Physical Properties and Cation Arrangement of Oxides with Spinel Structures I. Cation Arrangement in Spinels

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Physical Properties and Cation Arrangement of Oxides with Spinel Structures

I. Cation Arrangement in Spinels

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By means of a detailed x-ray study of a large number of oxides having a spinel structure, it has been established whether they crystallize in the "normal" spinel-type structure, XY_2O_4, or in the "inversed" type of structure, $Y(XY)O_4$, discovered by Barth and Posnjak. Certain rules can be derived which are also applicable to more complicated spinels or to solid solutions of different spinel oxides. Madelung constants have been calculated for different spinel types in order to investigate their stability on the basis of an ionic concept of the chemical bond (Born's lattice theory). The experimental results are only partially explainable on this basis. All exceptions to the electrostatic principles can be understood by assuming that Fe^{3+}, Ga^{3+}, In^{3+}, Zn^{2+}, and Cd^{2+} favor a configuration having the coordination number 4, because of a considerable covalent contribution to the chemical bond for that configuration.

1. INTRODUCTION

THERE are a great many oxides having the general formula XY_2O_4 which crystallize with the same general crystal structure as the mineral spinel, $MgAl_2O_4$. Certain groups of spinels show remarkable electrical and magnetic properties. The spinels are, therefore, of considerable interest from a technical point of view. They may be readily synthesized so that their properties, which are composition-sensitive, may be controlled within varying limits.

The spinel structure is cubic with a large unit cell containing 8 X, 16 Y, and 32 oxygen atoms. The positions of the oxygen atoms are more or less fixed but the arrangement of the cations varies considerably within certain limits. The
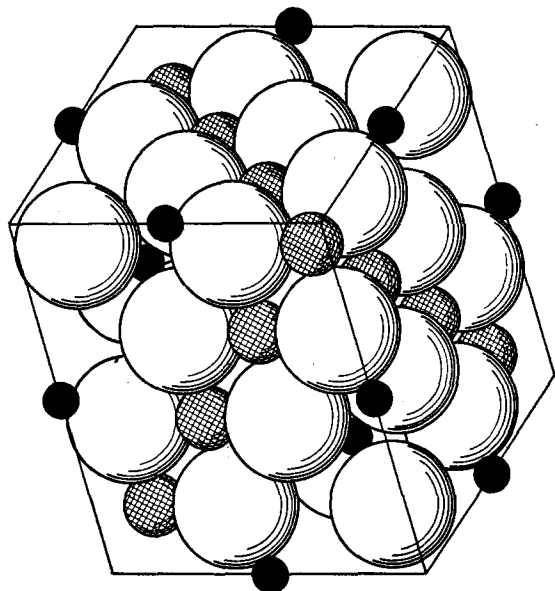

FIG. 1. Arrangement and packing of atoms in unit cell of ideal spinel-type ($u = 0.375$) containing $8[XY_2O_4]$. Large spheres represent oxygen, small black spheres represent fourfold coordination position and cross-hatched spheres sixfold coordination position.

* Deported to a concentration camp in the eastern part of Germany (July 1944), from which he never returned.
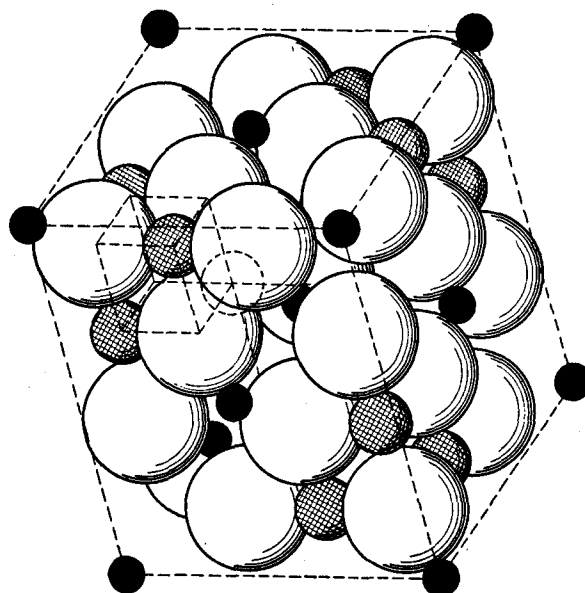

FIG. 2. Same as Fig. 1 but with unit cell shifted by one-half a cube edge. Small dashed-line cube shows NaCl-type structural motif with the cross-hatched ion in an octahedral interstice.

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variations in distribution of cations in the X and Y positions cause marked changes in some of the physical properties. One of these is the electrical conductivity which will be considered in a following paper (II). Equivalent lattice points may be occupied by different cations distributed statistically throughout the crystal. The permutations are often more complicated than those found in ordinary primary solid solutions.

We have investigated a large number of these compounds during the past few years. The present paper describes a detailed study of the structure of the oxide spinels. It contains the crystallographic results for those compounds in which we have established the arrangement of the cations and a general discussion of the factors determining their arrangement.

2. DISCUSSION OF THE SPINEL STRUCTURE

In most oxidic structures the oxygen ions are appreciably larger than the metallic ions and the spinel structure can be approximated by a cubic close packing of O^{2-} ions in which the Mg^{2+} and Al^{3+} ions occupy certain interstices. Each unit cell contains 8 $[MgAl_2O_4]$ and, therefore, 32 O^{2-} ions. This close packing contains 64 interstices surrounded by 4 O^{2-} ions (coordination number 4, tetrahedral) and 32 interstices surrounded by 6 O^{2-} ions (coordination number 6, octahedral). In the spinel structure, 8 of these tetrahedral holes and 16 of the octahedral holes are occupied. Unit cells of the "ideal" spinel structure are shown in Fig. 1 and Fig. 2; the only difference between them is that the cell unit has been shifted over one-half of the cube edge a in one of the three cubic cube edge directions in the crystal. It is convenient to subdivide the unit cell in 8 octants. The structure then may be described as a face-centered compilation of A- and B-cubes, where the A-cubes comprise a group Mg_2O_4 (Mg in 4-coordination) and the B-cubes a group Al_4O_4 (Al in 6-coordination).[1]

In all spinel-like substances the parameter u has a value in the neighborhood of 0.375. For $u = 0.375$, the case corresponding to Figs. 1–3, the arrangement of the O^{2-} ions equals exactly a cubic close packing. In actual spinel lattices this
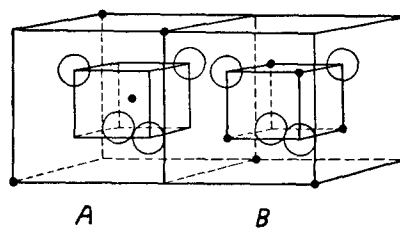

FIG. 3. Two octants of a unit cell. Spinel structure is a three-dimensional packing of A- and B-cubes in a checkerboard arrangement.

ideal pattern is slightly deformed, usually, corresponding to $u > 0.375$, in such a way that the oxygen tetrahedron in the A-cubes is somewhat expanded and the oxygen tetrahedron in the B-cubes is slightly contracted. Accordingly, in that case, the octahedrons formed by the 6 O^{2-} ions directly surrounding the positive ions in these B-cubes deviate somewhat from regular octahedrons.

In simple spinels the valencies of the cations may be either

$$X = 2+, \quad Y = 3+,$$

or

$$X = 4+, \quad Y = 2+.$$

The third possibility, $X = 6+$, $Y = 1+$, is very rare. In the present work, separate examples of the two common possibilities and their combinations in more complicated spinels are studied.

Originally, in accordance with classical principles of crystallography, it was assumed that in the spinels the X atoms or ions occupied the eightfold position (the tetrahedral holes of the A-cubes indicated in Fig. 3) and the Y atoms or ions were in the 16-fold positions (the octahedral interstices of the B-cubes). However, Barth and Posnjak[2] pointed out a second possibility of distributing the cations while retaining cubic symmetry; viz., one in which the tetrahedral interstices are occupied by half of the Y ions, the octahedral holes by the X ions, and the other half of the Y ions are distributed at random at these lattice points. For the sake of convenience, the first arrangement will be indicated as characteristic for "normal spinels," the Barth and Posnjak arrangement as that of "inversed spinels." A number of examples for both groups have

[1] E. J. W. Verwey, Zeits. f. Krist. 91A, 65 (1935).

[2] T. F. W. Barth and E. Posnjak, Zeits. f. Krist. 82, 325 (1932).

already been given by Barth and Posnjak, who based their conclusions upon a detailed discussion of the intensities of x-ray diffraction pictures. In addition to these two arrangements, there is the possibility of some intermediate arrangement with an averaged distribution of all ions about all spinel cation positions. As a matter of fact, this contingency constitutes in effect an infinite series of possibilities, as this type of distribution will generally occur in such a way that certain ions show a definite preference for one type of interstice according to a certain distribution factor. Machatschki[3] has described such an intermediate case ($MgGa_2O_4$).

3. CONSIDERATION OF THE STABILITY OF DIFFERENT ARRANGEMENTS BASED ON CALCULATIONS OF MADELUNG POTENTIALS

Before passing to an extension of the experimental facts and an attempt to find general rules as to the most stable arrangement in a given case as a function of the properties of the participating ions, it is useful to consider first what might be expected from a purely heteropolar point of view.

The chemical bonding in these spinel oxides can be treated to a first-order approximation as an ionic bond, in which the state of affairs is described by an equilibrium of Coulomb forces and Born repulsion forces. Comparing states with the same crystal structure, the former forces are described by the Madelung potential; the latter are roughly determined by the size of the different ions. The ionic radii will not vary over a very wide range, because the spinel structure is stable only if the cations are rather medium sized and, in addition, the radii of the different ionic species in the same compound do not differ too much. The ionic dimensions will have an influence upon the value of the parameter u; large values of u can be expected if the tetrahedral interstices are occupied by comparatively large ions. Values for this parameter, however, have been determined in only a few cases (where they were usually about 0.380). Accurate values are rather difficult to obtain and only very few are available.

Madelung summation constants have been calculated for spinels with the following values

of the valencies, where p and q are the valencies of the ions at tetrahedral and octahedral interstices, respectively:

(a) $p=4$, $q=2$,
(b) $p=2$, $q=3$,
(c) $p=3$, $q=2\frac{1}{2}$.

Case (a) will then give the Madelung constant of a normal 4-2 spinel, $X^{4+}Y_2^{2+}O_4$, and case (b) that of a normal 2-3 spinel, $X^{2+}Y_2^{3+}O_4$. In the inversed 4-2 spinel $Y^{2+}(X^{4+}Y^{2+})O_4$, the 16-fold position contains an averaged distribution of 4-valent and 2-valent ions and the corresponding Madelung constant will approximately be given by case (b) as the valency of the ions in the 16-fold position is on the average 3. In the inversed 2-3 spinel $Y^{3+}(X^{2+}Y^{3+})O_4$, the valency between the brackets is on the average $2\frac{1}{2}$ and the Madelung constant will be approximated by case (c).

The calculations have been carried out for different values of u in order to establish the effect of this parameter upon the stability.

The calculations have been done by a combination of the Ewald[4] and the Evjen[5] methods, for the following reasons. As a consequence of the large number of ions per unit cell the calculations are rather laborious, especially in those cases where the parameter u differs from 0.375 and the oxygen ionic lattice shows small deviations from the ideal face-centered cubic compilation.

Evjen's method, a direct summation over a restricted number of unit cells where electroneutrality is maintained by counting the ions in the outside planes $\frac{1}{2}$, etc., appears to lead to results accurate within 1 percent when the summation is carried out over a cube of 8 unit cells, with the ion under consideration in the corner common to all 8 cells (this has been checked by extending the calculations in one case over 27 and 64 cells). Accordingly, this method has been used for a calculation of the Madelung constant M for $u=0.375, 0.380, 0.385$, and 0.390. In some cases, including the present one, however, the Evjen method leads to M values which contain a constant error due to

[3] F. Machatschki, Zeits. f. Krist. **82**, 348 (1932).

[4] P. P. Ewald, Ann. d. Physik **64**, 253 (1921); Zeits. f. Krist. **56**, 129 (1921).
[5] H. M. Evjen, Phys. Rev. **39**, 675 (1932).

the circumstance that the outer part of the crystal fraction cut out of the crystal in this way gives rise to an electrical dipole layer. As this constant error will be independent of u, it is sufficient to eliminate it by calculating for the ideal parameter value $u = 0.375$, the Madelung constant according to an alternative method avoiding this constant error. For this calculation Ewald's method has been chosen. According to this method the summation over the infinitely large lattice is carried out by transforming the infinite series into the elliptical theta-functions, so that again a rapid convergency is obtained.

Calculating in this way the electrical potential at a tetrahedral lattice point, an octahedral lattice point, and an O-point, we find for the total Coulomb energy per "molecule" XY_2O_4:

$$V = -\tfrac{1}{2} \cdot (e^2/a)(p M_{tetra.} + 2q M_{oct.} + 8 M_O)$$
$$= -M \cdot (e^2/a)$$

where a = the length of the unit cell. The data obtained for the Madelung constant M are given in Table I. Hence, on the basis of the ionic picture of spinels, assuming that the cube edge of the unit cell is not altered by the inversion (we will see later on that this is not entirely true, but sufficiently true for our following conclusions), and also assuming that the Born repulsion potential is a constant fraction, amounting to about 10 percent of the Coulomb potential, we should arrive at the following results concerning the stability of different cation arrangements.

1. The normal 2-3 spinel (case (b)) is more stable than the inversed 2-3 spinel (case (c)), but the inversed 4-2 spinel (again case (b)) is more stable than the normal 4-2 spinel (case (a)).

2. This conclusion is not altered by the influence of the parameter, as the M values do not cross within the range of practically occurring u values.

The first conclusion can also roughly be explained on the basis of the principle of maximal charge neutralization; in both cases we find that the most stable arrangement is that in which the cations with the highest charge occupy the interstices with the highest coordination number.

Similarly it can easily be understood that the Madelung potential of a normal 4-2 spinel is increased by a decrease of u and that of a normal 2-3 spinel by an increase of u, as both variations of u correspond to a contraction of the oxygen ions around the cations with the highest charges.

TABLE I.

	(a) $p=4$; $q=2$	(b) $p=2$; $q=3$	(c) $p=3$; $q=2\frac{1}{2}$
$u=0.375$	142.1	150.3	143.6
$=0.380$	139.9	153.1	143.8
$=0.385$	137.7	155.7	144.1
$=0.390$	135.6	158.2	144.3

It is also understood that the intermediate case ($p=3$, $q=2\frac{1}{2}$) is less sensitive to variations of the parameter.

In the following section the extent of the agreement between the predictions given above concerning the relative stability of different arrangements and the cation distributions actually found will be shown.

4. X-RAY INVESTIGATION OF VARIOUS SPINELS

A large number of spinel oxides were prepared by mixing the pure oxides ("pro-analysis" quality) in the proper ratio, pressing the mixture into bars and heating the latter for several hours in an electric furnace at a constant temperature. The sintering temperature varied with the nature of the constituent oxides; for easily sintering samples it was mostly 1200°C, for oxides sintering with greater difficulty it was 1300°C, or even 1400°C (as in the case of $MgCr_2O_4$). Only in the instance last mentioned was it necessary to carry out the heating process in an atmosphere of oxygen; in the other cases air was sufficient to prevent reduction. The samples with Fe^{2+} form an exception to this rule and require special precautions to obtain the iron completely in the desired valency state.

The determination of the cation arrangement and, consequently, also of the detailed pattern of the oxygen ions (the latter described by the parameter u) was made in the usual way with the aid of x-ray powder diagrams.* The intensities of a great number of diffraction lines were measured and the observed values were compared with the calculated reflection intensities** for different arrangements and different

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* We wish to thank Dr. J. F. H. Custers and Mr. C. G. J. Jansen, both from this Laboratory, for the preparation of these x-ray pictures under carefully controlled, checked conditions.

** The intensities were measured visually by comparison with an intensity scale. In the calculations the usual angle-dependent factors were taken into account, including absorption.

TABLE II. Intensities.

Plane	Cu	$Cu_{0.5}Zn_{0.5}$	$Cu_{0.4}Zn_{0.6}$	Zn
(111)	5	4	3	1-
(220)	15	20	20	30
(311)	100	100	100	100

values of u. In several cases the difference in the scattering power of the constituent metal ions for arbitrarily chosen wave-length of x-radiation was too small to allow a decision between different arrangements. In that case it was often possible to arrive at the desired result by a special choice of the irradiating wave-length. The scattering power of an element is comparatively low for the characteristic $K\alpha$-radiation of the metal having an atomic number one higher than the scattering metal atom, as a consequence of the proximity of the absorption edge. Thus, the scattering power of Fe is reduced by about 20 percent for the same values of $\sin\theta/\lambda$ when Co $K\alpha$-radiation is used instead of, for instance, Cu $K\alpha$-radiation. Hence, we must replace the usual theoretical scattering factor by the experimental values, which in this case have been determined by Bradley and Hope.[6] In this way it was possible, for instance, to determine the arrangement in samples containing both Cu and Fe which normally would have been impossible to determine.

The following substances were investigated: $MgCr_2O_4$, $NiCr_2O_4$, $CdCr_2O_4$, $CuFe_2O_4$, $ZnFe_2O_4$, $Cu_xZn_{1-x}Fe_2O_4$, $CdFe_2O_4$, $TiZn_2O_4$, $SnZn_2O_4$, $SnCo_2O_4$, $Fe^{2+}Fe^{3+}AlO_4$, $LiAl_5O_8$, and a large number of solid solutions containing these and other spinels.

The following are the results obtained with the simpler spinels.

$MgCr_2O_4$. Radiation Cu $K\alpha$. Lattice dimension $a = 8.312$A. Intensities exclude the arrangement $Cr_8(Mg_8Cr_8)O_{32}$ and point definitely to $Mg_8Cr_{16}O_{32}$, hence all Mg in eightfold position (tetrahedral holes), and all Cr in 16-fold position (octahedral holes). Comparison of experimental and calculated intensities does not permit very accurate conclusions as to the value of u; the calculations were made with differences of $0.5/60$. The best agreement is found for $u = 23/60$ though

[6] A. J. Bradley and R. A. H. Hope, Proc. Roy. Soc. 136, 283 (1932).

also $u = 23.5/60$ cannot be excluded. Hence $u = 0.38_5 \pm 0.01$.

$NiCr_2O_4$. Radiation Cr $K\alpha$. $a = 8.299$A. For the scattering power of Cr for Cr $K\alpha$ a correction was made in view of the vicinity of the absorption edge. Arrangement definitely $Ni_8Cr_{16}O_{32}$. Intensities do not permit a decision between $u = 23/60$ and $u = 23.5/60$, hence $u = 0.38_5$ to 0.39 ± 0.01.

$CdCr_2O_4$. Radiation Cu $K\alpha$. $a = 8.567$A. Arrangement $Cd_8Cr_{16}O_{32}$. Best u value $23/60$ though $23.5/60$ cannot be excluded. Hence $u = 0.38_5 \pm 0.01$.

$CuFe_2O_4$. Radiation Co $K\alpha$. $a = 8.37$A. Very good agreement for inversed spinel arrangement: $Fe_8(Cu_8Fe_8)O_{32}$ with $u = 0.38_0 \pm 0.005$.

$ZnFe_2O_4$. Radiation Co $K\alpha$. $a = 8.416$A. Very good agreement for normal spinel positions: $Zn_8Fe_{16}O_{32}$ with $u = 0.38_0 \pm 0.005$.

$Cu_{0.5}Zn_{0.5}Fe_2O_4$. Radiation Co $K\alpha$. $a = 8.388$A. Arrangement $Zn_4Fe_4(Cu_4Fe_{12})O_{32}$ with $u = 0.380 \pm 0.005$.

$Cu_{0.4}Zn_{0.6}Fe_2O_4$. $a = 8.402$A. Arrangement $Zn_{4.8}Fe_{3.2}(Cu_{3.2}Fe_{12.8})O_{32}$ with $u = 0.380 \pm 0.005$.

It is not possible to distinguish between Cu and Zn. However, the gradual transition between the inversed spinel (copper) and the normal spinel (zinc), with each Zn and Cu keeping its own position, can very well be followed in the gradual change of the intensities as one goes from $CuFe_2O_4$ to $ZnFe_2O_4$. For example, the relative increase of the intensity of (220) or decrease of (111), in comparison with (311), which was a strong reflection arbitrarily set equal to 100 in all films, is shown in Table II.

$CdFe_2O_4$. Arrangement $Cd_8Fe_{16}O_{32}$.

$TiZn_2O_4$. Radiation Cu $K\alpha$. $a = 8.445$A. Arrangement $Zn_8(Ti_8Zn_8)O_{32}$ with $u = 0.380 \pm 0.005$.

$SnZn_2O_4$. Arrangement $Zn_8(Sn_8Zn_8)O_{32}$.

$SnCo_2O_4$. Arrangement $Co_8(Sn_8Co_8)O_{32}$.

$Fe^{2+}Fe^{3+}AlO_4$. Radiation Co $K\alpha$. Best agreement for the arrangement $Fe^{2+}(Al_8Fe_8^{3+})O_{32}$ or $Fe_8^{3+}(Al_8^{3+}+Fe_8^{2+})O_{32}$, with $u = 0.385 \pm 0.01$, though small deviations remain which can be explained by a small percentage of Al in eightfold position (less than 10 percent). The presence of a weak (111) reflection might even suggest that Fe^{2+} is at the 16-fold position, as for small reflection angles the scattering power of Fe^{2+} will be appreciably larger than that of Fe^{3+}.

$LiAl_5O_8$. The x-ray data used in the investigation of this substance were those found in the literature.[7] Of the two possible arrangements, $Al_8(Li_4Al_{12})O_{32}$ or $(Li_4Al_4)Al_{16}O_{32}$, the intensities are definitely in favor of the former, though the best agreement is obtained by assuming that the actual distribution is an intermediate one, with a small contribution of the second, $u = 0.385 \pm 0.01$. Hence, the most probable arrangement approaches the completely random distribution which would correspond to $(Li_{1\ 1/3}Al_{6\ 2/3})$ $(Li_{2\ 2/3}Al_{13\ 1/3})O_{32}$. As this substance is the only one investigated of the interesting type in which $Li^+ + Al^{3+}$ together take the role of two divalent ions, we merely give the results for this compound; in the following sections, which are concerned only with 2-3 and 4-2 spinels, it will be omitted from further consideration.

5. CONSIDERATION OF LATTICE DIMENSION; DISCUSSION

Including the results of Barth and Posnjak[2] (who found normal spinels with a number of Al spinels, inversed spinels for Mg_2TiO_4, Fe_2TiO_4, $MgFe_2O_4$, and $MgIn_2O_4$) and that of Machatschki ($MgGa_2O_4$ intermediate case), we arrive at the following conclusions:

(a) 4-2 spinels are always found in the inversed arrangement, in complete accordance with the lower Coulomb potential thereby realized.

(b) 2-3 spinels are often found in the normal arrangement, again in accordance with expectation on the basis of electrostatic considerations. Thus, all Al and Cr spinels investigated obey this electrostatic rule. The same holds for $ZnFe_2O_4$ and $CdFe_2O_4$. Obvious exceptions, however, are a number of other Fe spinels ($MgFe_2O_4$, $CuFe_2O_4$) and also $MgIn_2O_4$, $MgGa_2O_4$ (partially inversed).

In connection with these conclusions, it would be interesting to have more information as to the behavior of other Fe spinels, such as those containing Mn, Fe, Co, Ni as the divalent ion. Here, however, the difference in scattering power is so small that no information can be obtained from the x-ray intensities. We have investigated, therefore, whether there are regularities in the values of a, the cube edge of the unit cell, for the different spinels. This is shown in Table III, where most data concerning a were derived from the literature; in those cases for which more

[7] E. Kordes, Zeits. f. Krist. 91, 193 (1935).

than one value was found we used an average value.

Comparing all Al spinels, all Cr spinels, and those Fe spinels for which a normal arrangement was established in the present paper (Zn and Cd), it is seen that the lattice dimensions of these spinels run completely parallel to their composition and, apart from small deviations, go in the sequence to be expected from the divalent ionic radii. One finds an increase of 0.235A (average value maximal deviation only 0.015A) in a as one goes from Al to Cr spinels, and an increase of 0.12A as one goes from Cr to normal Fe spinels. This increase, practically independent of the nature of the divalent ion, can easily be understood on the basis of the different sizes of the Al^{3+}, Cr^{3+}, and Fe^{3+} ions, and it is in agreement with the gradual increase of the ionic radii established from more simple oxide structures.

Making the same comparison, but now with the other Fe spinels, we find the same parallelism and again a constant increase of a between Cr and inversed Fe spinels. Now, however, this increase is only 0.04 to 0.06A and, accordingly, on the average is 0.07A less than that found for the two normal Fe spinels (Zn and Cd). Since the Fe spinels of Cu and Mg were found to be inversed spinels, this may tentatively be considered as an indication *that the* Fe *spinels of* Mn, Fe^{2+}, Co, *and* Ni *are also inversed spinels;* simultaneously one can conclude that the Al and Cr spinels for which the normal arrangement was not established by x-ray intensity considerations are actually all normal spinels.

TABLE III. Cube edge a of unit cell for a number of 2–3 spinels XY_2O_4.

$Y^{3+} =$ $r_{Y^{3+}} =$		Al^{3+} 0.57		Cr^{3+} 0.64		Fe^{3+} 0.67
X^{2+}	$r_{X^{2+}}$	a	Δ	a	Δ	a
Ni^{2+}	0.78	8.05	0.25	8.30	0.06	8.36
Cu^{2+}	— *	8.07	—	—	—	8.37
Zn^{2+}	0.83	8.07	0.23	8.30	0.12	8.42
Mg^{2+}	0.78	8.07	0.24	8.31	0.05	8.36
Co^{2+}	0.82	8.08	0.24	8.32	0.04	8.36
Fe^{2+}	0.83	8.12	0.22	8.34	0.05	8.39
Mn^{2+}	0.91	8.26	0.23	8.49	(0.06)	(8.55)**
Cd^{2+}	0.97	—	—	8.57	0.12	8.69

* The value of $r_{Cu^{2+}} = 1.01$ found in many tables in the literature is obviously incorrect.
** The values for $MnFe_2O_4$ in the literature vary considerably, obviously as a consequence of differences in the valency states of Mn and perhaps also Fe.

TABLE IV.

Solid solutions of:			Formula
$Fe^{3+}(Fe^{2+}Fe^{3+})O_4$ and $Fe^{2+}(AlAl)O_4$			$Fe^{3+}(Fe^{2+}Al)O_4$
Fe	(Cu | Fe)O_4 and Zn	(FeFe)O_4	$(Fe_{1/2}Zn_{1/2})(Fe_{3/2}Cu_{1/2})O_4$
Fe	(Mg | Fe)O_4 and Mg	(CrCr)O_4	Fe (Mg Cr)O_4
Zn	(Fe | Fe)O_4 and Zn	(CrCr)O_4	Zn (Fe Cr)O_4
Zn	(Ti | Zn)O_4 and Fe	(MgFe)O_4	Zn (FeMg$_{1/2}$Ti$_{1/2}$)O_4
Mg	(Ti | Mg)O_4 and Fe	(MgFe)O_4	Fe (Ti$_{1/2}$Mg$_{3/2}$)O_4
Zn	(Fe | Fe)O_4 and $\begin{cases}Fe & (Fe_{1\,2/3})O_4 \\ =\gamma\cdot Fe_2O_3\end{cases}$		$(Zn_{1/2}Fe_{1/2})Fe_{1\,5/6}O_4$

Hence, we arrive at the conclusion that, contrary to electrostatic rules, all Fe spinels are inversed spinels, except those of Zn and Cd. The comparison of lattice dimensions is obviously not so conclusive as a direct derivation from the intensities, but our conclusions will be seen to be in complete accordance with other physical properties of the Fe spinels.

The shrinkage of about 0.07A found above for an inversed spinel in comparison with the corresponding normal arrangement must obviously be explained by a more dense structure in the former case. Actually, the arrangement which is electrostatically most stable for a 2-3 spinel, where the comparatively large divalent ions go into the smallest interstices, is not the most favorable one from a geometrical point of view, and a certain contraction of the whole lattice can reasonably be expected if, for some reason, the inversed spinel becomes the most stable configuration (the corresponding contraction is itself a factor in favor of the inversed configuration, but it is so small that its effect is negligible in comparison with the difference between the two Madelung potentials).

Since it is thus made plausible that all Fe spinels, except Zn and Cd, have the inversed cation spinel arrangement, the explanation of this abnormal behavior must obviously be found in the circumstance that these structures cannot be completely understood from a purely ionic point of view. Comparatively important homopolar contributions to the bond must be considered. Apparently the Fe^{3+} ion shows a certain preference for such a homopolar contribution if surrounded by 4 O^{2-} ions, and the same must be true for In^{3+} and Ga^{3+}. The fact that $ZnFe_2O_4$ and $CdFe_2O_4$ show again a normal behavior can

then easily be explained, as the Fe^{3+} will find in Cd^{2+} and Zn^{2+} a competitor for the tetrahedral interstices. The preference of Zn^{2+} and Cd^{2+} for a tetrahedral surrounding is well known; e.g., in ZnO, ZnS, Zn_2SiO_4, CdS, CdSe; and has been attributed to homopolar contributions to the chemical bond.[8] Zn^{2+} and Cd^{2+} have a filled d-band, and the distance between the d-band and the unoccupied s-band is only small; hence there is a possibility of hybridization of 3 d-electrons and 1 s-electron, forming 4 bonds in tetrahedral directions (sp^3 and d^3s form a hybrid with 4 equivalent tetrahedral bonds[9]). The same explanation would probably hold for In^{3+} and Ga^{3+} which have the same electronic configuration as Cd^{2+} and Zn^{2+}.

The general principles underlying the building up of oxidic spinels can thus be summarized as follows:

1. Trivalent and quadrivalent ions, in accordance with electrostatic rules, preferably occupy the octahedral interstices of the 16-fold position.
2. Exceptions are, however, certain trivalent ions: Fe^{3+}, In^{3+}, Ga^{3+} which show a preference for the tetrahedral interstices of the eightfold position.
3. Some divalent ions, Zn^{2+} and Cd^{2+} show a special preference for occupying the tetrahedral position, which can counteract the tendency mentioned under 2.

These general principles appear to hold their validity in more complicated spinels. The application of these rules may be illustrated with the aid of a few examples given in Table IV.*

The atomic configuration in all these cases has been confirmed by an analysis of the intensities of the x-ray diagram (for the first two cases this has already been given in Section 4 of the present paper) and other means of investigation.

The crystallographic points of view developed here will be used in a series of subsequent papers in which a study of various physical properties of many complicated spinels will be reported.

[8] F. A. Kröger, Thesis, Amsterdam, p. 104 (1940).
[9] G. E. Kimball, J. Chem. Phys. 8, 188 (1940).
* In this and the following paper we use a notation which is slightly different from that in mineralogical work. Fe(MgFe)O_4, for instance, expresses that the octahedral position contains together 1 Mg and 1 Fe for each Fe in the tetrahedral position.