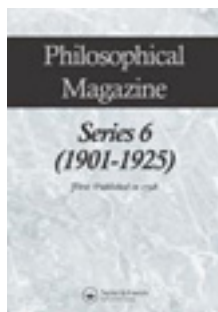


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XXX. The structure of the spinel group of crystals

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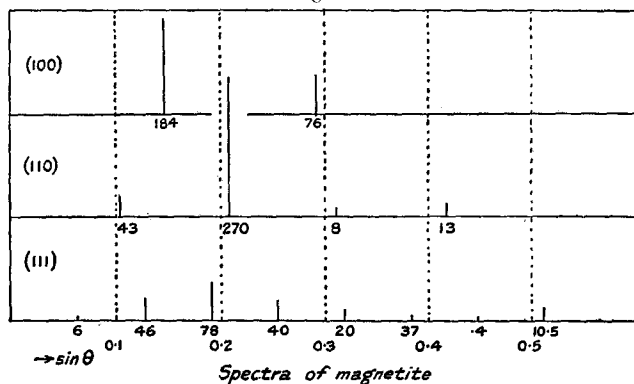
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XXX. *The Structure of the Spinel Group of Crystals.* By
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Physics in the University of Leeds* *.

THE spinel group of crystals is placed by crystallographers in their Class 32, the members of which are cubic and possess the highest possible number of symmetries. The composition is given by the formula $R''R_2'''O_4$, where the divalent metal R'' may be Mg, Fe, Zn, or Mn, and the trivalent metal R''' may be Fe, Mn, Cr, or Al. It is very interesting that a somewhat complicated composition should be associated with such complete crystalline symmetry.

Magnetite, $FeFe_2O_4$, is a member of this group. Its X-ray spectra are shown in fig. 1, the same method of

Fig. 1.



representation being used as in previous cases. The heights of the vertical lines represent the intensities of the various orders of reflexion by the three most important planes, and their positions represent the sines of the glancing angles of reflexion. The X-ray used is the α -ray of rhodium for which $\lambda = 0.614 \text{ \AA.U.}$

We first find the spacings of the three sets of planes. According to the usual formula, $\lambda = 2d \sin \theta$. For the (100) planes $\theta = 8^\circ 30'$.

$$\text{Hence } 2d_{100} = \frac{0.614}{0.1478} = 4.15 \text{ \AA.U.}$$

In the same way $2d_{110} = 5.88 \text{ \AA.U.}$, and $2d_{111} = 9.60 \text{ \AA.U.}$

We now try to connect these values with the molecular dimensions of the crystal.

* Communicated by the Author.

Let a be the length of the edge of the cube containing one molecule, that is to say the volume per molecule put into cubic form. The specific gravity of the crystal is 5.2 approximately, its molecular weight is $3 \times 56 + 4 \times 16 = 232$, and the weight of a hydrogen atom is 1.64×10^{-24} .

$$\begin{aligned} \text{Hence} \quad a^3 \times 5.2 &= 232 \times 1.64 \times 10^{-24}, \\ a^3 &= 73.2 \times 10^{-24}, \\ a &= 4.18 \text{ \AA.U.} \end{aligned}$$

The length of a face diagonal of such a cube is 5.92 \AA.U. and the length of the cube diagonal is 7.25 \AA.U. A cube containing eight molecules has twice these dimensions.

There is a clear connexion between these dimensions and the spacings of the planes which we have calculated. We may state it simply in the following form:—

The spacing of the (100) planes is a quarter of the edge of a cube containing eight molecules, the spacing of the (110) planes is a quarter of the face diagonal of such a cube, and the spacing of the (111) planes is a third of the cube diagonal.

Now this is exactly what has already been found to be true of the diamond, atoms of carbon replacing molecules of Fe_3O_4^* . We conclude, therefore, that magnetite has fundamentally the same structure as diamond, a molecule in the magnetite corresponding to an atom in the diamond.

It has been suggested by Barlow (Proc. Roy. Soc. xci. p. 1) that such arguments as this are ambiguous, and that atoms lying on any of the cubic space lattices may be shifted in a manner which he describes without the fact being betrayed by the X-ray spectrometer. This is not the case, however. The moves which he describes will, amongst other things, introduce a periodicity into the spacings of the (110) planes which is twice as great as before. If such a periodicity existed, it would be detected at once by the existence of a spectrum at half the normal glancing angle of the first order.

The structure described above, so long as each molecule is represented by a point, has all the full symmetries of Class 32.

We have now to place the atoms in the molecule: in doing which we are guided by two requirements.

- (1) The symmetry must not be degraded.
- (2) The relative intensities of the spectra of different orders must be explained.

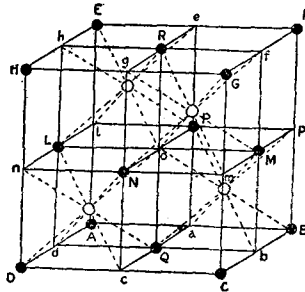
* 'X-rays and Crystal Structure' (G. Bell and Sons, 1915), pp. 102-6.

We begin with the oxygen atoms, of which there are four. In order to maintain the trigonal symmetries these must lie at the corners of a regular tetrahedron, so oriented that the lines drawn from the centre to the corners of the tetrahedron are parallel to the four diagonals of the crystal cube.

Such an arrangement does not interfere with the symmetries about the (100) and (110) planes, as may be seen in the following way.

Consider first the case of the diamond, the structure of which is shown in fig. 2 (*loc. cit.* p. 100). The black circles

Fig. 2.



and white circles both represent carbon atoms, but the blacks and whites can be considered separately as each forming face-centred lattices. They can be derived from one another by a shift along a cube diagonal equal to one quarter of the length of that diagonal. The symmetry about the plane *egca* is not an absolute mirror symmetry; but if all that is on the right of that plane is reflected in it and then shifted by an amount and in a direction represented for example by a move from D half way to *o*, the reflected right coincides absolutely with the left. White circles slip into the places of black circles, but since both represent carbon atoms no difference is made.

Suppose now that the oxygen tetrahedra take the place of the carbon atoms and are arranged, as already described, so that the four perpendiculars from the corners on the faces are parallel to the four cube diagonals. There are two ways of making this arrangement. We may describe them by saying that the coordinates of the four corners referred to rectangular axes are in one case (111) (1,-1,-1) (-1,1,-1) (-1,-1,1), in the other (-1,-1,-1) (-1,1,1) (1,-1,1) (1,1,-1).

Two tetrahedra so arranged are the reflexions of each other in the planes (*xy*), (*yz*), or (*zx*).

Let the carbon atoms of one face-centred lattice be replaced by oxygen tetrahedra of one orientation, and the atoms of the other lattice by the other orientation. It then follows that when the process of reflexion and shifting is carried out as in the case of the diamond, we still obtain the same absolute coincidence. From the crystallographic point of view the symmetry about the (100) plane is complete.

As regards the (110) planes the introduction of the oxygen tetrahedra in place of the carbon atoms does not disturb the simple mirror symmetry which already exists. Any (110) plane passing through a tetrahedron contains some one edge and bisects the opposite edge at right angles, thus dividing it into two halves which are the reflexions of each other in the plane.

A tetrahedron of one kind does *not* reflect into a tetrahedron of the other kind over a (111) plane, but the crystal of course possesses no symmetry of that kind; so the introduction of tetrahedra creates no difficulty.

Thus all the symmetries are maintained in full.

Next consider the effects of the substitution on the spectra.

As regards the (100) planes the spacing in the case of the diamond is one quarter of the edge of the cube shown in fig. 2, a cube which contains a volume associated with eight atoms of carbon. The (100) planes contain alternately all blacks and all whites; and when both blacks and whites are carbon atoms they are necessarily exactly similar. When the blacks represent oxygen tetrahedra of the one orientation and the whites tetrahedra of the other, the planes are still effectively identical. A (100) plane divides a tetrahedron so that two oxygen atoms lie on each side of it. All four are at the same distance from the plane, though the pair on one side is not the reflexion of the pair on the other. Each (100) plane of carbon atoms becomes, therefore, a pair of oxygen planes, and whether the original plane contained blacks or whites these sets of two are indistinguishable from an X-ray point of view. If they were not we should have a new spacing double as great as the old, and the (100) spectra would be interleaved by new ones bisecting the spaces between those of the diamond. We have nothing of this sort to account for, and the tetrahedra therefore still satisfy the conditions required.

As regards the (110) planes no difficulty arises because each (110) plane contains blacks and whites in equal numbers, and the spacing of the (110) planes does not

depend on whether the blacks and whites have the same or different significance.

As regards the (111) planes, the spacing in the case of the diamond (*loc. cit.* p. 100) is the distance from one plane containing blacks only to the next that contains blacks only; the planes containing only whites lie between those containing blacks and divide the spacings of the latter in the ratio 1 to 3. Whether or not the blacks and whites represent the same things again makes no difference in the spacings. It makes a difference in the intensities, of course: there is no second order spectrum in the diamond because the blacks and whites represent the same carbon atoms and there is perfect interference (*loc. cit.* p. 103). In zinc-blende they do not, and the second (111) spectrum is only partially destroyed (*loc. cit.* p. 98). In the present case the blacks and whites do not represent the same thing as regards the (111) planes, and so the second (111) spectrum remains as in the case of zinc-blende; but we are coming to this point presently.

Thus the replacement of the carbon atoms by oxygen tetrahedra does not interfere with the spacings of the (100) (110) and (111) planes, and we still have them of the same description as those of the diamond, which is in agreement with our experimental results. The placing of the oxygen atoms has been completed satisfactorily. The *size* of the tetrahedron remains undetermined as yet.

Let us next consider the iron atoms. We have three, of which chemical considerations would distinguish one as divalent from the other two as trivalent.

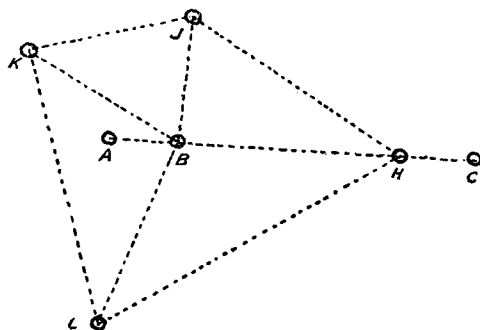
Symmetry considerations are in agreement with such a division. It is not possible to place three atoms round a point so as to have all the symmetries required. We may increase the three to six, provided that we so place each iron atom that it is shared equally by two oxygen tetrahedra, and that each oxygen tetrahedron has shares in four iron atoms. It does not seem possible to do this; nor do extensions of the number to nine, twelve, and so on seem to offer a solution. In any case, such a disposition would make no difference between the divalent and trivalent atoms. In the spinel $MgAl_2O_4$ the magnesium atoms must surely be placed in some different way to the aluminium or else we should, in securing the trigonal symmetries, be obliged to assume that Mg and Al behave alike to the X-rays, which would be contrary to all our experience.

Let us, therefore, take the divalent and trivalent irons separately. The most simple and obvious place for the single

divalent iron atom is the centre of the oxygen tetrahedron. It might of course be multiplied by four, provided each was placed at equal distances from four oxygen tetrahedra and each such tetrahedron had shares in four iron atoms; but this comes to the same thing as the first suggestion, since, owing to the peculiar diamond structure, a point which is equally distant from four oxygen tetrahedra is itself the centre of a tetrahedron.

We have two iron atoms left. These cannot be assigned entirely to a single tetrahedron so as to have the symmetries required. But if they are increased to four, each being placed on one of the four perpendiculars from the corners of the tetrahedron on the opposite faces, and halfway between two tetrahedra so as to be shared equally by them, every condition of symmetry and spacing is fulfilled, for it has already been shown that a properly oriented tetrahedron, such as that on which the trivalent atoms now lie, may be substituted for a single point centre without degrading the symmetry or increasing the spacings. We conclude that this is the real position of the trivalent atoms, and the structure is complete, except as regards (1) a knowledge of the dimensions of the tetrahedron and the determining whether two neighbouring tetrahedra point towards or away from each other, (2) a choice between two alternative positions of the iron atom which we will discuss immediately.

Fig. 3 a.



Arrangement of atoms on diamond. ABHC trigonal axis.

$$AB = 1.52 \text{ \AA.U.} \quad BH = 4.56 \text{ \AA.U.}$$

A very good way to realize the stage we have reached is to consider a small portion of the crystal consisting principally of atoms lying along a trigonal axis. Fig. 3 a shows four such atoms of carbon in the case of the diamond, viz., A, B,

H, and C. J, K, and L are the three other atoms which lie at the same distance from B as H does. H, J, K, and L form a regular tetrahedron. The length of AB is 1.52 \AA.U. , and of BH 4.6 \AA.U. , being three times as large as AB. The (111) spacing is not shown directly in the figure, but is four thirds of AB: a glance at the photograph of the model shown in 'X-rays and Crystal Structure,' p. 107, will make this clear.

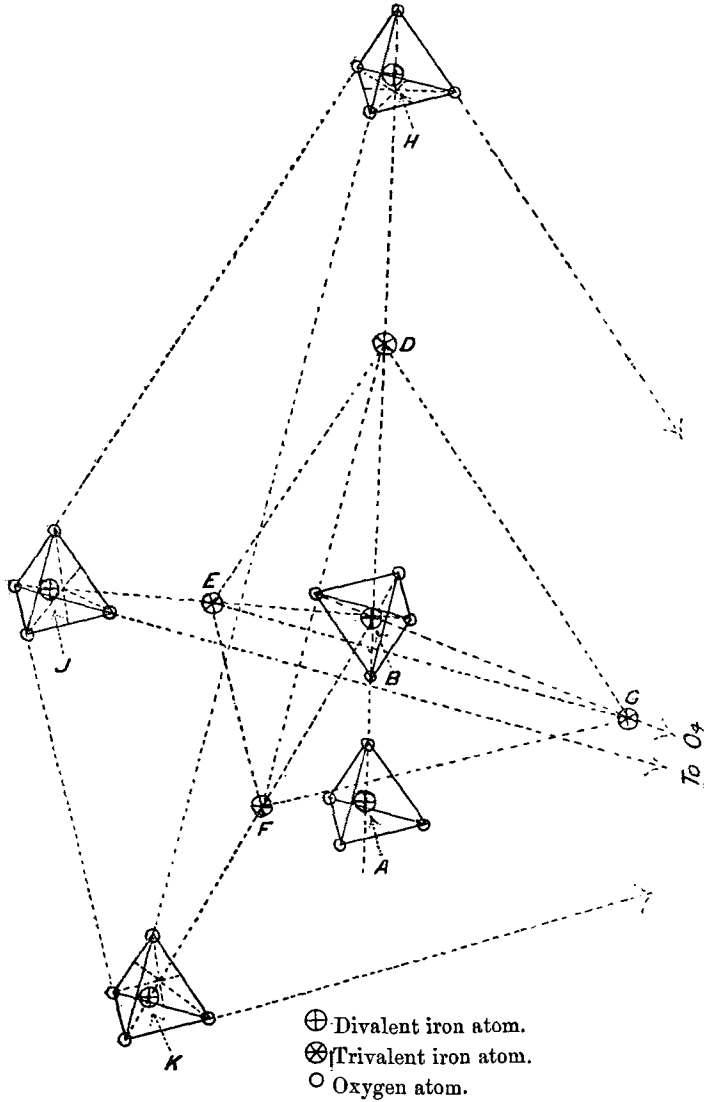
In magnetite the distance AB becomes 3.60 \AA.U. , and BD 10.80 \AA.U. In fig. 3*b* divalent iron atoms have replaced the carbon atoms at A, B, H, J, and K; L is not shown. The oxygen tetrahedra are shown, and it will be observed that there are two orientations, A, H, J, and K being of one description and B of the other. The former replace atoms belonging to one of the face-centred lattices of the diamond, the latter corresponds to the other. So far as our arguments have gone, the *size* of the tetrahedron has not entered into consideration: it might be of any size, but is drawn small enough to be clear of other atoms. The structure seems easier to grasp when this is done. We shall come presently to arguments which relate to the *size*, but they are based on quite new considerations. We may anticipate so far as to say that the oxygen tetrahedron is so much larger than it is drawn in the figure that it takes in five divalent iron atoms instead of one*. Probably it is not the same size in all the crystals of the spinel group.

Trivalent iron atoms are shown at D, E, F, and G. It will be observed that the positions of the divalent and trivalent atoms are essentially different. B lies inside a tetrahedron, D lies between the bases of two tetrahedra and has connexions with six oxygen atoms, whereas B has relation to four. This difference is quite independent of the size of the tetrahedron; if the latter is enlarged, other oxygen atoms than those shown move toward the iron atoms and the neighbours change. But it always remains true that the trivalent atom has three neighbours to the divalent atom's two.

Let us now take up the points we left undecided. The trivalent iron atom might be halfway between A and B or halfway between B and H, the latter being the position adopted in the figure. The reason for placing it as shown is derived from considerations of the (111) spectra, and in

* *Note added subsequently.* I see that the disposition of the oxygen atom here described as consisting of certain large tetrahedra pointing towards each other may with equal exactness be described as consisting of smaller tetrahedra each containing only one divalent iron atom and pointing away from each other.

Fig. 3 b.—Diagram illustrating structure of magnetite.
Oxygen tetrahedra shown correctly as regards form and position,
but *not* as regards size.



$$AB = 3.60 \text{ \AA.U.}$$

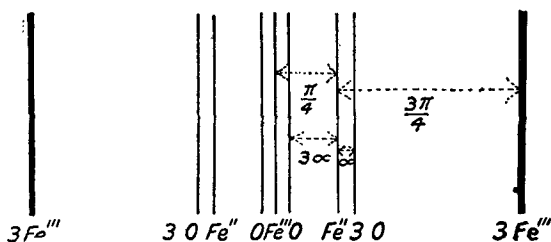
$$BD = DH = BE = EJ = BF = FK = BG = 5.40 \text{ \AA.U.}$$

BH, BJ, BK, BG are trigonal axes.

particular the fact that the first order spectrum is so very small. We gather from this fact that two sets of planes occur alternately at half the actual (111) spacing, and nearly balance one another. If we place the trivalent atom halfway between every pair of divalent neighbours such as A and B, we obtain the two sets of planes we want, but one set is so much stronger than the other that it would be hard to explain the weakness of the first order reflexion. If we place it as shown, viz., halfway between B and H, we again obtain the two sets of planes (it is rather hard to see without a model), but one consists of a single plane with three atoms in it, and the other three planes fairly close together each with a single atom. Thus they nearly balance, and so we make the first order reflexion small. In all this we are neglecting the oxygen atoms, it is true. But they are so much lighter than the iron atoms that it seems unlikely that they can make much difference.

Let us next consider the size of the oxygen tetrahedron. So far as we have gone we have made such a distribution of the atoms in the crystal that the distribution in the (111) planes will be found to be as shown in fig. 4; the distance

Fig. 4.



from $3Fe'''$ to $3Fe'''$ being 4.80 \AA.U. The constituents of two molecules are employed to represent the arrangement. We may represent the effect of such a distribution in the manner employed by W. L. Bragg in previous papers. Take the central Fe''' plane as the zero plane. We have then

- (1) The central Fe''' plane.
- (2) Two Fe'' planes having phases $\pi/4$ and $-\pi/4$ respectively.
- (3) One $3Fe'''$ plane having a phase π : the other is only a repeat of the first.

- (4) Two planes containing three oxygen atoms each and having phases $\pi/4 + \alpha$ and $-\pi/4 - \alpha$ respectively. If α is determined the size of the tetrahedron is known.
- (5) Two planes containing one oxygen atom each and having phases $\pi/4 - 3\alpha$ and $-\pi/4 + 3\alpha$ respectively.

The combination of the whole gives the same effect as that of a single plane having a weight

$$56 + 112 \cos \frac{n\pi}{4} + 168 \cos n\pi + 32 \cos n\left(\frac{\pi}{4} - 3\alpha\right) + 96 \cos n\left(\frac{\pi}{4} + \alpha\right),$$

where n is the order of the spectrum. We here assume what is no doubt an approximation only, that every atom contributes to every order of reflexion in proportion to its weight. In order to find a value for α let us first examine the effects of the iron atoms alone. Putting $n = 1, 2, 3 \dots$, the first three terms give us the following series of values:—

$$-34, 224, -190, 112, -190, 224, -34, 336.$$

We have to allow for the rapid decline in intensities as we proceed to higher orders, which seems an invariable effect. In the Bakerian lecture for 1915 it is ascribed to the fact that the centres scattering the X-rays are distributed through the volume of the atom and are not concentrated in one point. In general, we find that the intensity falls off inversely as the square of the order, where the reflecting planes are similar and similarly spaced. We may approximately allow for this fact by multiplying the experimental results, each by the square of its order, and then comparing them with the figures just found by calculation.

The experimental figures (see fig. 1) are

$$6 \quad 28.5 \quad 48 \quad 25 \quad 12.6 \quad 2.3 \quad .3 \quad 6.6,$$

which then become

$$6 \quad 114 \quad 432 \quad 400 \quad 315 \quad 84 \quad 14 \quad 424.$$

There is a steady rise to the 3rd or 4th followed by a steady fall and a large rise to the 8th.

Comparing these with the calculated figures due to the iron alone, we see that the latter are at fault in having the 2nd and 6th too large and the 4th too small. We shall want all the influence we can get from the oxygen

atoms in order to make these alterations, which we do by making the tetrahedra at A and B point towards each other and putting $4\alpha = \pi$. The oxygen terms in the formula then become simply $8 \times 16 \cos \frac{n\pi}{2}$: or, in the different orders

$$0 \quad -128 \quad 0 \quad +128 \quad 0 \quad -128 \quad 0 \quad +128$$

Combining these with the effects due to the iron atoms we get the calculated series

$$-34 \quad 96 \quad -190 \quad 240 \quad -190 \quad 96 \quad 34 \quad 464,$$

which has the proper rise and fall, though the maximum is actually at the 4th instead of between the 3rd and the 4th. The 8th is large as it should be. It is too large in fact: but that need not trouble us because the spectra of high order seem to diminish even faster than the inverse square of the order. At this stage the plus and minus signs have no significance.

When α is put equal to $\frac{\pi}{4}$ the structure becomes much simpler. The two oxygen tetrahedra round A and B in fig. 2 should be supposed to grow until the two corners on the line AB pass each other and finally lie each on a face of the other tetrahedron. The oxygen atoms then all lie on two planes. When a model is made it is seen that each trivalent iron atom lies at the centre of a regular octahedron of oxygen atoms and each divalent at the centre of a tetrahedron of oxygen atoms. The (100) planes consist of Fe_2O_4 planes having the spacing 2.07 Å.U. interleaved with Fe planes. This makes the second order spectrum more intense than is normally the case and agrees with experiment (see fig. 1). The (110) planes may be looked on as consisting of Fe_2O_2 planes of spacing 2.94 Å.U. interleaved with FeO_2 planes. The near equality of these two kinds of plane will readily account for the fact that the first (110) reflexion is so very small (fig. 1).

The results for spinel MgAl_2O_4 work out in exactly the same way, though it looks as if the oxygen tetrahedron was not quite so large. But these details may be left to be discussed hereafter.