_4 (X = S, Se, Te)

The same procedure which was carried out for the compounds of the AB_2O_4 type was applied to the compounds having the formula AB_2X_4 where X is S, Se, and Te. The results are listed in Tables III and IV and a plot is shown in Figure 4. Three major crystal structure areas exist: the spinel and Ag_2HgI_4, the $CaFe_2O_4$, and the Th_3P_4 structure areas. Two intermediate regions can be recognized, namely, a rhombohedral and an orthorhombic one. The broken lines in Figure 4 are the boundary lines corresponding to the areas shown in Figure 1. The square of the ratio of the radius of selenium to that of oxygen, $(r_{Se}/r_o)^2$, is 2 and in order to adjust the scale the force constant was multiplied by $^1/_2$. These transferred boundary lines produce regions which do not conflict with the areas occupied by the major crystal structure types. Inverse spinels lie in the inverse spinel region and the horizontal line separates the map into two areas of major structures. The similarity between the diagrams in Figure 1 and 4 is nevertheless somewhat tenuous because few compounds of the AB_2X_4 type having structures lying on the left side of Figure 4 are reported, while three major structure areas of compounds having the formula AB_2O_4 are located there.

An important feature in Figure 4 is that the spinel structure area and the Ag_2HgI_4 structure area are not separated. It is also interesting that no compound of the Ag_2HgI_4 structure is found among the AB_2O_4-type compounds. It can be postulated that in addition to the larger radius of the anions S, Se, and Te, which permit the cations to fit easily into the tetrahedral sites, some other force due to these anions becomes important, for instance, a site preference energy. This postulate is advanced on the basis that even though compounds with the formula AB_2O_4 have similar values for the force constants and radius ratios as compounds AB_2X_4 which have the Ag_2HgI_4 structure, they still do not crystallize with this structure. The Th_3P_4 structure to which no compound with the formula AB_2O_4 belongs is also present as a major structure type in Figure 4. No AB_2O_4-type compound has both the small force constant and appropriate radius ratio value to permit this crystallization. Thus it is not unreasonable that the Th_3P_4 structure is not observed among the compounds of the AB_2O_4 type if the congruence between Figures 1 and 4 holds.

The density distribution of the compounds having the formula AB_2X_4 is quite similar to that of the compounds with the formula AB_2O_4 shown in Figure 2. Superposition can be achieved by shifting every dot in Figure 2 by half the magnitude of the force constant. This figure immediately shows that many computer-generated compounds lie in the area where no AB_2X_4 compounds are found in Figure 4. The major structures similar to the AB_2O_4 types are expected to occupy this area.

Possible Structures for AB_2X_4 Stoichiometries

An expression relating various cation configurations around anions in close packing can be derived. Let

Table IV

Additional Compounds with the AB_2X_4 Stoichiometry[a]

MG	CE	S	2	3	.34	.58	.58	1 30	.06	.84	.94	structure unknown
MG	LA	S	2	3	.34	.62	.54	1.33	.05	.83	.91	
MG	PR	S	2	3	.34	.58	.59	1.32	.06	.84	.94	
MG	ND	S	2	3	.34	.57	.60	1.32	.06	.84	.95	
MG	SM	S	2	3	.34	.54	.62	1.32	.06	.84	.96	
MG	GD	S	2	3	.34	.53	.64	1.37	.06	.81	.97	
MG	TB	S	2	3	.34	.51	.67	1.35	.06	.81	.98	orthorhombic type A
MG	DY	S	2	3	.34	.50	.67	1.35	.06	.81	.99	
MG	Y	S	2	3	.34	.50	.67	1.37	.06	.81	.99	
MG	HO	S	2	3	.34	.49	.68	1.35	.06	.81	.99	
MG	ER	S	2	3	.34	.48	.70	1.37	.06	.81	1.00	
MG	TM	S	2	3	.34	.47	.71	1.37	.06	.81	1.00	cubic spinel
MG	YB	S	2	3	.34	.47	.72	1.30	.06	.84	1.01	
MG	LU	S	2	3	.34	.46	.73	1.40	.06	.78	1.01	
MG	SC	S	2	3	.34	.44	.77	1.48	.07	.74	1.03	
CA	LA	S	2	3	.51	.62	.82	1.12	.04	.70	.97	Th_3P_4
CA	CE	S	2	3	.51	.58	.87	1.10	.04	.71	1.00	
CA	PR	S	2	3	.51	.58	.88	1.11	.04	.71	1.00	
CA	ND	S	2	3	.51	.57	.89	1.11	.04	.71	1.01	
CA	SM	S	2	3	.51	.54	.93	1.11	.04	.71	1.02	
CA	GD	S	2	3	.51	.53	.96	1.15	.04	.68	1.03	
CA	TB	S	2	3	.51	.51	1.00	1.14	.04	.69	1.05	
CA	DY	S	2	3	.51	.50	1.01	1.14	.04	.69	1.05	
CA	Y	S	2	3	.51	.50	1.01	1.15	.04	.68	1.05	orthorhombic type A
CA	HO	S	2	3	.51	.49	1.02	1.14	.04	.69	1.05	
CA	ER	S	2	3	.51	.48	1.05	1.15	.04	.68	1.06	
CA	TM	S	2	3	.51	.47	1.07	1.15	.04	.68	1.07	
CA	YB	S	2	3	.51	.47	1.08	1.10	.04	.71	1.07	
CA	LU	S	2	3	.51	.46	1.09	1.19	.04	.66	1.08	structure unknown
CA	SC	S	2	3	.51	.44	1.15	1.25	.04	.63	1.09	
SR	LA	S	2	3	.57	.62	.92	1.07	.03	.67	1.00	Th_3P_4
SR	CE	S	2	3	.57	.58	.98	1.05	.03	.68	1.02	
SR	PR	S	2	3	.57	.58	.99	1.06	.03	.67	1.02	
SR	ND	S	2	3	.57	.57	1.01	1.06	.03	.67	1.03	
SR	SM	S	2	3	.57	.54	1.05	1.06	.03	.67	1.05	
SR	GD	S	2	3	.57	.53	1.09	1.10	.04	.65	1.06	
SR	TB	S	2	3	.57	.51	1.13	1.09	.04	.65	1.07	Orthorhombic type B
SR	DY	S	2	3	.57	.50	1.14	1.09	.04	.65	1.08	
SR	Y	S	2	3	.57	.50	1.14	1.10	.04	.65	1.08	
SR	HO	S	2	3	.57	.49	1.16	1.09	.04	.65	1.08	
SR	ER	S	2	3	.57	.48	1.18	1.10	.04	.65	1.09	
SR	TM	S	2	3	.57	.47	1.21	1.10	.04	.65	1.10	
SR	YB	S	2	3	.57	.47	1.22	1.05	.03	.68	1.10	
SR	LU	S	2	3	.57	.46	1.24	1.13	.04	.63	1.10	structure unknown
SR	SC	S	2	3	.57	.44	1.30	1.19	.04	.60	1.12	
BA	LA	S	2	3	.68	.62	1.10	1.05	.03	.65	1.04	Th_3P_4
BA	CE	S	2	3	.68	.58	1.18	1.03	.03	.67	1.06	
BA	PR	S	2	3	.68	.58	1.19	1.04	.03	.66	1.07	
BA	ND	S	2	3	.68	.57	1.21	1.04	.03	.66	1.07	
BA	SM	S	2	3	.68	.54	1.26	1.04	.03	.66	1.09	
BA	GD	S	2	3	.68	.53	1.30	1.08	.03	.64	1.10	Orthorhombic type B
BA	TB	S	2	3	.68	.51	1.35	1.07	.03	.64	1.12	
BA	DY	S	2	3	.68	.50	1.37	1.07	.03	.64	1.12	
BA	Y	S	2	3	.68	.50	1.37	1.08	.03	.64	1.12	
BA	HO	S	2	3	.68	.49	1.38	1.07	.03	.64	1.12	
BA	ER	S	2	3	.68	.48	1.42	1.08	.03	.64	1.13	
BA	TM	S	2	3	.68	.47	1.45	1.08	.03	.64	1.14	
BA	YB	S	2	3	.68	.47	1.46	1.03	.03	.67	1.14	
BA	LU	S	2	3	68	.46	1.48	1.11	.03	.62	1.15	structure unknown
BA	SC	S	2	3	.68	.44	1.56	1.16	.03	.59	1.17	

MG	LA	SE	2	3	.31	.58	.54	1.33	.05	.83	.93	structure unknown
MG	CE	SE	2	3	.31	.54	.58	1.30	.05	.84	.95	
MG	PR	SE	2	3	.31	.54	.59	1.32	.05	.84	.95	
MG	ND	SE	2	3	.31	.53	.60	1.32	.05	.84	.96	
MG	SM	SE	2	3	.31	.51	.62	1.32	.05	.84	.97	
MG	GD	SE	2	3	.31	.49	.64	1.37	.06	.81	.98	
MG	TB	SE	2	3	.31	.47	.67	1.35	.05	.81	1.00	
MG	DY	SE	2	3	.31	.46	.67	1.35	.05	.81	1.00	
MG	Y	SE	2	3	.31	.46	.67	1.37	.06	.81	1.00	cubic spinel
MG	HO	SE	2	3	.31	.46	.68	1.35	.05	.81	1.00	
MG	ER	SE	2	3	.31	.45	.70	1.37	.06	.81	1.01	
MG	TM	SE	2	3	.31	.44	.71	1.37	.06	.81	1.02	
MG	YB	SE	2	3	.31	.43	.72	1.30	.05	.84	1.02	
MG	LU	SE	2	3	.31	.43	.73	1.40	.06	.78	1.03	
CA	LA	SE	2	3	.47	.58	.82	1.12	.04	.70	.99	structure unknown
CA	CE	SE	2	3	.47	.54	.87	1.10	.04	.71	1.01	
CA	PR	SE	2	3	.47	.54	.88	1.11	.04	.71	1.01	
CA	ND	SE	2	3	.47	.53	.89	1.11	.04	.71	1.02	
CA	SM	SE	2	3	.47	.51	.93	1.11	.04	.71	1.03	
CA	GD	SE	2	3	.47	.49	.96	1.15	.04	.68	1.04	
CA	TB	SE	2	3	.47	.47	1.00	1.14	.04	.69	1.06	
CA	DY	SE	2	3	.47	.46	1.01	1.14	.04	.69	1.06	
CA	Y	SE	2	3	.47	.46	1.01	1.15	.04	.68	1.06	Rhombohedral
CA	HO	SE	2	3	.47	.46	1.02	1.14	.04	.69	1.07	
CA	ER	SE	2	3	.47	.45	1.05	1.15	.04	.68	1.07	
CA	TM	SE	2	3	.47	.44	1.07	1.15	.04	.68	1.08	
CA	YB	SE	2	3	.47	.43	1.08	1.10	.04	.71	1.08	
CA	LU	SE	2	3	.47	.43	1.09	1.19	.04	.66	1.09	
SR	LA	SE	2	3	.53	.58	.92	.07	.03	.67	1.01	Th_3P_4
SR	CE	SE	2	3	.53	.54	.98	.05	.03	.68	1.03	
SR	PR	SE	2	3	.53	.54	.99	1.06	.03	.67	1.04	
SR	ND	SE	2	3	.53	.53	1.01	1.06	.03	.67	1.04	
SR	SM	SE	2	3	.53	.51	1.05	1.06	.03	.67	1.06	
SR	GD	SE	2	3	.53	.49	1.09	1.10	.03	.65	1.07	
SR	TB	SE	2	3	.53	.47	1.13	1.09	.03	.65	1.08	Orthorhombic type B
SR	DY	SE	2	3	.53	.46	1.14	1.09	.03	.65	1.09	
SR	Y	SE	2	3	.53	.46	1.14	1.10	.03	.65	1.09	
SR	HO	SE	2	3	.53	.46	1.16	1.09	03	.65	1.09	
SR	ER	SE	2	3	.53	.45	1.18	1.10	.03	.65	1.10	
SR	TM	SE	2	3	.53	.44	1.21	1.10	.03	.65	1.11	
SR	YB	SE	2	3	.53	.43	1.22	1.05	.03	.68	1.11	
SR	LU	SE	2	3	.53	.43	1.24	1.13	.03	.63	1.11	
BA	LA	SE	2	3	.64	.58	1.10	1.05	03	.65	1.05	Th_3P_4
BA	CE	SE	2	3	.64	.54	1.18	1.03	03	.67	1.07	
BA	PR	SE	2	3	.64	.54	1.19	1.04	03	.66	1.08	
BA	ND	SE	2	3	.64	.53	1.21	1.04	03	.66	1.08	
BA	SM	SE	2	3	.64	.51	1.26	1.04	03	.66	1.10	Orthorhombic type B
BA	GD	SE	2	3	.64	.49	1.30	1.08	03	.64	1.11	
BA	TB	SE	2	3	.64	.47	1.35	1.07	.03	.64	1.12	
BA	DY	SE	2	3	.64	.46	1.37	1.07	.03	.64	1.13	
BA	Y	SE	2	3	.64	.46	1.37	1.08	.03	.64	1.13	
BA	HO	SE	2	3	.64	.46	1.38	1.07	.03	.64	1.13	
BA	ER	SE	2	3	.64	.45	1.42	1.08	.03	.64	1.14	
BA	TM	SE	2	3	.64	.44	1.45	1.08	.03	.64	1.15	
BA	YB	SE	2	3	.64	.43	1.46	1.03	.03	.67	1.15	
BA	LU	SE	2	3	.64	.43	1.48	1.11	.03	.62	1.16	

[a] The columns represent the ions A, B, X, valence state of A, valence of B, radius ratio r_a/r_x, radius ratio r_b/r_x, radius ratio r_a/r_b, electronegativity product $\chi_a\chi_b$, force constant K_{ab}, ratio K_{ab}/K_{bb}, and tolerance factor.

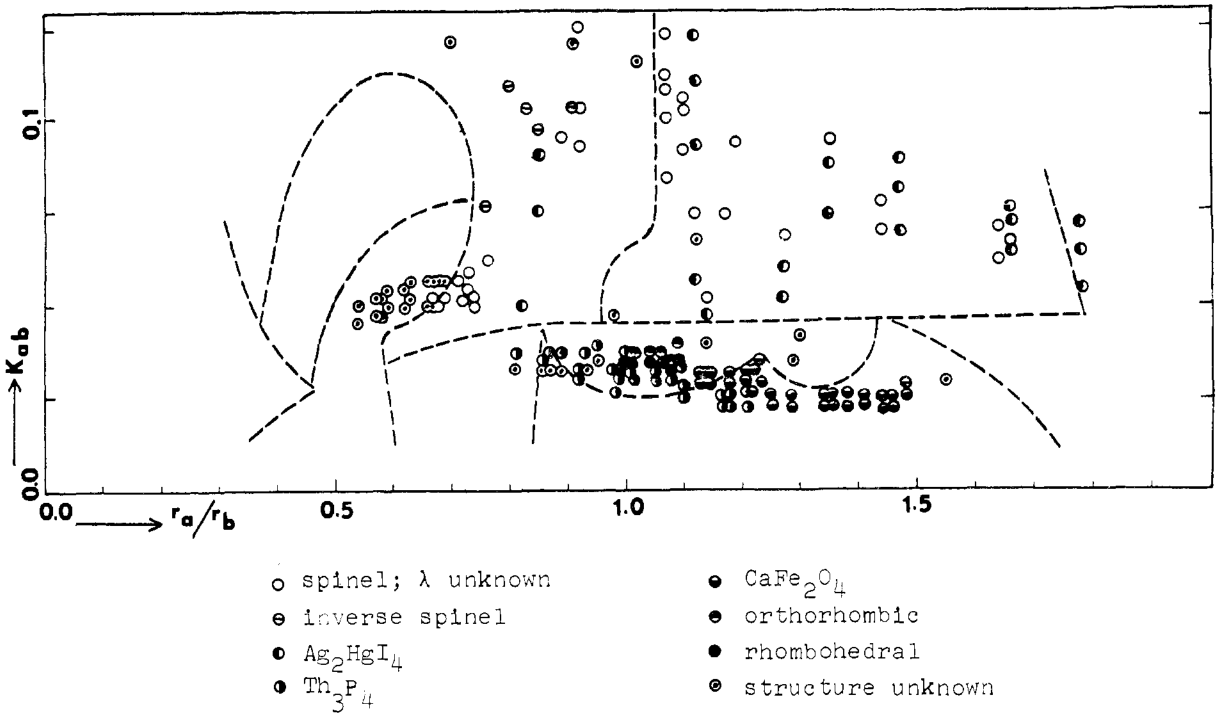

Figure 4.—Plot of K_{ab} vs. r_a/r_b for chalcogenide compositions AB_2X_4 (X = Se, Se, Te) for known and some unknown structures.

N_{tQ} and N_{oQ} be the number of atoms of type Q attached to n oxygen atoms in tetrahedral and in octahedral voids, respectively. Thus one-fourth of Q in a tetrahedral void and one-sixth of Q in an octahedral void belong to each oxygen, and on the average one-fourth of A and one-half of B in compounds with the formula AB_2O_4 are attached to an oxygen ion. The following equations can be derived

$$^1/_4N_{tA} + {}^1/_6N_{oA} = {}^1/_4n$$

$$^1/_4N_{tB} + {}^1/_6N_{oB} = {}^1/_2n$$

Thus

$$3N_{tA} + 2N_{oA} = 3n$$

$$3N_{tB} + 2N_{oB} = 6n$$

where all N's and n's are positive integers.

The degree of inversion λ of a spinel is related to N_{oQ} by

$$\lambda = \frac{N_{oA}}{N_{oA} + N_{oB}}$$

and usually $N_{oA} \leq N_{oB}$. Since for the inverse spinels

$$\frac{N_{tB}}{4} = \frac{N_{oB}}{6}$$

λ can be also expressed as

$$\lambda = \frac{1}{2}\left(\frac{N_{tB}}{n}\right)$$

For the case $n = 1$

$$3N_{tA} + 2N_{oA} = 3$$

$$3N_{tB} + 2N_{oB} = 6$$

and two solutions exist, (I) and (II).

$$\begin{matrix} N_{tA} = 1 & N_{oA} = 0 \\ N_{tB} = 2 & N_{oB} = 0 \end{matrix} \tag{I}$$

The Ag_2HgI_4 structure has this type of cation arrangement.

$$\begin{matrix} N_{tA} = 1 & N_{oA} = 0 \\ N_{tB} = 0 & N_{oB} = 3 \end{matrix} \tag{II}$$

The spinel structure and the olivine structure are examples of this type of cation arrangement.

For the case $n = 2$

$$3N_{tA} + 2N_{oA} = 6$$

$$3N_{tB} + 2N_{oB} = 12$$

Six solutions exist among which two solutions give the same cation distribution as (I) and (II) above, while a third solution

$$\begin{matrix} N_{tA} = 0 & N_{oA} = 3 \\ N_{tB} = 2 & N_{oB} = 3 \end{matrix} \tag{III}$$

describes the inverse spinel structure. One oxygen is associated with one B atom in the tetrahedral void, and two A atoms and one B atom are associated in the octahedral voids. The other solutions are

TABLE V

POSSIBLE COMBINATIONS OF ION DISTRIBUTIONS AROUND OXYGEN FOR SOLUTON III FOR THE CASE $n = 2$

Oxygen 1				Oxygen 2			
Tetrahedral elements		Octahedral elements		Tetrahedral elements		Octahedral elements	
A	B	A	B	A	B	A	B
0	0	0	0	0	2	3	3
		0	1			3	2
		0	2			3	1
		0	3			3	0
		1	0			2	3
		1	1			2	2
		1	2			2	1
		1	3			2	0
		2	0			1	3
		2	1			1	2
		2	2			1	1
		2	3			1	0
		3	0			0	3
		3	1			0	2
		3	2			0	1
		3	3			0	0
0	1	0	0	0	1	3	3
		0	1			3	2
		0	2			3	1
		0	3			3	0
		1	0			2	3
		1	1			2	2
		1	2			2	1[a]
		1	3			2	0

[a] This row represents arrangement for inverse spinel.

TABLE VI

THE CATION ARRANGEMENTS AROUND AN ANION FOR THE CASE $n = 4$ CORRESPONDING TO THE DISTRIBUTION IN $MgGa_2SO_4$

No. of anions in unit cell with same cation nearest neighbors	No. of Mg ions in octahedral voids	No. of Ga ions in tetrahedral voids
16	3	1
8	1	2
8	2	2
16	0	3

$$\begin{matrix} N_{tA} = 0 & N_{oA} = 3 \\ N_{tB} = 0 & N_{oB} = 6 \end{matrix} \tag{IV}$$

$$\begin{matrix} N_{tA} = 0 & N_{oA} = 3 \\ N_{tB} = 4 & N_{oB} = 0 \end{matrix} \tag{V}$$

$$\begin{matrix} N_{tA} = 2 & N_{oA} = 0 \\ N_{tB} = 2 & N_{oB} = 3 \end{matrix} \tag{VI}$$

Generally the number of solutions for the case $n = m$ is given by

$$([m/2] + 1)(m + 1)$$

where $[m/2]$ is $m/2$ if m is even and $[m/2]$ is $(m - 1)/2$ if m is odd, and all solutions for $n = m$ are contained in the solutions for $n = l$, if and only if m is a divisor of l.

There are several possible combinations of ion distributions around the two oxygens for each solution. In Table V the possible combinations for the third solution are shown. Mathematically all configurations are consistent with respect to charge distributions and stoichiometry, but a modifying principle can be introduced which will make some distributions more likely than others by assuming that the oxygen ions will prefer identical or nearly identical cation environments. The ion distribution around oxygens characterized by 0112 and 0121 is that of an inverse spinel. The cation arrangement of $MgGa_2S_4$[18] is an example of the case $n = 4$, which is a partially inverted structure of solution V, and the cation arrangement is listed in Table VI. The number of integral formula weights per unit cell will be given by the expression $I[\text{lcm}(4,n)/4]$, where I is an integer and the numerator is the least common multiplier of 4 and n.

It is quite possible that the local energy around oxygen due to the ionic charges becomes higher as n increases. If n is small, *e.g.*, 1, then each oxygen ion has the same cation environment. For $n = 2$ the cation environment becomes different for the inverted spinel structure and these differences among oxygen ions would become more pronounced as n increases. The fact that spinel, olivine, and Ag_2HgI_4 structures occur so frequently indicates that structures in which the local surroundings of anions differ greatly are unstable.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS 02139

The Crystal Structure of Cesium Tetrakis(hexafluoroacetylacetonato)yttrate(III). A Novel Stereoisomer Having Dodecahedral Eight-Coordination[1]

BY M. J. BENNETT, F. A. COTTON, P. LEGZDINS,[2] AND S. J. LIPPARD

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The crystal and molecular structures of cesium tetrakis(hexafluoroacetylacetonato)yttrate(III), $Cs[Y(CF_3COCHCOCF_3)_4]$, have been determined from 1650 independent, nonzero reflections collected with a counter diffractometer. The compound crystallizes in the orthorhombic space group Pbcn with four molecules in a unit cell of dimensions: $a = 8.679 \pm 0.005$ Å, $b = 21.518 \pm 0.008$ Å, and $c = 17.553 \pm 0.008$ Å ($\rho_{\text{obsd}} = 2.10$ g cm^{-3}; $\rho_{\text{calcd}} = 2.12$ g cm^{-3}). The structure, excluding hydrogen atoms, was solved from Patterson and electron density maps and refined by least-squares methods to a conventional R factor of 6.5%. The molecules are monomeric with the yttrium being dodecahedrally coordinated to the eight essentially equivalent oxygen atoms (average Y–O, 2.323 (4) Å). Both coplanar ligands show dihedral folding of 7.6° along the O–O line in the chelate rings. In contrast with other dodecahedral ML_4 (L = bidentate ligand) structures, each ligand in this structure spans adjacent vertices *between* the two bisphenoids constituting the dodecahedron, resulting in over-all D_2 symmetry. The monomeric anions are linked together in infinite columns parallel to the crystallographic a axis by a close Cs–F association (3.2–3.7 Å), but other intermolecular distances are not unusual. The structure is in accord with the mass spectral evidence for the existence of a strong ion pair.

Introduction

During the course of our investigation of the solid-state and solution properties of several anionic eight-coordinate β-diketonate complexes of yttrium(III),[3,4] it was discovered that certain large but flexible organic cations, such as $(C_6H_5)_4As^+$, gave rise to a polymorphism that was not observed for the simple inorganic cations (Na^+, K^+, Cs^+).[4,5] It was considered possible that this polymorphism might correspond to geometric isomerism for the eight-coordinate anions. This type of isomerism, although considered to be a possibility,[6] has never been observed in tetrachelate metal atom complexes.[7] As part of an investigation to test this structural possibility, it was decided to carry out a single-crystal X-ray analysis of $Cs[Y(HFA)_4]$, where HFA represents the hexafluoroacetylacetonate ion, $CF_3COCHCOCF_3^-$.

Experimental Procedures

Crystalline $Cs[Y(HFA)_4]$ was prepared by the reaction of Cs(HFA) with YCl_3 in aqueous ethanol as described previously[8] and was recrystallized from the same solvent. *Anal.* Calcd for $CsYC_{20}H_4O_8F_{24}$: C, 22.85; H, 0.38; F, 43.43. Found: C, 22.71; H, 0.46; F, 43.27. The analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

The well-formed, transparent, needle-like crystals showed mmm morphology under optical examination, and preliminary Weissenberg ($0kl$ and $1kl$ levels) and precession ($h0l$, hll, $hk0$, and $hk1$ levels) photographs, taken with Cu Kα radiation, confirmed this as the Laue symmetry. Moreover, the observed systematic absences—$0kl$ for $k \neq 2n$, $h0l$ for $l \neq 2n$, and $hk0$ for $h + k \neq 2n$—suggested the unique choice of the orthorhombic space group Pbcn (no. 60). The following unit cell dimensions were obtained, at 22°, by a method described earlier,[9] with 2θ values measured on a General Electric XRD-5 manually operated single-crystal diffractometer using Cu Kα radiation (λ(Kα_1)

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