

**X-Ray Studies on Magneto-Plumbite,  $PbO \cdot 6 Fe_2O_3$ , and other Substances resembling "Beta-Alumina",  $Na_2O \cdot 11 Al_2O_3$ .**

By

**VOLRATH ADELSKÖLD.**

With 3 figures in the text.

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**Introduction.**

During recent years A. WESTGREN and his collaborators have investigated aluminates and ferrites of Ca, Sr, and Ba by means of X-rays. It was found that  $CaO$  and  $SrO$ <sup>1</sup>, as well as  $BaO$ <sup>2</sup>, when melted together with  $Al_2O_3$  in large excess form aluminates with a structure closely resembling that of the so-called  $\beta$ -alumina, the composition of which has been recently determined by C. A. BEEVERS and S. BROHULT to be  $Na_2O \cdot 11 Al_2O_3$ .<sup>3</sup> As found by N. SCHREWELIUS and T. ALEXANDERSON of this institute, phases of the same kind are present also in the systems  $SrO-Fe_2O_3$  and  $BaO-Fe_2O_3$ , but no calcium-ferrite of this type seems to exist.<sup>4</sup>

Several years ago G. AMINOFF described a new mineral, a lead-ferrite, that he called magneto-plumbite<sup>5</sup>, which, be-

<sup>1</sup> K. LAGERQVIST, S. WALLMARK and A. WESTGREN, *Zeitschr. f. anorg. u. allg. Chemie* 234, 1. 1937.

<sup>2</sup> S. WALLMARK and A. WESTGREN, *Arkiv f. kemi etc.* Bd 12 B, N:r 35. 1937.

<sup>3</sup> C. A. BEEVERS and S. BROHULT, *Zeitschr. f. Kristallogr.* 95, 472. 1936.

<sup>4</sup> Investigations still unpublished.

<sup>5</sup> G. AMINOFF, *Geol. Fören. Förhandl. Stockholm* 47, 283. 1925.

cause of its lattice dimensions and symmetry properties, must be assigned to this group of substances also. On the suggestion of AMINOFF it has recently been chemically re-analyzed by R. BLIX, who has come to the conclusion that it consists of  $PbO \cdot 5 Fe_2O_3$ .<sup>1</sup>

In their reports on aluminates of Ca, Sr, and Ba, WESTGREN and his collaborators have suggested formulae of the type  $3 CaO \cdot 16 Al_2O_3$  for the phases of the kind mentioned, basing their choice partly on the analysis of BLIX and partly on the apparent isomorphy of these substances with  $\beta$ -alumina. They have, however, also emphasised that this conclusion should be checked by a structure determination.

For such a determination the lead-ferrite seemed most appropriate since it contained metal atoms with high scattering power and formed good crystals. The problem of its crystal structure has now been solved, and surprisingly enough it has been found that this ferrite is composed according to the formula  $PbO \cdot 6 Fe_2O_3$ . Though very similar in structure to  $\beta$ -alumina, it is thus not completely isomorphous to it.

As well known,  $\beta$ -alumina has been the subject of many X-ray investigations. A successful attack upon the problem of its structure was made by W. L. BRAGG, C. GOTTFRIED, and J. WEST, who were the first to advance an approximate solution of it.<sup>2</sup> After BEEVERS and BROHULT had established the true composition of  $\beta$ -alumina, the research on this problem could be pursued, and quite recently BEEVERS and M. A. S. ROSS have reported a more complete solution of it.<sup>3</sup> They were kind enough to report the structure found to this institute before their work was published, with the result that the present author has had an early opportunity of testing whether it could also explain the X-ray data of the lead-ferrite. This was found not to be the case, and the structure problem of magneto-plumbite had thus to be independantly and more radically treated.

### The Composition and Structure of Magneto-Plumbite.

In order to obtain pure samples of the lead-ferrite, solutions of lead and iron nitrates, mixed in different proportions, were precipitated by ammonia or ammonium carbonate.

<sup>1</sup> R. BLIX, Geol. Fören. Förhandl. Stockholm 59, 300. 1937.

<sup>2</sup> W. L. BRAGG, C. GOTTFRIED, and J. WEST, Zeitschr. f. Kristallogr. 77, 255. 1931.

<sup>3</sup> C. A. BEEVERS and M. A. S. ROSS, Zeitschr. f. Kristallogr. 97, 59. 1937.

The hydroxides thus obtained were dried and then heated to about  $1000^{\circ}$  C for about a day. The series of substances produced in this way was investigated by means of the X-ray powder method. From the photographs it could be concluded that there are at least two intermediate phases present in the system  $\text{PbO}\text{-Fe}_2\text{O}_3$ , one tetragonal corresponding to about  $5 \text{ PbO} \cdot 2 \text{ Fe}_2\text{O}_3$ , the other hexagonal containing 1 PbO per about  $6 \text{ Fe}_2\text{O}_3$ .<sup>1</sup> The latter phase corresponds to the mineral magneto-plumbite. Its lattice dimensions are  $a=5.877$  and  $c=23.02$  Å.

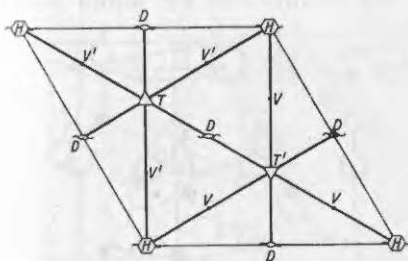


Fig. 1. Projection of unit cell on (001).

No crystals were obtained from the synthetic samples. Therefore, a crystal of magneto-plumbite had to be used for taking Laue and rotation photographs. It was found necessary to etch the crystal with HCl in order to remove a surface layer which to a great extent absorbed the X-rays. Some of the rotation photographs as well as a WEISSENBERG diagram of the equator zone about [001] were produced employing Cu-K radiation. The attempts to determine the structure could therefore be based upon a rather plentiful supply of X-ray data. It proved especially valuable that the intensity was established for a large number of prism and basal reflections.

The Laue symmetry proved to be  $D_{6h}$ , as AMINOFF has shown. All reflections  $hhl$  with  $l$  odd were found to be missing, and as no piezoelectric effect could be demonstrated,

<sup>1</sup> The mineral plumbo-ferrite, described by K. JOHANSSON (*Z. f. Kristallogr.* 68, 87, 1928) is a third lead-ferrite, composed according to the formula  $\text{PbO} \cdot 2 \text{ Fe}_2\text{O}_3$ . It is evidently formed under conditions which were not prevailing during the syntheses performed by the author. — According to a private communication of Mr. SCHREWELIUS of this institute, the tetragonal phase has its analogies in the systems  $\text{SrO}\text{-Fe}_2\text{O}_3$  and  $\text{BaO}\text{-Fe}_2\text{O}_3$ . It is probably also related to the mineral haematophanite,  $\text{Pb}(\text{Cl}, \text{OH})_2 \cdot 4 \text{ PbO} \cdot \text{Fe}_2\text{O}_3$ , likewise described by K. JOHANSSON (*loc. cit.*). Its lattice dimensions seem to be about the same as those of this mineral.

the most probable space-group seemed to be the same as that of  $\beta$ -alumina, *viz.*  $D_{6h}^4-C6/mmc$ .

As mentioned above, it was first assumed that the number of atoms in the unit cell of magneto-plumbite was about the same as in that of  $\beta$ -alumina. The latter contains 2 Na, 22 Al, and 34 O. It seemed reasonable to suppose that the oxygen lattice was the same in the two substances, and that consequently there were 34 O present in the cell of magneto-plumbite also. Further, it seemed most likely that the latter also contained 2 Pb. In order that the electro-neutrality might be maintained, its number of Fe would then be only  $21\frac{1}{3}$ ,

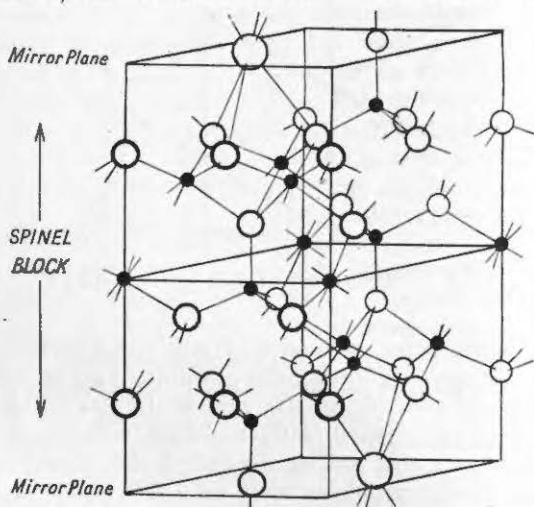


Fig. 2. The structure of  $\text{Na}_2\text{O} \cdot 11 \text{Al}_2\text{O}_3$  according to BEEVERS and ROSS. Half of the unit cell. The large circles represent Na, the small ones O, and the black dots Al.

that is some of the points occupied by Al in the lattice of  $\beta$ -alumina would be vacant in that of magneto-plumbite. Its composition would thus correspond to  $3 \text{PbO} \cdot 16 \text{Fe}_2\text{O}_3$ , as suggested by WESTGREN. Density measurements, performed in order to check this hypothesis, gave in fact somewhat too high a value, but since the discrepancy was considered to be due to experimental errors, its significance was not at first appreciated.

As a lack of only 2 Fe from every third unit cell volume of the lattice could hardly have any noticeable influence upon the intensities, the attempts to determine the structure were started on the assumption that the elementary prism of magneto-plumbite contained 2 Pb, 22 Fe, and 34 O. As mentioned above, it was at first tested whether the structure of

$\text{Na}_2\text{O} \cdot 11 \text{Al}_2\text{O}_3$ , determined by BEEVERS and ROSS, reappeared in magneto-plumbite. But, even if the parameters were somewhat varied about the values given, it was impossible to obtain a complete agreement between observed and calculated intensities.

Much time was then lost upon fruitless attempts to find an arrangement of the 58 atoms in the cell which might fulfill the conditions of the X-ray data. During these efforts, in conformity with BRAGG, GOTTFRIED and WEST, it was assumed that all the atoms were arranged in columns parallel to the

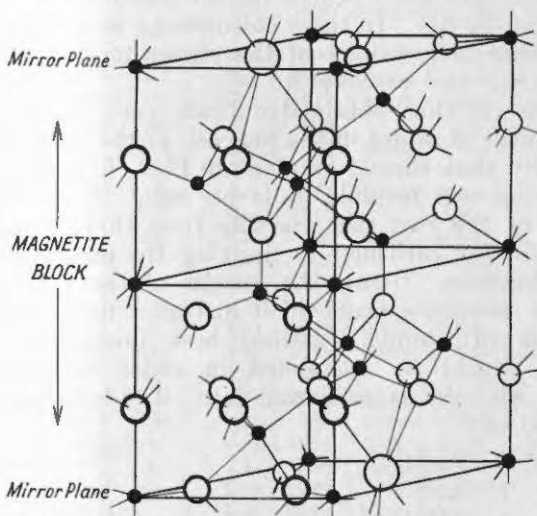


Fig. 3. The structure of  $\text{PbO} \cdot 6 \text{Fe}_2\text{O}_3$ . Half of the unit cell. The large circles represent Pb, the small ones O, and the black dots Fe.

c-axis and passing through the points H, T, D, V, and V' (Fig. 1). In order to find the distribution of atoms amongst these columns a very great number of arrangements was tried. The only result of these attempts was a confirmation of the idea that the structure of magneto-plumbite must be very similar to that of  $\beta$ -alumina. A satisfactory final solution of the structure problem was not attained.

For some time the author was at a loss to understand how the problem should be attacked with a prospect of success, but finally a fact was established that completely changed the whole aspect of the question. The density of magneto-plumbite is in reality not as low as had been assumed but instead even somewhat higher than the author had found experimentally. S. HILPERT and R. SCHWEINHAGEN have very carefully

determined the density of strontium and lead ferrites of quite a series of different compositions.<sup>1</sup> From their diagrams it may be gathered that the densities of lead and strontium ferrites, composed according to the formulae  $\text{PbO} \cdot 5 \text{Fe}_2\text{O}_3$  and  $\text{SrO} \cdot 5 \text{Fe}_2\text{O}_3$ , are 5.69 and 5.11 respectively while those of  $\text{PbO} \cdot 6 \text{Fe}_2\text{O}_3$  and  $\text{SrO} \cdot 6 \text{Fe}_2\text{O}_3$  are 5.62 and 5.12 respectively. If we assume the first-mentioned formulae to be valid, the number of atoms in the unit cell is calculated to be 62.7 for the lead-ferrite, and 63.6 for the strontium-ferrite, and if the compositions correspond to the latter formulae the number of atoms in the cells must be 63.4 for the lead-ferrite, and 64.1 for the strontium-ferrite. In these calculations the following values of the lattice dimensions of the strontium-ferrite have been used:  $a=5.864$ , and  $c=23.03 \text{ \AA}$ .

The figures thus obtained indicate very strongly that the correct number of atoms in the unit cell of the ferrites is 64 and consequently that their formulae are  $\text{PbO} \cdot 6 \text{Fe}_2\text{O}_3$  and  $\text{SrO} \cdot 6 \text{Fe}_2\text{O}_3$ , giving two formula units per cell. This conclusion is confirmed by the fact that starting from these new data there is no longer any difficulty in deriving the atomic grouping of magneto-plumbite. Using the results of the previous discussion of the structure problem, it was soon discovered how that combination of atomic locations best suiting the intensity conditions should be completed in order to give a perfect agreement with the experimental data. The following structure was arrived at:<sup>2</sup>

- 2 Pb in 2 (d);
- 2 Fe in 2 (a);
- 2 Fe in 2 (b);
- 4 Fe in 4 (f);  $2 \pi z_1=10^\circ$ ;
- 4 Fe in 4 (f);  $2 \pi z_2=68^\circ$ ;
- 12 Fe in 12 (k);  $2 \pi x_3=60^\circ$ ,  $2 \pi z_3=39^\circ$ ;
- 4 O in 4 (e);  $2 \pi z_4=54^\circ$ ;
- 4 O in 4 (f);  $2 \pi z_5=-18^\circ$ ;
- 6 O in 6 (h);  $2 \pi x_6=67^\circ$ ;
- 12 O in 12 (k);  $2 \pi x_7=60^\circ$ ,  $2 \pi z_7=18^\circ$ ;
- 12 O in 12 (k);  $2 \pi x_8=180^\circ$ ,  $2 \pi z_8=54^\circ$ .

As may be seen from Table 1, the agreement between the observed intensities and those calculated under the assumption of this structure is excellent. The estimated intensity values are classified in the usual way by v. w.=very weak, w=weak, m=medium, st=strong, and v. st.=very strong.

<sup>1</sup> S. HILPERT and R. SCHWEINHAGEN, Zeitschr. f. physik. Chemie B 31, 1. 1935.

<sup>2</sup> Notations according to »Internationale Tabellen zur Bestimmung von Kristallstrukturen», Berlin 1935.

Table 1.

 Powder Photographs of  $\text{PbO} \cdot 6 \text{Fe}_2\text{O}_3$ . Cr-K Radiation.

h k l	$\sin^2 \theta$		I		h k l	$\sin^2 \theta$		I	
	Obs.	Calc.	Obs.	Calc.		Obs.	Calc.	Obs.	Calc.
006	0.0890	0.0887	w.	0.8	215	0.4145	0.4142	v. w.	0.6
104		0.0898		1.1	216	0.4418	—	0.3	
105	0.1122	0.1120	w.	1.4	2010	0.4484	0.4479	v. w.	0.3
106		0.1391	—	0.09	300	0.4544	0.4534	w.	3.4
110	0.1518	0.1511	m.	9	301		0.4559	—	0
008	0.1581	0.1578	w.	2.8	302	0.4638	0.4633	v. w.	0.7
112	0.1618	0.1610	w.	2.5	1013	0.4678	0.4670	v. w.	0.3
107	0.1716	0.1712	st.	17	217	0.4732	0.4734	st.	8
114	0.1909	0.1905	st.	18	303		0.4756	—	0
200	0.2018	0.2015	v. w.	1.8	0014	0.4822	0.4832	w.	1.8
201		0.2040	—	0.4	304	0.4931	0.4928	m.	4.0
108	0.2080	0.2082	v. w.	0.7	2011	0.5001	0.4998	m.	6.1
202		0.2114	—	0.02	1112		0.5061	w.	1.2
203	0.2238	0.2237	m.	7.6	218	0.5105	0.5104	v. w.	0.3
116		0.2398	—	0.001	305		0.5150	—	0
204		0.2409	—	0.006	1014		0.5336	—	0.2
0010	0.2464	0.2465	v. w.	0.2	306		0.5421	—	0
109	0.2498	0.2500	w.	1.2	219	0.5512	0.5522	v. w.	0.8
205	0.2632	0.2631	st.	4.6	2012	0.5561	0.5565	v. w.	0.4
206	0.2904	0.2902	m.	2.8	307		0.5742	—	0
1010	0.2968	0.2969	v. w.	0.7	2110	0.5995	0.5991	v. w.	0.4
118	0.3091	0.3080	v. w.	0.7	220	0.6043	0.6045	st.	9
207		0.3223	—	0.001	1015	0.6066	0.6050	v. w.	0.7
1011	0.3493	0.3487	w.	1.4	308	0.6120	0.6112	v. w.	0.4
210		0.3526	—	0.02	222		0.6144	—	0.1
0012	0.3555	0.3550	v. w.	0.08	2013	0.6175	0.6181	v. w.	0.3
211		0.3551		1.2	0016	0.6313	0.6310	v. w.	0.3
208	0.3593	—	0	1114	0.6343		—		0.9
212		0.3625	—	0.4	224	0.6439	—	0.1	
213	0.3761	0.3748	v. w.	1.0	2111	0.6505	0.6509	w.	0.5
214		0.3920	—	0.3	309		0.6530	—	0
1110	0.3978	0.3976	v. w.	1.1	1016	0.6819	0.6814	m.	1.4
209	0.4008	0.4011	w.	1.8	2014		0.6847		3.1
1012		0.4054	—	0.02	226	0.6924	0.6932	v. w.	0.6

It seemed at first difficult to reconcile the conclusion, that the formula of magneto-plumbite should be  $\text{PbO} \cdot 6 \text{Fe}_2\text{O}_3$ , with BLIX's analytical results, which without doubt are very careful determinations. The author has, however, microscopically examined some magneto-plumbite crystals taken from the specimens analysed and found that they contained several minute inclusions, probably consisting of kentrolite, a lead-manganese-silicate, comparatively rich in lead. This contamination may explain why BLIX has obtained somewhat too high a lead-content in his analysis.

Table 2.

 $\beta$  Alumina and Magneto-Plumbite Phases.

Structure Type	Formula	a	c
$\beta$ -Alumina	$\text{Na}_2\text{O} \cdot 11 \text{ Al}_2\text{O}_3$	5.584 Å	22.45 Å
	$\text{K}_2\text{O} \cdot 11 \text{ Al}_2\text{O}_3$	5.584 Å	22.67 Å
	$\text{K}_2\text{O} \cdot 11 \text{ Fe}_2\text{O}_3$	5.915 Å	23.68 Å
	$\text{Rb}_2\text{O} \cdot 11 \text{ Fe}_2\text{O}_3$	5.915 Å	23.88 Å
Magneto-Plumbite	$\text{CaO} \cdot 6 \text{ Al}_2\text{O}_3$	5.536 Å	21.825 Å
	$\text{SrO} \cdot 6 \text{ Al}_2\text{O}_3$	5.557 Å	21.945 Å
	$\text{BaO} \cdot 6 \text{ Al}_2\text{O}_3$	5.577 Å	22.67 Å
	$\text{SrO} \cdot 6 \text{ Fe}_2\text{O}_3$	5.864 Å	23.03 Å
	$\text{BaO} \cdot 6 \text{ Fe}_2\text{O}_3$	5.876 Å	23.17 Å
	$\text{PbO} \cdot 6 \text{ Fe}_2\text{O}_3$	5.877 Å	23.02 Å

**Discussion of the Structure. Survey of »Beta-Alumina»  
and Magneto-Plumbite Phases.**

Fig. 2. borrowed from the report of BEEVERS and ROSS, shows how the atoms are arranged in  $\beta$ -alumina. In Fig. 3 the structure of magneto-plumbite is correspondingly demonstrated. If the two figures are compared, it may be seen that they are to a large extent identical. No less than 50 of the 58 and 64 atoms of the unit cells are arranged in the same way, forming large blocks of spinel and magnetite structure. Only the linking of these blocks is different in the two substances. In  $\beta$ -alumina the spinel layers are linked by 2 Na, 4 Al, and 2 O per unit cell, with the linking Al atoms situated in oxygen tetrahedra; in magneto-plumbite the magnetite blocks are kept together by 2 Pb, 6 Fe, and 6 O, the Fe atoms being surrounded by either 6 or 5 oxygen atoms.

The two large metal atoms in the unit cell of these substances, consisting of Na, K, Rb, Ca, Sr, Ba, or Pb, seem to be essential to the stability of their structure. From the survey, given in Table 2 of the now known phases of this type, in order for these structures to be formed, it seems necessary that the size of the two large atoms bear a certain ratio to the dimensions of the aluminate and ferrite lattices. As already mentioned, no calcium-ferrite of the magneto-plumbite type seems to exist and the author has tried to pro-



duce the whole series of alkali-ferrites corresponding to  $\beta$ -alumina but has only succeeded in making  $K_2O \cdot 11 Fe_2O_3$  and  $Rb_2O \cdot 11 Fe_2O_3$ . Li and Na seem to have too small and Cs too large atoms to be able to form ferrites of this kind. As building-stones of aluminates, the Na and Ca atoms are evidently sufficiently large to build up phases of the  $\beta$ -alumina type. The reason for this is probably that the aluminates have smaller lattice dimensions than the ferrites. In view of these facts it would not be astonishing if Rb and Cs will be found to have too large atoms to be able to form aluminates of the  $\beta$ -alumina type.

As may be seen in Table 2, quite a number of  $\beta$ -alumina and magneto-plumbite phases have so far been discovered. However, as Al and Fe in these substances may be replaced by related metals such as Cr, Mn, Co, Ni, or Ga a still greater number of such phases may certainly be produced.

The author wishes to express his sincere thanks to Professor A. WESTGREN for suggesting this work and for much advice during its performance. He also thanks Professor G. AMINOFF for his helpful interest and for his kindness in supplying suitable material for the investigation. The author is also indebted to K. Vetenskapsakademien for a grant from its Scheele Fund for this work.

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