Accurate determination of the cell dimensions of magnetite.

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Summary. An analysed magnetite from Bisperg, Säter, Dalecarlia, Sweden, gave the formula $Fe^{2+}_{1\cdot024}Mg^{2+}_{0\cdot010}Fe^{3+}_{1\cdot984}O_{4\cdot000}$, which corresponds closely to the ideal composition. A precise determination of the cell dimensions gave a $8\cdot3963\pm$ $0\cdot0005$ Å. at $18°$ C. Gentle heating of the powdered magnetite in evacuated silica glass tubes, before X-ray examination, resulted in sharply defined lines with high Bragg angles; an improvement which enabled precision data to be obtained. Four other new analyses of magnetites are also given and their lattice parameters are determined in the same way and are found to range from $8\cdot3960$ Å. to $8\cdot3970$ Å. The Bisperg magnetite being the purest sample examined, the value of its cell edge is taken as representative of pure magnetite.

The effect of the different ionic substitutions on the cell dimensions of natural magnetites is discussed. An attempt is also made to explain the great variations among the published values of cell dimensions of artificial preparations; one main reason being the presence of defect structures with varying oxygen contents in excess of the formula requirements.

MANY elements may substitute either the divalent or the trivalent atoms in Fe_3O_4, and as a result pure magnetite is the exception and not the rule. A knowledge of the exact value of the cell dimensions of pure natural magnetite is important for any investigation of these different substitutions and their effect on the size of the unit cell.

During a recent study of the system $FeO-Fe_2O_3-TiO_2$ and the magnetite solid solutions, the author could not find in the literature any reliable data for the unit-cell dimensions of magnetite (Basta, 1953). Holgersson (1927) gave measurements[1] of two natural magnetites from

[1] Throughout this paper, measurements are given in Ångstrom units, converted

Sweden: one from Dalarne with a cell edge of $8\cdot416\pm0\cdot003$ Å., and the other from Nordmarken with a cell edge of $8\cdot429\pm0\cdot003$ Å. However, such measurements are of little value, as they are not accompanied by chemical analyses. Newhouse and Glass (1936), in their study of some physical properties of iron oxides, gave $8\cdot395$ Å. for the cell edge of an almost pure magnetite from Lovers' Pit, Mineville, U.S.A.; an averaged value that could not be accepted, especially as it is not known what precautions were adopted in its determination. Very recently, Schmidt and Vermaas (1955) using a $57\cdot3$ mm.-diameter camera and unfiltered cobalt radiation gave the values for cell dimensions of five samples of magnetites, from different localities, which range from $8\cdot386$ to $8\cdot398$ $(\pm0\cdot001)$ Å. Such relatively large variations of the lattice parameters were attributed to the presence of appreciable amounts of Mg, Al, and in one case Ni; FeO varied between 25 and 28 % indicating an excess of Fe_2O_3. Schmidt and Vermaas plotted the values for cell dimensions against the sum of the molecular proportions of MgO and NiO and concluded that a magnesium-free magnetite should have a cube edge of $8\cdot402$ Å. $(\pm0\cdot002)$. In view of the fact that complete chemical analyses were not given, it is difficult to accept such a conclusion, as other oxides such as TiO_2, MnO, and γ-Fe_2O_3 may enter in the lattice of magnetite and will modify the cell dimensions.[1] A more useful value, however, is $8\cdot392\pm0\cdot001$ Å. given by the same authors for the unit-cell dimensions of the relatively pure Mineville magnetite.

The unit-cell dimensions of magnetite are better known for the artificial compound, but the measurements by different workers range widely from $8\cdot36$ Å. to $8\cdot45$ Å. (table V).

It is evident that there is a need for reliable and accurate data on the lattice dimensions of such a common mineral as magnetite. A number of chemically analysed magnetite samples were available from an unpublished study of the system FeO–Fe_2O_3–TiO_2. It was therefore decided to utilize some of these samples in the precision determination of the unit-cell dimensions of magnetite; at the same time an attempt was made to explain the considerable variations in the values given by the previous investigators for the artificial preparations. An additional purpose of the work was the possibility of correlating the variations in composition and cell edge of naturally occurring magnetites with the

when necessary from the original values in the references cited (W. L. Bragg, Journ. Sci. Instr., 1947, vol. 24, p. 27). In the absence of a statement of the wavelength used, particularly before 1943, the measurements, although usually specified as being in Ångstroms, were presumed to be in kX.

[1] See below, p. 436.

changes in their physical properties, and thus trying to account for some of the contradictory statements as to the appearance of magnetite in polished sections. This part of the work has, however, not progressed sufficiently, and is therefore left for a later publication.

Technique and results of analyses.

Small fragments of selected material were crushed into a fine powder of about 0·1 mm. particle diameter. To avoid iron contamination that

TABLE I. Chemical analyses of magnetites.

	1.	2.	3.	4.	5.	6.		1′.	
FeO	31·43	30·58	31·05	30·76	30·65	31·03	Fe^{2+}	1·024	
MgO	0·18	0·28	0·46	0·19	0·43	—	Mg^{2+}	0·010	3·018
MnO	0·05	0·27	0·03	0·29	0·27	—	Fe^{3+}	1·984	
CaO	0·01	tr.	0·00	tr.	tr.	—	O	4·000	4·000
Fe_2O_3	67·55	66·92	66·42	65·08	68·59	68·97			
Al_2O_3	0·04	tr.	0·37	1·54	tr.	—			
V_2O_3	0·01	n.d.	0·27	n.d.	n.d.	—			
Cr_2O_3	0·02	0·00	0·00	0·00	0·00	—			
TiO_2	0·05	0·28	0·27	0·36	tr.	—			
SiO_2	0·73	1·08	1·22	1·20	0·00	—			
	100·07	99·41	100·09	99·42	100·00	100·00			

1. Magnetite, Bisperg, Säter, Dalecarlia, Sweden. Analyst, H. B. Milner.
2. Magnetite, Barras Nose, Tintagel, Cornwall. Analyst, W. H. Herdsman.
3. Magnetite, Arendal, Norway. Analyst, H. B. Milner.
4. Magnetite, Hall, Ottawa, Canada. Analyst, W. H. Herdsman.
5. Magnetite, recalculated after deduction of 2·02% SiO_2 as quartz, Binnenthal, Switzerland. Analyst, W. H. Herdsman.
6. Theoretical composition of magnetite, Fe_3O_4.
1′. Atomic ratios calculated from analysis 1 on basis of 4 O.

might result if hardened steel mortars were used, the preliminary crushing was carried out between two horizontal disks of non-magnetic Cu–Be alloy under a pressure of 3 to 4 tons per sq. in. The powder was subjected to magnetic and heavy-liquid separations in order to remove impurities (see Basta, 1953, for details). A check for homogeneity was made under the microscope and by X-ray powder photographs.

A specimen of magnetite (Bristol No. 636) from Bisperg, Säter, Dalecarlia, Sweden, was found by chemical and spectrochemical analysis (table I, col. 1) to be exceedingly close to the ideal stoichiometric composition Fe_3O_4. A portion of the analysed sample was studied by X-ray diffraction methods using iron-filtered cobalt radiation in a 114·59 mm.-diameter powder camera of the type described by

W. Parrish and E. Cisney.[1] The change of temperature of the camera during the period of exposure ($1\frac{1}{2}$–2 hours) did not exceed 2° C. under operating conditions. The wave-lengths of the X-rays from the cobalt target were taken as $K\alpha_1 = 1.78890$, $K\alpha_2 = 1.79279$, $K\alpha = 1.79020$ Å., and the measurements were made for the specimen at 18° C.

Although the low θ values were indicated by sharp lines, the more important back-reflection lines were diffuse, possibly as a result of lattice distortion or strain of the crystal structure due to the grinding process. Although such a phenomenon is frequently encountered in metals, it has only rarely been reported in minerals, for example by B. Wasserstein[2] in his work on galena; guided by his experience, the powdered magnetite sample was heated to about 400° C. for a few minutes; to safeguard against oxidation, the heating was carried out in evacuated silica glass tubes. X-ray powder photographs of the annealed samples showed a remarkable improvement in definition, which could be attributed to recrystallization. That such recrystallization takes place at the temperature of annealing is supported by the observation made by Gheith (1952), in his work on the differential thermal analysis of iron oxides, that for natural magnetite there is a small exothermic peak at 380–395° C., which he considered to be due to the recrystallization of the finer particles.

Measurements on the films were carried out by means of a Thornton Heath precision instrument equipped with a travelling microscope. Duplicate measurements showed a precision of 0·02 mm. The diffraction lines were measured on either side of the entrance and exit holes of the X-ray beam, and as the Straumanis method of film mounting[3] was used, it was possible to apply accurately the 'shrinkage correction'.

The lattice parameters based on measurements of eight lines from 1·0922 to 0·9386 Å. (see table II) were extrapolated according to the method of Nelson and Riley[4]; the cell edge determined by this extrapolation was 8·3963 Å. (fig. 1).

Another photograph of the same specimen taken with nickel-filtered copper radiation (Cu-$K\alpha_1 = 1.5405$, Cu-$K\alpha_2 = 1.5443$, Cu-$K\alpha = 1.5418$ Å.), although slightly fogged owing to fluorescent radiation, gave the result of 8·3965 Å. for the cell edge, which, despite a small error, shows with what precision results can be duplicated. It was also

[1] Philips Techn. Review, 1948, vol. 10, p. 157 [M.A. 11–278].
[2] Amer. Min., 1951, vol. 36, p. 102 [M.A. 11–316].
[3] M. E. Straumanis, Journ. Appl. Physics, 1949, vol. 20, p. 726.
[4] J. B. Nelson and D. P. Riley, Proc. Phys. Soc., London, 1945, vol. 57, p. 160.

possible to duplicate the results when different samples from the same locality were similarly examined; a sample of Bisperg magnetite (British Museum, No. 89240) showed very little variation in results from those of the original chemically analysed sample. The complete measurements
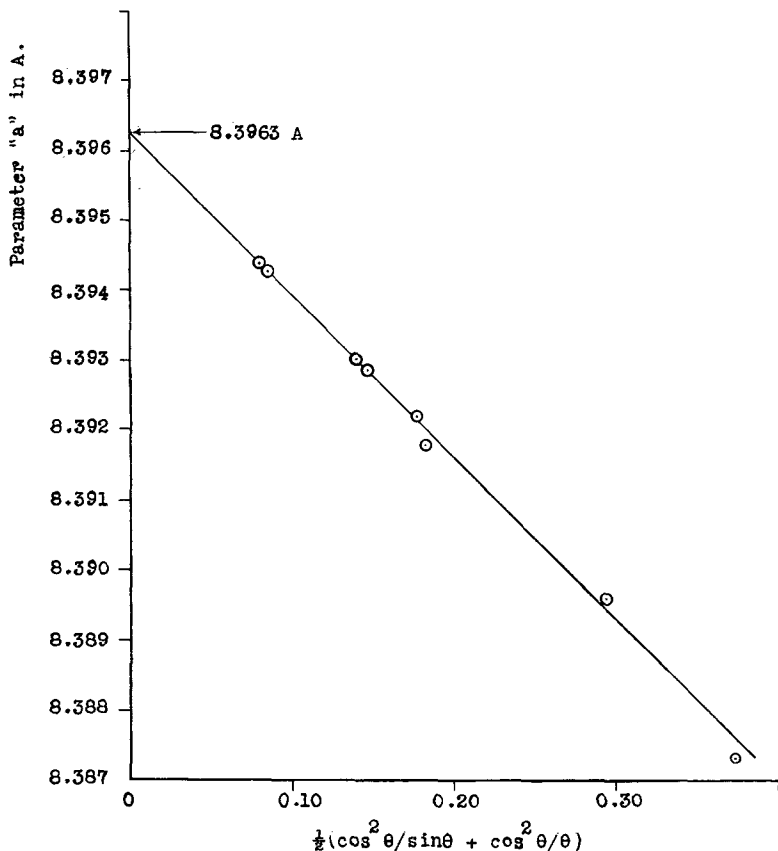

Fig. 1. Extrapolation for the accurate determination of the lattice parameter of Bisperg magnetite at 18° C.

of the X-ray powder pattern of the Bisperg magnetite are given in table II; the spacings recorded show fairly good agreement with the calculated data.

Errors in temperature are considered to be less than one degree, which in terms of the value of cell dimension amounts to an error of less than 0·0001 Å. The positive correction for refraction for magnetite is 0·0001 Å.,

calculated according to the method of Lipson and Wilson[1] (1941), and has been neglected. Taking into account factors of X-ray absorption, thermal expansion, sharpness of the lines, elimination of strain, and the like, the limit of error can be safely taken as 0·0005 Å.

Four other samples of practically pure magnetite from different localities, which have also been chemically analysed (table I, cols. 2

TABLE II. X-ray powder pattern of magnetite, Bisperg, Säter, Sweden; Co-$K\alpha$ radiation. Camera diameter 114·59 mm. Intensities estimated visually. a 8·3963± 0·0005 Å. Spacings are compared with those from the A.S.T.M. index card d 1–1120, recommended by the Joint Committee as the best data for magnetite. These data are given by J. D. Hanawalt, H. W. Rinn, and L. K. Frevel, Ind. Eng. Chem., 1938, vol. 10, p. 457.

I.	d(obs.)	hkl.	d(calc.)	$1-\frac{d}{1120}$	I.	d(obs.)	hkl.	d(calc.)	$1-\frac{d}{1120}$
mw	4·847	111	4·847	4·85	ms	1·0922α_1	553, 731	1·0930	1·09
s	2·966	220	2·968	2·97	mw	1·0489α_1	800	1·0495	1·05
vvs	2·530	311	2·532	2·53	vvw	0·9890α_1	660, 822	0·9895	—
vvw	2·419	222	2·423	2·42	vvw	0·9890α_2	660, 822	0·9895	—
s	2·096	400	2·098	2·10	mw	0·9692α_1	555, 751	0·9695	0·97
ms	1·712	422	1·714	1·71	w	0·9692α_2	555, 751	0·9695	0·97
vs	1·614	333, 511	1·616	1·61	w	0·9386α_1	840	0·9387	0·94
vs	1·483	440	1·484	1·48	vw	0·9386α_2	840	0·9387	—
vw	1·327	620	1·328	1·33	mw*	0·8794α_1	931	0·8800	0·88
w	1·279	533	1·281	1·28	m*	0·8565α_1	844	0·8589	0·86
vvw	1·264	622	1·266	—	w*	0·8565α_2	844	0·8589	0·85
vw	1·2112	444	1·2120	1·21	mw*	0·8113α_1	951	0·8115	0·81
w	1·1214	642	1·1220	1·12	vw*	0·8113α_2	951	0·8115	0·81

* Measurements of these five lines were obtained from a photograph taken with Cu-$K\alpha$ radiation.

to 5), were examined in the same way and the values of their lattice parameters were found to range from 8·3960 to 8·3970 Å. In view of the fact that the Bisperg magnetite was the purest sample examined, it is proposed to take its value, 8·3963±0·0005 Å., as representative of pure magnetite until such time as a purer specimen is measured.

Discussion.

Analyses of natural magnetites show that they frequently contain other cations, which may substitute either the divalent or the trivalent iron and may modify the cell dimensions. Table III shows that among the divalent elements that may enter the crystal structure of magnetite, only Mn^{2+} has an ionic radius greater than that of Fe^{2+}, while all the trivalent elements have an ionic radius less than that of Fe^{3+}. From the table it is clear that the cell dimensions of magnetite are increased only when replacement by Mn^{2+} or Ti^{4+} takes place; the cell-edge values of the spinels $MnFe_2O_4$ and Fe_2TiO_4 thus formed are 8·51

[1] H. Lipson and A. J. C. Wilson, Journ. Sci. Instr., 1941, vol. 18, p. 144.

and 8·50 Å. respectively (Bénard and Chaudron, 1937; Pouillard, 1949). However, manganese is rarely present in appreciable amount and natural magnetite ores usually contain less than 3 % MnO corresponding to 10 % $MnFe_2O_4$. Ulvöspinel, Fe_2TiO_4, on the other hand, has been shown

TABLE III. Ionic radii of the elements that may enter the crystal structure of magnetite, and the cell dimensions (in Å) of the spinels thus formed (various authorities).

Metal.	Ionic radius.	Al^{3+} 0·57.	Cr^{3+} 0·64.	Fe^{3+} 0·67.	Ti^{4+} 0·64.
Ni^{2+}	0·78	a 8·05	a 8·30	a 8·36	—
Mg^{2+}	0·78	8·07	8·31	8·37	—
Co^{2+}	0·82	8·08	8·32	8·38	—
Zn^{2+}	0·83	8·07	8·30	8·40	—
Fe^{2+}	0·83	8·12	8·34	8·40*	a 8·50
Mn^{2+}	0·91	8·26	8·49	8·51	—

* The value of cell edge for magnetite as determined in this paper, simplified to three significant figures.

TABLE IV. Chemical analyses of some substituted magnetites and their cell dimensions.

	1.	2.	3.		1′.	2′.	3′.
FeO	42·33	21·83	12·75	$FeFe_2O_4$	33·18	39·9	35·1
MgO	2·07	7·18	0·91	$MgFe_2O_4$	4·67	28·8	4·6
MnO	0·72	1·82	0·18	$MnFe_2O_4$	2·31	6·0	—
CaO	—	0·94	0·76	$CaFe_2O_4$	—	3·7	2·4
Fe_2O_3	26·88	57·11	80·63	γ-Fe_2O_3	—	—	53·0
Al_2O_3	0·40	3·62	0·30	$MgAl_2O_4$	—	5·1	—
V_2O_3	—	0·10	0·12				
Cr_2O_3	—	0·01	0·01	Fe_2TiO_4	32·48	10·3	—
TiO_2	24·86	6·98	2·54	γ-$FeTiO_3$	27·36	6·2	4·9
SiO_2	2·64	0·38	0·84				
	99·90	99·97	99·04		100·00	100·0	100·0

1. Titanomagnetite separated from basalt, Giant's Causeway, Ireland. Anal. W. H. Herdsman. $a = 8·4697 \pm 0·0005$ Å.

2. Titanomagnetite from Magnet Cove, Arkansas, U.S.A. Anal. H. B. Milner. $a = 8·3960 \pm 0·001$ Å.

3. Magnetite-maghemite separated from basalt, Co. Antrim, Ireland. Anal. H. B. Milner. $a = 8·369 \pm 0·001$ Å.

1′, 2′, 3′ are the percentages of the end-members calculated from the analyses 1, 2, and 3.

to be more common than had previously been supposed (Basta, 1953; Ramdohr, 1953; Vincent and Phillips, 1954). The present author, working on carefully separated homogeneous titanomagnetites from volcanic rocks, has found up to 32·5 % Fe_2TiO_4 (table IV, col. 1), a substitution that results in a continuous increase in the cell dimensions.

Replacements of Fe^{2+} or Fe^{3+} in magnetite by other divalent or

trivalent ions, e.g. Mg^{2+}, Co^{2+}, Ni^{2+}, Al^{3+}, and Cr^{3+}, also occur, but the effect in these cases is a decrease in the cell dimensions of magnetite. Exceptionally up to 8 % MgO (table IV, col. 2) and up to 7 % Al_2O_3 have been recorded in the analyses of magnetites, but such values are uncommon. Contents of ZnO, NiO, CoO, and Cr_2O_3 are usually too low to influence the cell-edge value of natural magnetite significantly. Zn reported by Vincent and Phillips (1954) in their analyses of magnetites from the Skaergaard intrusion, East Greenland, did not exceed 0·2 %; Schmidt and Vermaas (1955) determined 1·76 % NiO in one of their specimens of magnetite from Witbank, S. Africa; Cr_2O_3 is usually less than 0·5 %. V_2O_3 rarely exceeds 2 %, corresponding to a replacement of less than 3 % of the Fe^{3+} ions by V^{3+}, but its effect on the cell dimensions is not known. Another possibility leading to a decrease in the size of the unit cell of natural magnetites is partial oxidation to maghemite ($a = 8\cdot32$ Å.). In an unpublished study (Basta, 1953), the author was able to prove, by chemical and X-ray analyses, the existence in nature of minerals intermediate in composition between Fe_3O_4 and γ-Fe_2O_3; one of the analyses is given in table IV, col. 3.

Since several substitutions are possible, some increasing and some decreasing the cell dimensions, it is impossible to deduce the chemical composition of natural magnetite from the cell dimensions alone; even if the unit cell has the size of that of pure Fe_3O_4 there may be substantial substitutions, as in the Magnet Cove titanomagnetite (table IV, col. 2).

Variations in the chemical composition and cell edge of naturally occurring magnetite may account for the considerable differences in its physical properties reported in the literature; thus figures for the specific gravity vary between 4·96 and 5·3. From the present X-ray data on the Bisperg magnetite, its specific gravity was calculated as 5·192.

Literature data for the cell dimensions of artificial magnetite show marked variations (table V).

The values given by earlier workers up to 1940 may not be quite as precise as indicated, for at the time when these measurements were made the nature of the systematic errors was not fully known, the wavelength values assumed for the various radiations differ appreciably from the present values, and the cited lattice parameters were usually averages of the values calculated from all the lines of both low and high angle θ. Thus the measurement of Clarke, Ally, and Badger (1931), which is that given in the 7th edition of Dana's System of Mineralogy[1]

[1] C. Palache, H. Berman, and C. Frondel, Dana's System of Mineralogy, 7th edn, New York, 1944, vol. 1, p. 698.

and in Wyckoff's Crystal Structures[1], requires revision. In their original paper, the value of $8\cdot374\pm0\cdot003$ Å. was obtained from measurements with a scale reading directly in lattice spacings. The two values listed in table V were obtained by conversion, firstly to Ångstrom units from the wave-length 0·712 [kX] quoted for the Mo radiation used, secondly from the wave-length 0·70783 kX then known for Mo-K, by which the scale may have been calibrated. The exceptionally high value obtained by Van der Marel (1951) is most probably owing, as the author himself indicated, to the presence of impurities, possibly Na, in his

TABLE V. Cell edge of Fe_3O_4 (Å.).

Holgersson (1927)	8·434
Clarke, Ally, and Badger (1931)	$8\cdot361\pm0\cdot003$ or $8\cdot389\pm0\cdot003$
Hägg (1935)	8·397
Gaglioti and D'Agostino (1936)	8·427
Bénard (1939)	$8\cdot390\pm0\cdot002$
Frank-Kamenecky (1939)	8·437
Pouillard (1949)	8·413
Van der Marel (1951)	$8\cdot441\pm0\cdot004$
Tombs and Rooksby (1951)	$8\cdot3940\pm0\cdot0005$
Abrahams and Calhoun (1953)	$8\cdot3940\pm0\cdot0005$
Basta, on Bisperg magnetite, this paper	$8\cdot3963\pm0\cdot0005$

samples, which were prepared by precipitation. Michel (1937, p. 37) has found that up to 7 % of the Fe^{2+} ions of synthetic magnetites may be replaced by Na^+ and Fe^{3+}, a replacement that causes the cell dimensions to rise from 8·41 to 8·43 Å.

An important possibility that may account for the distinct range of 8·36 to 8·44 Å. in values of the cell edge obtained by different workers on artificial preparations is the presence of oxygen in excess of the stoichiometric formula requirements, as has already been mentioned in the case of natural magnetite. Hägg (1935) found that magnetite, when oxidized at up to 300° C., may vary continuously in composition from Fe_3O_4 to $Fe_{8/3}O_4$, i.e. to γ-Fe_2O_3, the cell edge decreasing uniformly from 8·40 to 8·32 Å. Furthermore, from the work of Greig and his co-workers (1935), magnetite is capable of containing about 30 % Fe_2O_3 at 1452° C.; the product gives an X-ray powder pattern of the spinel type but with a value of the cell edge slightly lower than that of pure Fe_3O_4. The artificial preparations of Fe_3O_4 on which the cell dimensions quoted in table V were measured were made either from slags, the so-called hammer-scale (Holgersson, 1927); or by heating at up to 1300° C. preparations containing Fe^{2+} and Fe^{3+} in the atomic

[1] R. W. G. Wyckoff, Crystal Structures, 1952, vol. 2, New York.

ratio 1:2 (Clark, Ally, and Badger, 1931); or by reducing hematite at high temperatures, up to 1400° C., with hydrogen. In none of these preparations was a check made on the $Fe^{2+}:Fe^{3+}$ ratio after heating. An increase of oxygen, i.e. a decrease in iron beyond the formula require-ment, may well have occurred, and may be the reason for the low values of the cell edge as observed in some of the preparations. Starke (1939) sought to explain the relation of the structure of synthetic magnetite to its stability by assuming that the unit cell of precipitated magnetite contains: 16 Fe^{3+}, $5\frac{1}{3}$ Fe^{2+}, $26\frac{2}{3}O^{2-}$, $5\frac{1}{3}OH^-$, and not $16Fe^{3+}$, $8Fe^{2+}$, $32O^{2-}$, as in the case of the high-temperature magnetite.

Recalculation of the chemical analysis of the Bisperg magnetite (table I, col. 1′) gave the formula $Fe^{2+}_{1\cdot024}Mg^{2+}_{0\cdot010}Fe^{3+}_{1\cdot984}O_{4\cdot000}$; the ratio of total cations to oxygen was 3·018:4·000, which shows that such a magnetite is free from vacant cation positions. Similar calculations on the four other new analyses in table I led to the same conclusion.

Another factor that may influence the cell dimensions of magnetite is the possibility of cation rearrangement. The equality of the scattering power of Fe^{2+} and Fe^{3+} makes it impossible to decide from the X-ray data whether magnetite is a normal spinel, $X^{2+}Y^{3+}_2O_4$, with divalent atoms in the eightfold and trivalent in the sixteenfold positions, or an inversed spinel, $Y^{3+}(X^{2+}Y^{3+})O_4$, with trivalent atoms in the eight-fold positions and the sixteenfold positions divided between di- and trivalent atoms.

Verwey and De Boer (1936) assigned magnetite to the inversed group on account of its high electrical conductivity, and Verwey and Heil-mann (1947) arrived at the same conclusion from a consideration of the cell dimensions of a large number of spinels.[1]

It is possible that at high temperatures there is a more random distribution of the cations, or that a partial change to the normal spinel structure takes place. If this is so, small variations in the cell dimensions of pure Fe_3O_4 may occur after heating, varying with the temperature attained and the rate of cooling; further work is needed to test this suggestion. A change in the cation arrangement at high temperatures has been found for some other members of the spinel group ($AlFe_2O_4$, Verwey, Hayman, and Raneijn, 1947; $MnFe_2O_4$, McAndrew, 1952).

[1] Verwey and Heilmann found that normal ferrites generally have a unit cell about 0·12 Å., larger than that of the corresponding chromites, while for inversed ferrites the increase is only about 0·05 Å.; for the pair $FeCr_2O_4$–Fe_3O_4 the increase is 0·06 Å (see table III).

Conclusions.

The great variation among the reported cell dimensions of artificially prepared magnetites is mainly owing to the formation of defect structures with varying oxygen contents in excess of the formula requirements. Another possible cause of variation is change in the cation arrangement in the spinel structure of magnetite at high temperatures, depending on the method of preparation.

The Bisperg magnetite, which has the formula

$$Fe^{2+}_{1\cdot024}Mg^{2+}_{0\cdot010}Fe^{3+}_{1\cdot984}O_{4\cdot000},$$
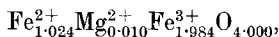
is substantially free from defect structures, and from accurate X-ray determinations carried out on annealed specimens free of crystal distortion the following result was obtained for its cell edge and is suggested to be the best known value for pure natural magnetite: a at $18°$ C. $= 8\cdot3963\pm0\cdot0005$ Å.

An appreciable increase in the cell dimensions of natural magnetite above this value probably indicates the presence of Fe_2TiO_4 or $MnFe_2O_4$ in solid solution, while an appreciable lowering of the above value may indicate partial oxidation to γ-Fe_2O_3. Other substitutions of Fe^{2+} or Fe^{3+} in the magnetite lattice by Mg^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cr^{3+}, Al^{3+}, or V^{3+} occur but they are of minor importance, either because the cell dimensions of the resultant spinel are not much different from those of pure magnetite or because the extent of substitution is very limited in natural ores. In all cases it is impossible to predict the exact composition from cell dimensions alone.

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