A NEW TYPE OF CRYSTAL FINE-STRUCTURE:
LITHIUM FERRITE ($Li_2O \cdot Fe_2O_3$)

BY E. POSNJAK AND TOM. F. W. BARTH

GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION, WASHINGTON, D. C.

(Received October 9, 1931)

ABSTRACT

The interpretation of the x-ray diffraction obtained from the isometric modification of lithium ferrite resulted in the conclusion that the smallest "unit" of this structure contains four anions and four cations. The anions, oxygens, occupy the four equivalent points 4b while the cations, iron and lithium, occupy together the four equivalent points 4c. The large difference in the scattering power of iron and lithium makes it possible to arrive at the definite conclusion that in the structure of lithium ferrite the same set of equivalent positions is occupied by the two chemically different elements (variate atom equipoints). It is shown that the distribution of iron and lithium in this set of equipoints is not regular, that is, there are not always two of each cation present in the "unit"; the distribution is one of chance, which, however, must comply with the requirement that an equal number of each of the cations is always present within a relatively small space. In view of these findings the conception of the unit cell loses its traditional chemical significance and becomes strictly a geometric conception. The "unit cell" of lithium ferrite has a meaning only if its lattice be regarded as geometric points in space. The lattice of lithium ferrite is then identical with the one of the "sodium chloride" structure (4b, 4c); the unit cube contains one molecule of $Li_2O \cdot Fe_2O_3$, and the length of its edge is 4.141 ± 0.005A. The density of lithium ferrite is 4.368 and its refractive index $n_{Li} = 2.40 \pm 0.04$.

INTRODUCTION

IN THE course of studies of ferrites it became of interest to prepare and examine the properties of the alkali ferrites. Although sodium and potassium ferrites have been described in the literature, there is apparently no record of the preparation of lithium ferrite. It will be appropriate therefore to mention that the experiments showed that this compound could be prepared in two modifications, an isotropic and an anisotropic one. The latter resulted from the interaction of a concentrated solution of lithium hydroxide and ferric oxide when heated in a pressure bomb somewhat below 600°C, while above this temperature the cubic modification was formed. The isometric modification was also prepared by heating the appropriate mixture consisting of lithium carbonate and ferric oxide, at red heat. The relation of the two modifications of lithium ferrite has not been determined. In this paper we shall be concerned only with the one formed at the higher temperature which is isotropic, and which was found not to invert when cooled to and kept at room temperature. The optical examinations were kindly made by Dr. George Tunell of this Laboratory, who found that the isotropic modification has a refractive index $n_{Li} = 2.40 \pm 0.04$. The determination of the density of this modification by the pycnometer method[1] resulted in the value of 4.368.

---

[1] J. Johnston and L. H. Adams, J. Am. Chem. Soc. **34**, 563 (1912).

X-ray Diffraction Measurements

When lithium ferrite was prepared in the bomb by crystallization from solution, minute single octahedral crystals were obtained, the edges and corners of which were modified by rounded faces which were apparently dodecahedra and cubes. They were, however, too small to be utilized singly for x-ray measurements. Diffraction was therefore obtained only by the powder method. The apparatus was one made by the General Electric Company, equipped for using K_α radiation of molybdenum. The spacings were standardized in the usual way by exposure of sodium chloride on the same film alongside of lithium ferrite. Data obtained from such a powder spectrogram are given in Table I. By using the customary equation

TABLE I. *Powder diffraction data from lithium ferrite* ($Li_2O \cdot Fe_2O_3$).

Planar spacing	Intensity (estimated)	Indices	a_0
2.39	4	111(1)	4.143
2.07	10	100(2)	4.142
1.461	9	110(2)	4.128
1.247	3	113(1)	4.144
1.195	4	111(2)	4.144
1.035	2	100(4)	4.141
0.949	1	133(1)	4.140
0.925	5	120(2)	4.139
0.845	4	112(2)	4.143
0.798	1	111(3) 115(1)	4.150
0.732	1 −	110(4)	4.144
0.690	2	100(6) 122(2)	4.132
0.654	2	130(2)	4.139
0.624	1	113(2)	4.141
0.575	1 −	230(2)	4.145
0.553	1	123(2)	4.138

$$a_0 = 4.141 \pm 0.005\text{A}$$

$m = a_0^3 \rho / M$, where m is the number of molecules of $Li_2O \cdot Fe_2O_3$ within the unit, M the mass of a molecule of the substance, ρ its density, and a_0 the length of the edge of the unit cube, we find $m = 0.993$. This is, within experimental error, a whole number, as it should be, and one may therefore assume that one molecule of $Li_2O \cdot Fe_2O_3$ is associated with the unit cube.

Application of Space Group Criteria

From the reflections given in Table I it is immediately obvious that the lattice underlying the structure of lithium ferrite is a face-centered one. An examination of the tabulation of the results of the theory of space groups shows, however, that there is no space group with an underlying face-centered lattice, or for that matter of any other cubic lattice, which would accommodate two lithium, two iron, and four oxygen ions. This fact would suggest that it may be necessary to multiply the number of molecules of $Li_2O \cdot Fe_2O_3$, and therefore the length of the edge of the unit cell in which they are contained, by a simple integer, as for instance by two; however, we shall show later that this will be found to conflict with the experimental data.

ATOMIC ARRANGEMENT OF $Li_2O \cdot Fe_2O_3$

The comparison of the diffraction data from lithium ferrite with those of magnesium and ferrous oxides presents a clue for the solution of the problem. Thus it was found that the diffraction from lithium ferrite bore a very close similarity to that of the two substances just mentioned. The powder diffraction patterns of all three are reproduced in Fig. 1 and it will be readily seen how small the differences in spacings and intensities are. In view of recent experience in the study of spinels[2] in which the present authors had shown that different elements occupy crystallographically equivalent positions, it was thought not to be improbable that lithium ferrite presented another case of variate atom equipoints. Both magnesium oxide[3] and ferrous oxide[4] had been shown to have the sodium chloride structure containing four cations and four anions per unit cell in a face-centered arrangement ($4b$, $4c$). In the case of lithium ferrite it was thought that by analogy lithium and iron together may occupy four equivalent positions and the oxygens the other four; thus com-
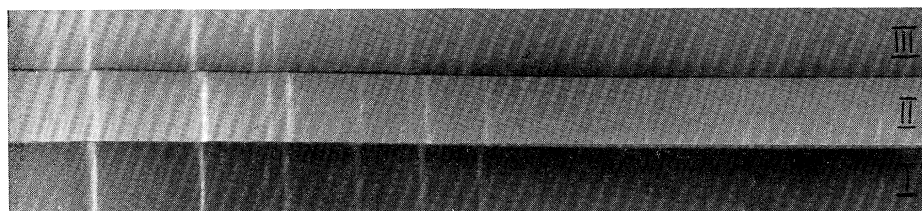

Fig. 1. Spectrograms of I, MgO; II, $Li_2O \cdot Fe_2O_3$; and III, FeO.

plying with the experimental evidence of the presence of two lithium, two iron, and four oxygen ions per unit cell of the lithium ferrite structure.

By making this assumption, the next question that arises concerns the interrelation between the lithium and iron ions within the crystal: are the points in arrangement $4c$ occupied in a regular or an irregular fashion by the two different kinds of ions? The following discussion will prove that it is necessary to conclude that the distribution of lithium and iron among the points of arrangement $4c$ must be one of chance, complying only with the requirement of an equal number of each within a relatively very small space.

The simplest regular arrangement which we may assume would be obtained by placing the lithium and iron ions alternately between the oxygens. Then in the direction of the edge of the cube we would have O–Fe–O–Li–O—. It is quite obvious that in this case the length of the edge of the unit cube would be twice that of the "sodium chloride" arrangement where it extends only from one oxygen over a cation to the next oxygen. The length of the edge of the unit cell given in Table I corresponds to the one in the "sodium chloride" structure, and if we assume the regular distribution of iron and

[2] Tom. F. W. Barth and E. Posnjak, J. Wash. Acad. Sci. **21**, 255 (1931).

[3] W. P. Davey and E. O. Hoffmann, Phys. Rev., [2], **15**, 333 (1920); W. Gerlach and O. Pauli, Zeits. f. Physik **7**, 116 (1921); R. W. G. Wyckoff, Am. J. Sci. [5], **1**, 138 (1921).

[4] R. W. G. Wyckoff and E. D. Crittenden, J. Am. Chem. Soc. **47**, 2876 (1925).

lithium it would therefore be necessary to conclude that the true length of the edge of the cube is $2a_0$. This would of course result in the necessity of re-assigning all our indices to higher orders—they would all be multiplied by two, which means that no first order reflections at all would occur in the lithium ferrite structure. However, such a conclusion can be shown to be incompatible with the established theory of the interaction of x-rays and crystals. The proof in this case is identical with that advanced by L. Vegard and H. Schjelderup[5] and more precisely brought out by M. v. Laue[6] in clearing up the theory of diffraction in the case of mixed crystals. The discussion may be confined to the consideration of the structure factor of the face-centered cubic crystal resulting from the regular arrangement of lithium and iron mentioned above, the length of the edge of the unit cell of which is A_0 $= 2a_0$. The structure factor can be expressed as the product of the following three parts:

$$F_1 = \left[1 + e^{2\pi i(h+k)/2} + e^{2\pi i(h+l)/2} + e^{2\pi i(k+l)/2}\right]^2$$

$$F_2 = \left[1 + e^{2\pi i(h+k)/4} + e^{2\pi i(h+l)/4} + e^{2\pi i(k+l)/4}\right]^2$$

$$F_3 = \left[\overline{O}(1 + e^{2\pi i(h+k+l)/2}) + \overline{Li}\cdot e^{-2\pi i(h+k+l)/2} + \overline{Fe}\cdot e^{2\pi i(h+k+l)/2}\right]^2.$$

The part F_1 is due to the fact that the whole lattice is made up of face-centered lattices; the part F_2 because from such a lattice three other identical lattices will be developed by the displacements $A_0/4$, 0, $A_0/4$; 0, $A_0/4$, $A_0/4$ and $A_0/4$, $A_0/4$, 0; and part F_3 shows that in the direction parallel to a body diagonal there are situated equally spaced O–Li–O–Fe. With the help of this structure factor all reflections which can occur may be calculated. When this is done it is found that while all the reflections which have been observed should occur in this structure, there should in addition be present reflections which, however, were not found in the spectrogram. For instance, the reflection from 111(1), the spacing of which would be 4.78A, has the structure factor 16.16 $(\overline{Fe}-\overline{Li})$ and, owing to the difference in the scattering power of iron and lithium, the intensity of this reflection should be stronger than any of those observed. As a matter of fact there is no indication of a diffraction line in this position, and therefore the assumption of the regular distribution of iron and lithium which required doubling the length of the edge of our unit cell must be discarded.

We now have to evaluate our experimental data in regard to the other assumption, namely, the chance distribution of iron and lithium in the four equipoints (4c) of the "sodium chloride" arrangement. Taking into consideration not too small a portion of the crystal an equal number of points is occupied by iron and by lithium. Therefore in calculating the intensities the average of the scattering power of the two may be taken, $(Fe+Li)/2$. The position of the atoms are: O in (4b) i.e. 0 0 0, $\frac{1}{2}\frac{1}{2}$ 0, $\frac{1}{2}$ 0 $\frac{1}{2}$, 0 $\frac{1}{2}\frac{1}{2}$; and 2Fe+2Li in (4c) i.e. $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}$ 0 0, 0 $\frac{1}{2}$ 0, 0 0 $\frac{1}{2}$. The intensities of reflection were calculated on the basis of the equation

[5] L. Vegard and H. Schjelderup, Phys. Zeits. **18**, 93 (1917).

[6] M. v. Laue, Ann. d. Physik [4], **56**, 497 (1918).

$$I = j \frac{1 + \cos^2 2\theta}{\sin 2\theta} F^2,$$

employing the F-values published by W. L. Bragg and J. West[7] for iron and oxygen. For lithium the F-curve given recently by R. W. James and G. W. Brindley[8] was used. The results are given in Table II from which it will be

TABLE II. *Comparison of observed and calculated diffraction intensities from lithium ferrite* $(Li_2O \cdot Fe_2O_3)$.

Indices	Estimated	Calculated	Indices	Estimated	Calculated
(111)	4	1.4	(333) (115)	1	1.3
(200)	10	10.4			
(220)	9	8.8	(440)	1 —	0.8
(113)	3	2.3	(600) (244)	2	1.6
(222)	4	3.1			
(400)	2	1.3	(260)	1	1.0
(133)	1	1.5	(226)	1	0.8
(240)	5	4.0	(460)	1 —	0.5
(422)	4	2.8	(246)	1	0.8

seen that the calculated intensities are in very good agreement with the estimates made from the spectrogram. Therefore we must conclude that this is the correct structure and that iron and lithium together occupy four equipoints of the "sodium chloride" arrangement filling these points in equal molecular ratio by chance distribution. The holohedral symmetry required by the "sodium chloride" arrangement is in accord with the observed external crystal faces and it may also be mentioned that the lattice dimensions of lithium ferrite agree well with the accepted values of the atomic radii.

CONCLUSIONS

In a recent study of the structure of spinels the authors[9] have shown that the 16 equivalent positions (16c) of this structure are not all occupied by chemically equivalent ions, but that eight of them are of one kind, such as the trivalent Fe^{+++}, Al^{+++}, Ga^{+++}, etc., while the other eight are bivalent ions like Mg^{++}, Fe^{++}, etc. The present study of the structure of lithium ferrite, which structurally is the simplest possible case and therefore an even more convincing one, again proves that crystallographically equivalent positions in a crystal may be occupied by chemically different ions (Fe^{+++} and Li^{+}). Such crystals with variate atom equipoints challenge in a certain way our usual conceptions of "crystal" and "chemical compound." Crystallographically, in crystals with variate atom equipoints we find that the usual symmetry requirements (symmetry operations) cannot be extended to its smallest unit, that is, the unit cell. Such an extension can only be accomplished if the atoms are regarded purely as geometrical points in space. Crystals with variate atom equipoints do not exhibit in their lattice the regular

[7] W. L. Bragg and J. West, Zeits. f. Krist. **69**, 118 (1929).

[8] R. W. James and G. W. Brindley, Phil. Mag. [7] **12**, 81 (1931).

[9] Tom. F. W. Barth and E. Posnjak, J. Wash. Acad. Sci. **21**, 255 (1931).

periodicity in regard to the chemical character of the atoms composing it, which is usually associated with our conception of compounds. However, it should be remembered that the conception of the molecule also found no support from the crystal structure of such simple substances as the alkali halides, some oxides, etc.; indeed, the conception of the "unit cell" was introduced and in a sense replaced it, but only as a convenient descriptive term, for it would be very arbitrary to think of the chemical molecule as being identical with the unit cell. In the solid state the only logical limitation of the molecule is the macrocrystal itself.

It may be suggested that the structure with variate atom equipoints be regarded as representing the general case of which the other structures are special cases. We know that the possession of a (geometrical) unit cell of indefinite chemical composition (which is identical with having variate atom equipoints) is apparently the property of all mixed crystals and is therefore a very common phenomenon. There seems to be no obvious reason from the point of view of geometrical and descriptive crystallography why compounds would not require similar treatment.

Several cases are on record in which the same problem arose. For instance, ammonium-oxy-fluoro-molybdate,[10] $(NH_4)_3MoO_3F_3$, whose x-ray diffraction data indicate that the O and F ions occupy crystallographically equivalent positions. In this case it was possible to explain the structure by assuming a larger unit cell, the existence of which, however, could not be brought out by the x-ray spectrograms on account of the similarity of the scattering power of O and F. Other cases were potassium cyanate,[11] KCNO, in which C and N seemed to occupy crystallographically equivalent positions and $Co(NH_3)_5H_2OSO_4I$,[12] in which the NH_3 groups are partly replaced by H_2O. In these cases again the explanation given for ammonium-oxy-fluoro-molybdate appeared reasonable. In the case of lithium ferrite, however, it can be shown in view of the large difference in the scattering power of the cations that an enlargement of the unit cell is inadequate to explain this structure, and thus it becomes much more reasonable to assume that the iron and lithium ions are irregularly distributed within the same set of equipoints.

While very few cases of this type of structure have so far been encountered in compounds, and it is also impossible at present to say what significance attaches to this fact, further studies will show whether or not these cases are fortuitous.

[10] L. Pauling, J. Am. Chem. Soc. 46, 2738 (1924).
[11] S. B. Hendricks and L. Pauling, J. Am. Chem. Soc. 47, 2904 (1925).
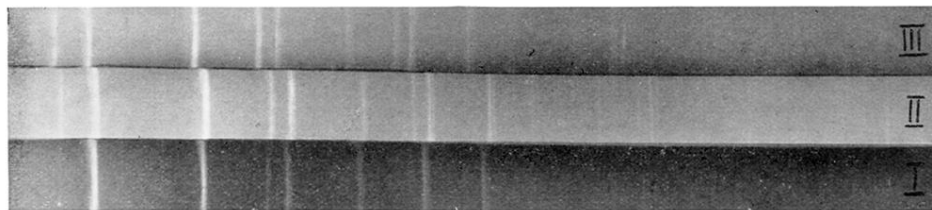[12] O. Hassel, Norsk. Geol. Tidsskrift. 10, 33 (1928). See also idem, p. 92.

Fig. 1. Spectrograms of I, MgO; II, $Li_2O \cdot Fe_2O_3$; and III, FeO.