

## ELECTRONIC STRUCTURES OF THE SPINELS

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## ABSTRACT

**Crystal structure of the spinels.**—(1) The most probable *arrangement of valence electrons* is that in which there is a pair on or near each centerline between adjacent atoms. The valence shell of each oxygen and divalent metal atom is a tetrahedron of electronpairs; that of each trivalent metal atom is an octahedron of pairs. (2) *The distances between adjacent atomic centers* are calculated (from the densities) and the *positions of the oxygen centers* determined in crystals of  $ZnAl_2O_4$ ,  $ZnCr_2O_4$ ,  $ZnFe_2O_4$ ,  $MgAl_2O_4$ ,  $MgCr_2O_4$ ,  $MnAl_2O_4$ ,  $MnCr_2O_4$ ,  $CdCr_2O_4$ , and  $FeFe_2O_4$  by means of the assumptions that the Zn–O distance in the first three equals that in ZnO and that corresponding interatomic distances in different spinels are equal. (3) *Densities of  $MgFe_2O_4$  and  $MnFe_2O_4$*  are computed to be 4.47 and 4.90 gm/cm<sup>3</sup>, respectively, on the basis of these same assumption. (4) *Chemical formulæ.* There is no physical basis in the arrangement of atoms and electrons for the formulæ  $R''O \cdot R_2'''O_3$  or  $R''(R'''O_2)_2$ .

**Atomic radii of divalent Zn, Fe, Mg, Mn, and Cd and of trivalent Al, Cr, and Fe** are computed (Table III.), assuming the radius of oxygen to be 0.65 Å.

**Association of ferromagnetism with a particular distribution of electrons,** such as a concentration of triplets in the same end of the kernel of each trivalent iron atom (in a fully magnetized crystal), is suggested.

**Arrangement of the atoms.**—The group of minerals known as the spinels, the general formula of which is  $R''R_2'''O_4$ ,  $R''$  being a divalent metal (Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb) and  $R'''$  a trivalent metal (Al, Cr, Fe, Co), has been studied by means of x-rays by W. H. Bragg,<sup>1</sup> Nishikawa,<sup>2</sup> and Vegard.<sup>3</sup> According to their results, the  $R''$  atoms are at the points of a "diamond type" of structure (Fig. 1), the other atoms being distributed around these as indicated in Figs. 2 and 3. Each  $R''$  atom is surrounded by four equidistant, tetrahedrally disposed oxygen atoms. Around each  $R'''$  atom are six oxygen atoms, at the corners of an octahedron. Each oxygen atom is surrounded by three equidistant  $R'''$  atoms and one  $R''$  atom.

**Arrangement of electrons.**—According to the Lewis theory of atomic structure<sup>4</sup> and the author's extension of it to the heavy elements,<sup>5</sup> there

<sup>1</sup> W. H. Bragg, *Phil. Mag.* **30**, 305 (1915).

<sup>2</sup> Nishikawa, *Math. Phys. Soc. Tokyo* **8**, 199 (1915).

<sup>3</sup> Vegard, *Phil. Mag.* **32**, 65 (1916).

<sup>4</sup> G. N. Lewis, *J. Am. Chem. Soc.* **38**, 762 (1916).

<sup>5</sup> Huggins, *Science* **55**, 459 (1922); *J. Phys. Chem.* **26**, 601 (1922).

are six valence electrons per oxygen atom, two per  $R''$  atom, and three per  $R'''$  atom, a total of 32 per "molecule." This is exactly the number required to form a tetrahedron of electronpairs, a stable "group of eight" or "octet," around each oxygen kernel. Since in every other oxygen-containing crystal studied there is a similar tetrahedron of pairs

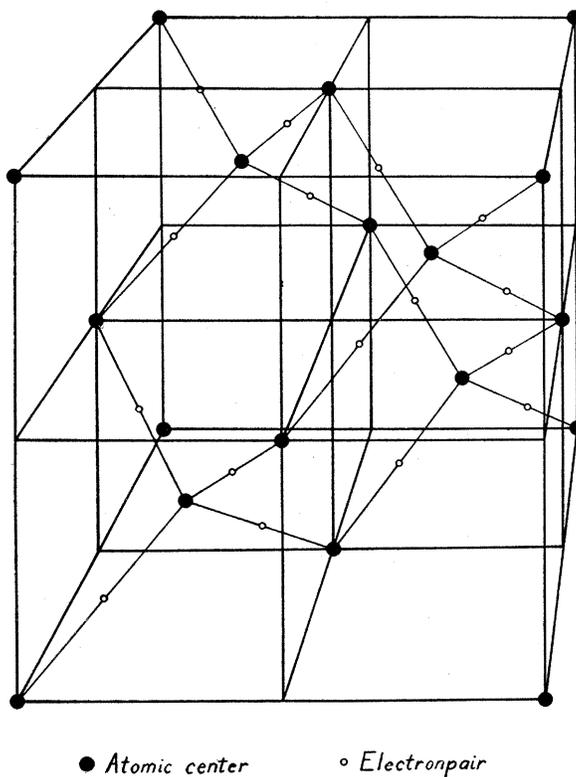


Fig. 1. Arrangement of atomic centers and valence electronpairs in the unit cube of the diamond crystal.

around each oxygen kernel, we may assume that to be the case in these crystals, if such an assumption leads to a structure which is otherwise reasonable. These valence tetrahedra may be oriented in either of three ways in accord with the threefold symmetry about the  $R''-O$  centerlines. Two of these orientations give structures quite unlike those which other crystals have been found to possess. If the third is correct, each electronpair is on (or very near) the centerline between an oxygen and one of the four surrounding atoms. Such an arrangement is in full accord with the author's theory, which has been fully verified in other crystals,<sup>1</sup>

<sup>1</sup> Huggins, J. Am. Chem. Soc. **44**, 1841 (1922); Phys. Rev. **19**, pp. 346, 354, 363, 369 (1922); **21**, 379 (1923).

that the valence electrons tend to be in pairs on or near the centerlines between adjacent atoms<sup>1</sup> and opposite the faces of the polyhedra formed by the outermost electronpairs or triplets in the kernels of the atoms thus joined.<sup>2</sup>

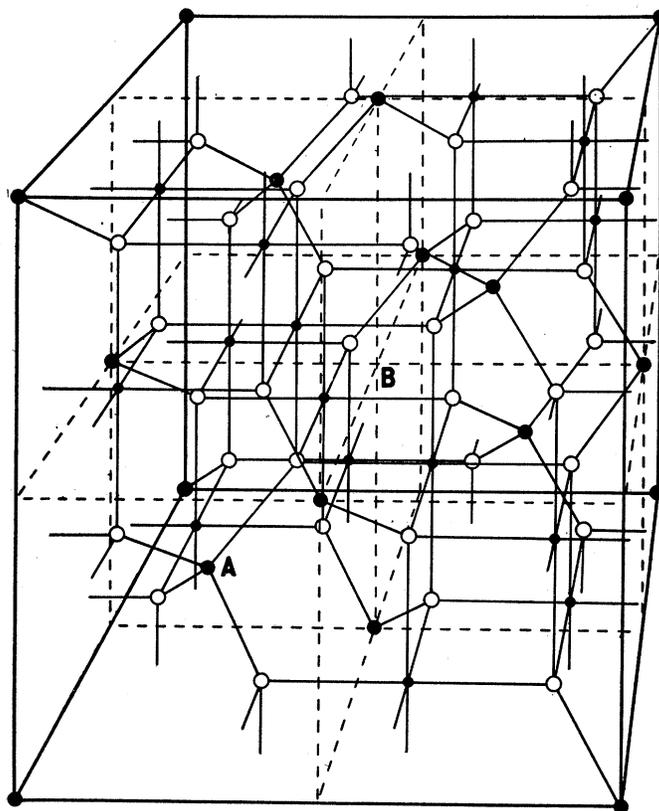


Fig. 2. Arrangement of atomic centers in a unit cube of a spinel crystal.  
 ●R'', ●R''', ○O.

The probable atomic formulæ of the metals concerned, according to the author's theory, are given in Table I. The first parenthesis in each represents the nucleus and each succeeding parenthesis an atomic shell, in order from the nucleus out, the number of electrongs and the number of electrons in each group being given for each shell except the last or valence shell.<sup>3</sup> The outermost kernel shell in each of the

<sup>1</sup> Exceptions to this tendency are found in the alkali halides, the alkaline earth oxides and sulfides, the metals, and a few other crystals.

<sup>2</sup> In an electropositive atom a kernel tetrahedron is sometimes surrounded by a valence *octahedron*. Cf. Huggins, Phys. Rev. **19**, 354 (1922).

<sup>3</sup> For the derivation of these structures and the further interpretation of the formulæ, see Huggins, J. Phys. Chem. **26**, 601 (1922).

divalent atoms is a tetrahedron, and the valence shell is a tetrahedron (one pair opposite each face of the kernel shell), if the structure assumed in the preceding paragraph is correct. The outermost kernel shell of each trivalent atom is a (distorted) cube or a tetrahedron; and the valence shell, in these crystals, is an octahedron.

TABLE I

Mg	(+ 12)(2 × 1)(4 × 2)(2)
Mn	(+ 25)(2 × 1)(1 × 3 + 5 × 2)(4 × 2)(2)
Fe	(+ 26)(2 × 1)(2 × 3 + 4 × 2)(4 × 2)(2)
Co	(+ 27)(2 × 1)(3 × 3 + 3 × 2)(4 × 2)(2)
Ni	(+ 28)(2 × 1)(4 × 3 + 2 × 2)(4 × 2)(2)
Cu	(+ 29)(2 × 1)(5 × 3 + 1 × 2)(4 × 2)(2)
Zn	(+ 30)(2 × 1)(6 × 3)(4 × 2)(2)
Cd	(+ 48)(2 × 1)(8 × 3)(6 × 2)(4 × 2)(2)
Pb	(+ 82)(2 × 1)(8 × 3)(6 × 3)(8 × 2)(6 × 2)(4 × 2)(2)
Al	(+ 13)(2 × 1)(4 × 2)(3)
Cr	(+ 24)(2 × 1)(3 × 3 + 5 × 2)(3)
Fe	(+ 26)(2 × 1)(5 × 3 + 3 × 2)(3) or (+ 26)(2 × 1)(1 × 3 + 5 × 2)(4 × 2)(3)
Co	(+ 27)(2 × 1)(6 × 3 + 2 × 2)(3) or (+ 27)(2 × 1)(2 × 3 + 4 × 2)(4 × 2)(3)

**The positions of the oxygen centers.**—With the atomic marshalling found for the spinels, it is impossible that the tetrahedron of electron-pairs around each oxygen kernel should be a *regular* tetrahedron, and at the same time that the octahedron of pairs around each R''' kernel should be a *regular* octahedron. If the former were the case, the R''-O distance would be just two thirds *AB* (Fig. 3); if the latter, it would be

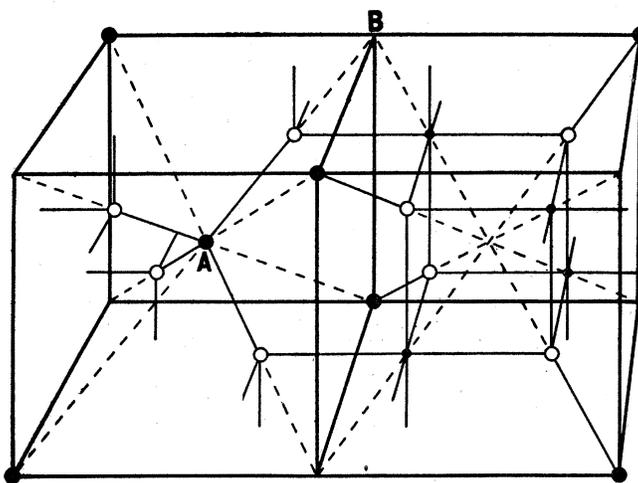


Fig. 3. Arrangement of atomic centers within two of the eighth-unit cubes of a spinel crystal. ●R'', ●R''', ○O.

exactly half  $AB$ <sup>1</sup> (assuming throughout that the valence pairs are *on the centerlines* between atoms). Actually we should expect  $R''-O$  to be intermediate between  $0.500 AB$  and  $0.667 AB$ , and we shall see that this is the case. For simplicity in making the figures, perfect octahedra have been assumed,  $R''-O$  being taken equal to one half  $AB$ .

Experimentally, by considering the relative intensities of the different orders of x-ray reflection from various crystal faces, Bragg found that in magnetite,  $FeFe_2O_4$ , the oxygen centers are *roughly* half-way between cube centers and cube corners. In spinel,  $MgAl_2O_4$ , his experiments indicated that the  $R''-O$  distance is slightly greater. Nishikawa estimated  $R''-O/AB$  as about 0.54 in spinel and between 0.50 and 0.53 in magnetite.

It will now be shown how the oxygen positions can be more accurately obtained in an entirely different way.

In a crystal of  $ZnFe_2O_4$ ,  $ZnAl_2O_4$ , or  $ZnCr_2O_4$ , each zinc atom is bonded by single bonds to four tetrahedrally disposed oxygen atoms, and each oxygen atom to four metal atoms, at tetrahedron corners. This disposition is essentially the same as that in a crystal of  $ZnO$ , hence we may be quite sure that the distance between zinc and oxygen centers is practically the same in each of these crystals. If we assume this, the position of each oxygen center relative to the surrounding atoms is determined. From the dimensions of the unit cells calculated from the densities, the  $Cr-O$ ,  $Al-O$  and  $Fe-O$  distances may then be easily obtained.

Then, assuming the  $Cr-O$  distance to be the same in the chromites of magnesium, manganese, and cadmium as in  $ZnCr_2O_4$ , and the  $Fe'''-O$  distance to be the same in  $FeFe_2O_4$  as in  $ZnFe_2O_4$ , the  $R''-O$  distances in these substances are similarly found (see Table II.). In the magnesium and manganese aluminates, we might either take the  $Al-O$  distances calculated for  $ZnAl_2O_4$ , and from it calculate the  $R''-O$  distances, or we might assume the  $R''-O$  values calculated for the corresponding chromates, and from them calculate the distance between  $Al$  and  $O$  centers. The latter procedure is probably the better of the two, since the  $Al-O$  distances computed through the  $Mg$  and  $Mn$  compounds check much more closely with each other than with that computed for  $ZnAl_2O_4$ , and since the density given for the latter compound is probably not very accurate. (If the  $Al-O$  distance in  $ZnAl_2O_4$  were 1.915 Å, as calculated for  $MnAl_2O_4$ ,  $Zn-O$  being 1.960 Å, the density would be 4.550 rather than 4.58 gm/cm<sup>3</sup>.)

<sup>1</sup>Symmetry considerations place the centers of the  $R'''$  atoms on the small cube diagonals at about half the distance between the cube centers and the cube corners. They would be *exactly* in these positions if their kernels possessed cubic or octahedral symmetry. For our present purposes we shall assume them to be so situated.

TABLE II

Formula	Density <sup>1</sup> (gm/cm <sup>3</sup> )	Edge of unit cube	R''-O	R'''-O	R''-O/AB
ZnCr <sub>2</sub> O <sub>4</sub> .....	5.30	8.34Å	1.96*A	2.00A	.54
ZnAl <sub>2</sub> O <sub>4</sub> .....	4.58	8.09	1.96*	1.89	.56
ZnFe <sub>2</sub> O <sub>4</sub> .....	5.33	8.42	1.96*	2.03	.54
MgCr <sub>2</sub> O <sub>4</sub> .....	4.415	8.32	1.94	2.00*	.54
MgAl <sub>2</sub> O <sub>4</sub> .....	3.57	8.08	1.94*	1.92	.56
MgAl <sub>2</sub> O <sub>4</sub> .....	3.59 <sup>2</sup>	8.06 <sup>2</sup>	1.94*	1.91	.56
MgFe <sub>2</sub> O <sub>4</sub> .....	4.47 <sup>3</sup>	8.39 <sup>3</sup>	1.94*	2.03*	.54
MnCr <sub>2</sub> O <sub>4</sub> .....	4.87	8.45	2.04	2.00*	.56
MnAl <sub>2</sub> O <sub>4</sub> .....	4.12	8.22	2.04*	1.91	.57
MnFe <sub>2</sub> O <sub>4</sub> .....	4.90 <sup>3</sup>	8.53 <sup>3</sup>	2.04*	2.03*	.55
CdCr <sub>2</sub> O <sub>4</sub> .....	5.79	8.61	2.16	2.00*	.58
FeFe <sub>2</sub> O <sub>4</sub> .....	5.23	8.36	1.92	2.03*	.53
FeFe <sub>2</sub> O <sub>4</sub> .....	5.16 <sup>2</sup>	8.40 <sup>2</sup>	1.95	2.03*	.54

\* Assumed.

Good density data for the ferrites of magnesium and manganese are not available. However, by assuming the interatomic distances in these compounds to be the same as the corresponding distances in other spinels, we can compute them to be 4.47 and 4.90 gm/cm<sup>3</sup>, respectively.

In the last column of Table II. are given the values of the ratio R''-O/AB for each of these crystals. This ratio is in each case between one half and two thirds (as was predicted before the computation was made).

**Atomic radii.**—In Table III. are given the atomic radii of the various elements present in these crystals, calculated from the R-O distances on the assumption that the oxygen radius (the distance from atomic center to valence electronpair) is 0.65 Å.<sup>4</sup> Should this value prove to be lower than the true value, the radii calculated for the other elements in the

TABLE III

*Atomic Radii*

(O <sup>+6</sup> )(4 × 2)(4 R).....	0.65Å
(Zn <sup>+2</sup> )(4 × 2)(4 O <sup>+6</sup> ).....	1.31
(Fe <sup>+2</sup> )(4 × 2)(4 O <sup>+6</sup> ).....	1.27-1.30
(Mg <sup>+2</sup> )(4 × 2)(4 O <sup>+6</sup> ).....	1.29
(Mn <sup>+2</sup> )(4 × 2)(4 O <sup>+6</sup> ).....	1.39
(Cd <sup>+2</sup> )(4 × 2)(4 O <sup>+6</sup> ).....	1.51
(Fe <sup>+3</sup> )(6 × 2)(6 O <sup>+6</sup> ).....	1.38
(Al <sup>+3</sup> )(6 × 2)(6 O <sup>+6</sup> ).....	1.26
(Cr <sup>+3</sup> )(6 × 2)(6 O <sup>+6</sup> ).....	1.35

<sup>1</sup> From Groth's *Chemische Krystallographie*, Vol. II. (Engelmann, Leipzig, 1908), except as otherwise noted.

<sup>2</sup> Calculated from the "chamber angles" given by W. H. Bragg and W. L. Bragg in "X Rays and Crystal Structure," G. Bell and Sons, London, 1916, p. 172.

<sup>3</sup> Calculated from the assumed R''-O and R'''-O distances.

<sup>4</sup> Huggins, *Phys. Rev.* **21**, 205 (1923); W. L. Bragg, *Phil. Mag.* **40**, 169 (1920), also gives this value for the oxygen radius.

table are correspondingly higher than the true distances, and vice versa. The accuracy of these radii values, except those for oxygen and zinc, depends largely on the accuracy of the values of the densities used, hence if any of the latter are later found to be much in error, the radii calculated therefrom will be correspondingly in error.

It is worthy of note that the radius of the iron atom is by no means the same when the kernel has a net charge of  $+2$  and is surrounded by *four* electronpairs as when the kernel has a charge of  $+3$  and is surrounded by *six* valence pairs.

**The correct formula for the spinels.**—In the arrangement pictured in Figs. 2 and 3 and described in the preceding pages, the atoms are obviously not divided into  $R''O$  and  $R_2'''O_3$  groups, nor into  $R''$  and  $R'''O_2$  ions. The whole crystal is a single molecule, each atom being held by single bonds to those adjacent. Hence the empirical formula  $R''R_2'''O_4$  is the only one which correctly represents the structure of these substances in the crystalline state.

**Ferromagnetism.**—The electronic structures of these crystals and of their component atoms suggest a possible partial explanation of the cause of ferromagnetism.

Atoms of chromium, manganese, iron, cobalt, and nickel each possess a kernel shell, according to the author's theory, containing *both* pairs and triplets of electrons. In general, we should not expect electrons to shift from one electrongroup to another (thereby changing the distribution of pairs and triplets) in an atom in a crystal, but in some crystals this might be possible. Ferromagnetism in iron, magnetite, etc., then, might be the result of a concentration of electron *triplets* in the *same* end of each atomic kernel (or at least in a large number of them), somewhat as shown

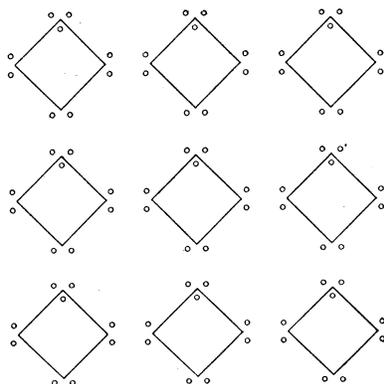


Fig. 4. Illustrating the electron arrangement in a hypothetical fully-magnetized two-dimensional crystal.

in Fig. 4 for an imaginary two-dimensional crystal. In magnetite it is probably the trivalent atoms which can assume this regular orientation, for the other ferrites (of Mg, Mn, Co, Ni, Cu, Zn, Pb) are ferro-magnetic, while ferrous aluminate and chromite are not so.

Why an unsymmetrical distribution of electrons in an atom should give it magnetic properties is not now evident. The writer hopes at a later date, however, to be able to present a more complete theory.

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