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The crystal structure and refinement of ferrimagnetic barium ferrite, $BaFe_{12}O_{19}$*

By **W. D. Townes, J. H. Fang** ** and **A. J. Perrotta**

Institute for Exploratory Research, U. S. Army Electronics Command
Fort Monmouth, New Jersey

Dedicated to Prof. Dr. G. Menzer on the occasion of his 70th birthday

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Auszug

Die Kristallstruktur von $BaFe_{12}O_{19}$ wurde bestimmt und dreidimensional verfeinert. Die Raumgruppe ist $P6_3/mmc$; die Elementarzelle, mit $a = 5{,}893$ Å, $c = 23{,}194$ Å, enthält zwei Formeleinheiten. Die Struktur ist aufgebaut aus kubischen und hexagonalen dichtesten Kugelpackungsschichten mit der Folge *BAB'ABCAC'AC* in Richtung der c-Achse. (Die gestrichenen Buchstaben deuten Schichten im Verhältnis von einem Ba-Atom zu drei O-Atomen an.) Die Verfeinerung beruht auf 900 beobachteten Interferenzen; sie wurde bis $R = 0{,}059$ getrieben. Das Ergebnis führte zur Bestätigung der Isotypie mit Magnetoplumbit $PbFe_{12}O_{19}$. Das Anionengerüst zeigt beträchtliche Störung der dichtesten Packung. Die Struktur ist ungewöhnlich in zweierlei Hinsicht. Erstens: Eisenatome, die ihrer Anzahl nach auf den horizontalen Spiegelungsebenen liegen sollten, sind daraus um 0,156 Å, statistisch in beiden c-Richtungen, herausgerückt. Zweitens: Einige Oktaeder um Fe-Atome kommen in Paaren mit gemeinsamer Fläche vor; sie bilden Koordinationsgruppen Fe_2O_9, in denen der Fe—Fe-Abstand um 0,45 Å vergrößert, der O—O-Abstand um 0,35 Å verkleinert ist. Eine beachtenswerte Ausnahme von einigen Pauling-Regeln.

Abstract

The crystal structure of barium ferrite, $BaFe_{12}O_{19}$, has been determined and refined with the use of three-dimensional counter data. The symmetry is $P6_3/mmc$; the unit cell whose dimensions are $a = 5.893$ Å and $c = 23.194$ Å, contains two formula units. The structure is built up of ten close-packed (both cubic and hexagonal) layers of barium and oxygen atoms. The sequence of the layering in

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** Permanent address: Department of Geology, Southern Illinois University, Carbondale, Illinois.

the c axial direction is $BAB'ABCAC'AC$. The primed letters denote layers consisting of one barium to three oxygen atoms. The refinement was based on 900 observed reflections and was taken to a final R value of 5.9%. The result confirmed the isotypic relationship with magnetoplumbite, $PbFe_{12}O_{19}$. The anion framework was found to be significantly distorted from close-packed geometry. The structure is unusual in two respects: (1) one set of iron atoms, which are on the horizontal mirror planes, is in trigonal-bipyramidal coordination. This iron atom is split into two half atoms 0.156 Å away from the mirror plane, and (2) some iron octahedra occur in pairs which share a common face to form Fe_2O_9 coordination groups. The distortion that occurs in these groups increases the Fe—Fe distance by 0.45 Å, while the decrease in the O—O distance in the shared face is 0.35 Å. The compound is a notable exception to some of Pauling's rules.

Introduction

Barium ferrite ($BaFe_{12}O_{19}$) has a mixed hexagonal and cubic close-packed structure, with a barium atom substituting for an oxygen position, and iron atoms occupying interstices. It is one of the so-called hexagonal ferrites (ferroxdure) which have been extensively studied in recent years because of their high coercive force as compared with the well-known cubic ferrites (ferroxcube).

Kohn and Eckart (1964 *a*, *b*; 1965) of this laboratory have discovered a number of hexagonal ferrite mixed-layer structures, most of which are based on the M phase ($BaFe_{12}O_{19}$) and Y phase ($Ba_2Me_2^{2+}Fe_{12}O_{22}$). Braun (1957) has refined the structure of the Y phase; however, no refinement of the M phase has been carried out. Therefore, it was decided to undertake the refinement of the crystal structure of the M phase in order to establish a basis for further analysis in the mixed-layer structures and also to aid in the magnetic study of the M phase where iron is partially substituted by other transition elements. A least-squares refinement using counter data was thought desirable, permitting the determination of more accurate atomic positions.

Unit cell and space group

Precise lattice parameters for the hexagonal unit cell were determined with the General Electric single-crystal orienter using Mo$K\alpha$ radiation, a 0.02 degree detector slit and a 1.0 degree take-off angle. The wavelength of Mo$K\alpha_1$ was taken to be 0.70926 Å. Values from four $h0\cdot0$ reflections in the range $33° < \theta < 57°$ were extrapolated against the Nelson-Riley (1945) function to obtain $a = 5.893$ Å, and a similar extrapolation based on six $00\cdot l$ reflections in the range $44° < \theta < 72°$ yielded a value of $c = 23.194$ Å. Laue and Weissenberg photographs were consistent with the space groups $P\overline{6}_3mc$, $P62c$, and $P6_3/mmc$. The subsequent refinement of the structure has justified the choice of the centrosymmetric space group $P6_3/mmc$.

Collection and corrections of intensity data

Two sets of intensity data were collected. Both sets were counter data measured with a G. E. XRD-6 diffractometer equipped with a Tl-activated NaI scintillation counter and pulse-height analyzer. Mo$K\alpha$ radiation was used to record reflections within $(\sin\theta)/\lambda = 1.186$. The first set of data was two dimensional, namely $h0\cdot l$ and $hk\cdot 0$, and a total of 578 reflections were measured by the stationary-crystal, stational-counter technique employing balanced filters. A constant counting rate of 40 seconds was employed. The $\alpha_1\alpha_2$ resolution was corrected by using a curve similar to that of Tulinsky *et al.* (1959). A standard reflection, $30\cdot 0$, was measured at the beginning of each day throughout the experiment. The day-to-day fluctuations in this reflection were found to be less than $4^0/_0$. Also a few equivalent reflections were measured, and their differences did not exceed $10^0/_0$. A second set of intensity data, which was three-dimensional, was measured by the moving-crystal, moving-counter technique, and a total of 900 reflections were collected.

The crystal used in this study was a sphere with a radius of 0.26 mm. The linear absorption coefficient is 155.9 cm^{-1}. The data were corrected for absorption and the usual Lorentz-polarization effect in order to obtain a set of structure factors.

Structure determination and refinement

Barium ferrite is isotypic with magnetoplumbite ($PbFe_{12}O_{19}$), whose structure has been determined by Adelsköld (1938) from powder data. The positional parameters reported by him were used as a starting point for the subsequent refinement. The scattering curve for Fe^{+3} was taken from the *International tables for x-ray crystallography* (1962) and for Ba^{2+} from Thomas and Umeda (1957); both were corrected for the real part of dispersion. The form factor for O^{2-} was obtained from Suzuki (1960).

The unusually large number of unobserved reflections (about 1/3 of all the reciprocal-lattice points within $2\theta = 115\,°$) can be attributed to the fact that the majority of the atoms are located at or near special positions of the type $(x, 2x, z)$ with $x = \frac{1}{3}$ and $\frac{1}{6}$. There was little or no contribution to reflections of the type $h-k = 3n$, $l = 2n + l$.

Table 1. *Final atomic coordinates and isotropic temperature factors*
Left columns are from three-dimensional data and right from two-dimensional data

Atom		Equipoint		x		y		z		B	
Ba	Ba	$2c$	$2c$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	$\frac{1}{4}$	.31(1) Å^2	.46(5) Å^2
Fe(1)	Fe(1)	$2a$	$2a$	0	0	0	0	0	0	.20(3)	.36(10)
$\frac{1}{2}$Fe(2)	Fe(2)	$4e$	$2b$	0	0	0	0	.2567(1)	$\frac{1}{4}$	.36(5)	1.30(11)
Fe(3)	Fe(3)	$4f$	$4f$	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	.0272(1)	.0272(2)	.21(2)	.44(7)
Fe(4)	Fe(4)	$4f$	$4f$	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	.1902(1)	.1901(2)	.22(2)	.35(7)
Fe(5)	Fe(5)	$12k$	$12k$	.1687(1)	.1691(5)	$2x$	$2x$	.1083(1)	.1082(1)	.23(1)	.41(3)
O(1)	O(1)	$4e$	$4e$	0	0	0	0	.1501(4)	.1499(14)	.29(10)	.07(38)
O(2)	O(2)	$4f$	$4f$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	.0546(4)	.0528(12)	.46(11)	.75(35)
O(3)	O(3)	$6h$	$6h$	.8159(10)	.8166(34)	$2x$	$2x$	$\frac{1}{4}$	$\frac{1}{4}$	.44(9)	.52(23)
O(4)	O(4)	$12k$	$12k$	.8447(7)	.8480(21)	$2x$	$2x$	.0522(2)	.0521(5)	.31(6)	.78(16)
O(5)	O(5)	$12k$	$12k$	.4967(8)	.4980(24)	$2x$	$2x$	.1495(2)	.1495(6)	.41(5)	.63(16)

Table 2. *Interatomic distances in* $BaFe_{12}O_{19}$

(*a*) Fe—O distances:		
Fe(1) octahedron	Fe—O(4)	1.995 ± 0.006 Å
Fe(4) octahedron	Fe—O(3)	2.060 ± 0.007
	—O(5)	1.975 ± 0.008
Fe(5) octahedron	Fe—O(1)	1.977 ± 0.005
	—O(2)	2.091 ± 0.006
	—O(4)	2.106 ± 0.004
	—O(5)	1.928 ± 0.005
Weighted-mean Fe—O octahedral distance: 2.012		
Fe(3) tetrahedra	Fe—O(2)	1.897 ± 0.011
	—O(4)	1.936 ± 0.009
Fe(2) trigonal bipyramids	Fe′—O(1)*	2.170 ± 0.011
	Fe″—O(1)	2.472 ± 0.011
	Fe′—O(3)	1.886 ± 0.010
	Fe″—O(3)	1.886 ± 0.010
(*b*) Ba—O distances:		
	Ba—O(3)	2.952 ± 0.001
	—O(5)	2.865 ± 0.006
(*c*) O—O distances:		
	O(1)—O(3)	2.982 ± 0.010
	—O(4)	2.769 ± 0.010
	—O(5)	2.947 ± 0.001
	O(2)—O(4)	2.949 ± 0.001
	—O(4)	3.049 ± 0.001
	—O(5)**	2.762 ± 0.011
	O(3)—O(3)	3.255 ± 0.017
	—O(3)	2.625 ± 0.017
	—O(5)	2.849 ± 0.006
	O(4)—O(4)**	2.746 ± 0.012
	—O(4)	3.147 ± 0.012
	—O(5)	2.896 ± 0.009
	—O(5)	2.872 ± 0.007
	O(5)—O(5)	2.888 ± 0.014
	—O(5)	3.005 ± 0.014
(*d*) Fe—Fe distances (within 3.5 Å):		
	Fe(1)—Fe(3)	3.460 ± 0.001
	—Fe(5)	3.045 ± 0.001
	Fe(3)—Fe(5)	3.495 ± 0.001
	Fe(4)—Fe(4)	2.778 ± 0.001
	Fe(5)—Fe(5)	2.910 ± 0.003
	—Fe(5)	2.983 ± 0.003

* If Fe(2) is on the mirror plane at $z = \frac{1}{4}$, then Fe—O(1) = 2.316 Å and Fe—O(3) = 1.893 Å. See the text for details.

** Denotes shared edges.

Table 3. *Observed and calculated structure factors*

h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$
2	0	0	1419	1548
3			2131	2327
4			1133	1146
6			3549	3820
8			605	578
9			925	860
10			415	426
12			1512	1624
1	1	0	2822	2864
4			1825	1801
7			1146	1185
10			788	809
4	2	0	923	907
5			1339	1310
6			665	644
8			2291	2355
10			332	376
11			563	576
3	3	0	1634	1679
6			1061	1060
9			742	834
4	4	0	3055	3266
6			517	517
7			785	804
8			370	397
5	5	0	980	1065
8			598	684
6	6	0	1728	2009
7	7	0	605	742
1	0	1	526	447
2			864	859
3			211	23
4			773	724
5			237	239
6			214	7
7			273	271
8			443	399
10			366	343
2	1	1	355	356
3			404	390
5			291	300
6			293	304
9			209	218
3	2	1	367	365
4			590	567
6			435	418
4	3	1	210	224
5			278	289
5	4	1	223	252
6			376	377
8			319	336
1	0	2	736	623
2			488	403
3			762	782
4			217	158
5			206	158
1	1	2	900	926
2			278	281
3			413	418
4			652	630
5			220	242
6			311	324
7			439	405
10			248	240
3	2	2	472	480
5			396	486
9			207	252
3	3	2	584	583
5			239	254
6			370	375
5	4	2	290	315
7			272	282
5	5	2	327	338
2	0	3	2259	2605
3			360	328
4			1886	1932
5			327	315
8			1048	987
9			289	265
10			802	788
4	1	3	212	204
5			322	212
8			224	181
4	2	3	1480	1529
5			269	283
6			1110	1127
7			257	249
4	3	3	255	272
6			213	199
6	4	3	866	902
7			268	232
8			639	728
1	0	4	442	353
3			2692	2846
4			331	301
5			318	291
8			213	166
9			1071	1079
10			214	176
1	1	4	2860	3454
2	1	4	363	335
3			284	286
4			2040	2165
5			270	271
7			1336	1369
8			203	218
10			893	925
3	2	4	205	211
4			296	247
5			1535	1611
6			245	197
7			213	225
3	3	4	1863	1973
4			255	268
6			1258	1267
7	4	4	965	996
5	5	4	1136	1194
2	0	5	2071	2209
4			1375	1342
5			217	206
10			458	434
2	1	5	249	241
3			221	236
5			221	253
4	2	5	1016	1016
6			714	711
5	3	5	210	229
6	4	5	537	542
8			345	389
0	0	6	1637	1709
1			768	285
2			1788	1855
3			612	545
4			1204	1126
5			287	235
6			793	716
8			547	558
9			201	213
10			380	396
12			251	227
1	1	6	777	663
2			370	325
3			215	148
4			402	328
2	2	6	1183	1139
4			890	863
5			249	258
6			605	612
7			214	155
8			470	397
3	3	6	325	244
4			220	164
6			203	185
4	4	6	651	603
6			485	496
8			319	367
6	6	6	334	314
1	0	7	2867	3050
2			401	323
4			217	147
5			1776	1766
7			1255	1233
11			730	781
2	1	7	2465	2604
3			2126	2187
5			1606	1585
6			1330	1339
8			1029	1031
9			872	904
3	2	7	1843	1882
7			1102	1099
9			781	843
4	3	7	1438	1475
5			1268	1261
7			934	984
8			815	872
5	4	7	1070	1112
6	5	7	857	914
7			801	812
0	0	8	2726	2922
1			877	973
2			382	316
3			348	381
4			263	141
5			853	793
6			1420	1361
7			211	152
9			201	177
11			441	438
12			586	603
1	1	8	532	421
2			1129	1067
3			713	665
4			371	343
5			620	566
6			320	276
7			256	239
8			475	433
9			251	211
2	2	8	2090	2079
3	2	8	443	395
5			321	274
7			583	546
8			897	863
3	3	8	353	330
4			660	637
5			398	348
6			229	216
7			365	345
4	4	8	1170	1175
5	5	8	208	200
6			456	450
7			277	248
6	6	8	708	739
1	0	9	517	576
2			1426	1446
4			1097	1014
5			453	398
7			267	282
8			510	503
10			364	376
2	1	9	583	531
3			501	492
5			397	407
6			327	342
8			243	262
9			218	247
3	2	9	397	417
4			835	801
6			583	586
7			278	242
4	3	9	372	354
5			310	351
7			223	276
5	4	9	229	262
6			429	451
8			298	338
6	5	9	207	201
0	0	10	262	364
1			356	496
2			1038	1048
3			828	790
4			814	722
5			505	466
6			235	224
8			448	393
9			343	309
10			376	338
11			248	289
1	1	10	972	938
2			627	550
3			434	407
4			699	679
5			398	397
6			209	216
7			512	494
8			313	321
10			339	317
2	2	10	252	214
3			273	265
4			629	564
5			511	495
6			486	435
7			351	352
3	3	10	656	667
4			411	414
5			245	283
6			414	416
7			242	279
4	4	10	211	214
6			407	370
7			298	289
5	5	10	434	457
6			293	311
6	6	10	222	256
1	0	11	1126	1140
4			2922	2947
5			815	750
7			522	487
8			1606	1570
10			1244	1226
11			341	335
2	1	11	1113	1025
3			952	899
5			746	724
6			582	586
8			520	498
9			405	432
3	2	11	764	749
4			2337	2361
6			1777	1765
7			483	484
9			294	307
4	3	11	666	659
5			577	604
7			440	499
8			345	372
5	4	11	458	449
6			1377	1432
6	5	11	426	417
7	5	11	379	419
1	0	12	341	428
2			1062	1127
3			1126	1075
4			895	793
5			393	348
6			202	228
8			463	410
9			468	468
10			399	376
11			204	184
1	1	12	1301	1240
2			547	471
3			341	286
4			894	875
5			286	244
7			609	581
8			238	187
2	2	12	347	313
4			683	617
5			744	686
6			527	482
7			282	240
3	3	12	833	809
4			315	280
5			222	155
6			529	543
7			200	152
6	4	12	435	390
7			425	429
5	5	12	490	501
6			234	193
2	0	13	1218	1192
4			900	832
5			365	368
8			521	476
10			412	372
2	1	13	413	416
3			318	323
5			301	301
6			205	207
8			223	204
3	2	13	270	252
4			721	662
6			549	498
4	3	13	279	312
5			212	221
6	4	13	434	437
1	0	14	559	587
2			2369	2505
3			797	730
4			1947	1860
6			2016	1936
7			448	431
8			1091	1064
9			360	312
10			813	811
1	1	14	929	834
2			440	377
3			498	480
4			678	628
5			329	306
6			400	405
7			476	451
9			254	295
2	2	14	2751	2810
3			529	528
4			1978	1524
5			503	479
6			1202	1158
8			1232	1258
9			299	327
3	3	14	634	607
5			315	337
8			261	309
4	4	14	1692	1693
5			373	390
6			937	967
7			328	290
5	5	14	382	409
1	0	15	994	915
5			618	571
7			494	477
11			217	215
2	1	15	853	801
3			785	763
5			623	603
6			558	546
8			427	400
9			402	410
3	2	15	708	677
7			313	349
9			319	322
4	3	15	513	512
5			532	541
7			426	430
8			345	368
5	4	15	461	442
6	5	15	299	305
0	0	16	1348	1315
2	0	16	375	354
3			1282	1217
4			282	240
6			726	680
9			550	542
1	1	16	1471	1398
4			1081	1024
7			738	728
2	2	16	1044	993
4			231	193
5			778	794
8			401	405
3	3	16	980	976
6			620	658
4	4	16	598	588
7			491	507
5	5	16	600	658
1	0	17	598	591
2			1291	1214
4			1012	977
7			408	368
8			593	559
9			232	218
10			463	452
2	1	17	432	371
3			457	404
5			259	226
6			358	312
9			266	232
3	2	17	494	445
4			858	821
5			206	218
6			634	639
5	3	17	265	234
8			271	271
5	4	17	344	334
6			521	514
1	0	18	1561	1358
3			2049	2010
5			892	841
7			795	758
9			998	988
11			415	453
1	1	18	2326	2260
2			1281	1136
3			1168	1074
4			1732	1663
5			895	820
6			787	768
7			1198	1154
8			581	580
9			525	531
3	2	18	1069	1019
5			1351	1356
7			552	583
3	3	18	1565	1547
4			816	744
5			727	707
6			1085	1106
7			567	565
8			495	520
5	4	18	681	681
7			907	918
5	5	18	964	1010
6			487	523
2	0	19	960	853
4			731	686
8			378	380
10			276	289
4	2	19	621	575
6			433	439
6	4	19	358	342
0	0	20	2917	2799
1			496	486
3			418	396
5			375	350
6			1641	1549
7			257	251
11			228	212
1	1	20	510	448
2			440	437
3			367	358
4			408	372
5			282	278
6			243	241
7			302	309
8			229	211
2	2	20	2239	2151
3			331	329
5			269	271
7			263	258
8			1015	1011
3	3	20	371	389
4			315	293
5			208	218
6			238	245
7			211	182
4	4	20	1348	1365
5			238	231
5	5	20	250	304

Table 3. *(Continued)*

h	k	l	$\|F_o\|$	$\|F_c\|$
6	5	20	233	219
1	0	21	1448	1271
2			224	234
4			220	200
5			842	815
7			799	771
2	1	21	1214	1102
3			1146	1068
5			884	838
6			815	814
8			570	568
9			594	608
3	2	21	1050	1010
4			220	187
7			524	525
4	3	21	756	731
5			748	766
7			594	603
5	4	21	717	715
6			211	188
6	5	21	437	457
0	0	22	2109	2012
1			452	388
2			1087	947
3			358	328
4			869	790
6			1312	1237
7			388	379
8			541	528
10			407	395
1	1	22	422	357
2			237	223
3			323	332
4			301	292
6			338	321
7			207	213
2	2	22	1735	1640
3			425	413
4			768	691
5			266	234
6			562	548
8			836	856
3	3	22	297	287
5			229	237
6			205	189
4	4	22	1094	1108
5			331	340
6			494	482
1	0	23	476	447
4			356	357
5			443	444
7			208	190
8			230	209
2	1	23	496	486
3			390	389
5			364	369
6			262	246
8			272	277
3	2	23	302	304
4			299	307
6			239	250
7			284	333
4	3	23	379	391
5			257	272
7			230	237
0	0	24	1297	1171
1			279	269
2			609	640
3			508	516
4			530	559
6			856	777
7			229	184
8			375	391
9			230	253
10			340	371
1	1	24	610	565
3			231	213
4			474	457
7			344	339
2	2	24	1073	973
3	2	24	224	211
4			495	489
5			351	368
6			410	431
8			615	618
3	3	24	451	443
6			289	305
4	4	24	753	725
5			220	175
6			364	382
5	5	24	283	303
1	0	25	953	827
2			2875	2699
4			2349	2295
5			749	681
7			477	435
8			1517	1489
10			1164	1197
2	1	25	916	811
3			795	737
5			694	667
6			574	537
8			490	517
3	2	25	700	624
4			2073	2008
6			1582	1632
7			499	499
4	3	25	626	625
5			538	577
7			481	514
5	4	25	429	413
6			1377	1382
0	0	26	496	305
1			416	340
2			385	406
3			240	250
4			401	339
5			304	290
6			309	261
7			218	173
1	1	26	285	282
2			345	336
3			349	307
4			200	236
5			290	286
6			248	220
8			215	235
2	2	26	357	281
3			302	259
7			220	229
3	3	26	233	246
4			257	272
5			252	244
7			201	226
4	4	26	261	262
1	0	27	589	544
5			503	461
7			314	307
2	1	27	585	535
3			520	478
5			438	422
6			340	347
8			291	307
3	2	27	443	421
7			315	332
4	3	27	417	411
5			328	352
7			277	289
5	4	27	292	285
0	0	28	1978	1832
2			331	300
4			283	257
5			437	432
6			1270	1271
8			208	192
1	1	28	231	207
2			417	385
5			320	299
8			292	306
2	2	28	1687	1582
4	2	28	229	235
6			210	179
7			382	403
4	3	28	382	389
4	4	28	1121	1164
1	0	29	1149	1046
5			844	791
7			709	707
2	1	29	1066	964
3			1007	925
5			849	783
6			763	741
8			574	577
3	2	29	910	879
7			562	573
4	3	29	712	723
5			714	710
5	4	29	665	663
0	0	30	979	927
1			389	333
2			288	236
3			216	230
4			237	200
5			287	278
6			632	597
1	1	30	247	258
2			342	323
3			264	303
5			294	278
6			216	226
2	2	30	863	790
3			265	263
7			224	215
3	3	30	214	239
4			269	262
5			234	243
4	4	30	522	524
1	0	31	321	330
2			1029	942
4			894	822
5			274	269
7			289	276
8			534	524
10			359	403
2	1	31	302	294
3			305	276
5			278	228
6			239	235
3	2	31	299	293
4			743	724
6			559	584
7			226	237
4	3	31	247	242
5			232	197
5	4	31	271	255
0	0	32	329	261
1			511	467
2			369	292
3			1632	1501
4			219	270
5			388	364
7			347	315
9			916	938
1	1	32	1729	1587
2			476	431
3			457	418
4			1454	1357
5			390	360
6			327	327
7			1049	1078
2	2	32	233	226
3			411	400
5			1184	1190
6			213	232
3	3	32	1305	1304
4			327	340
5			373	318
6			955	1034
5	4	32	308	285
2	0	33	557	521
4	0	33	489	465
8			316	317
4	2	33	415	417
6			312	358
0	0	34	602	566
1			349	306
2			884	800
4			803	714
6			400	391
7			295	281
8			513	519
2	1	34	257	234
3			298	280
5			211	207
6			283	263
2	2	34	513	493
3			331	309
4			664	653
6			532	544
5	3	34	229	226
4	4	34	326	355
1	0	35	282	278
2			482	542
4			525	519
8			457	468
3	1	35	243	261
5			210	222
6			200	222
3	2	35	208	244
4			481	500
6			446	475
5	3	35	222	223
0	0	36	2119	1979
1			208	173
2			1065	961
3			859	753
4			959	866
6			1504	1490
8			615	621
9			466	461
1	1	36	898	802
4			775	705
2	2	36	1837	1779
4			797	789
5			652	603
6			646	662
3	3	36	705	699
4	4	36	1338	1379
1	0	37	283	269
2			203	243
5			281	260
2	1	37	283	282
3			248	246
5			239	235
3	2	37	206	204
4	3	37	260	237
0	0	38	938	871
1			341	308
2			335	310
4			291	291
5			227	196
6			725	724
7			239	260
8			211	214
2	1	38	275	255
3			289	278
5			233	218
6			246	241
2	2	38	859	811
3			322	298
4			252	268
4	3	38	209	187
1	0	39	257	241
2			1364	1275
4			1196	1167
5			271	248
8			835	863
2	1	39	233	262
3			200	226
5			216	228
3	2	39	214	178
4			1040	1077
4	3	39	241	230
2	0	40	265	238
3			581	571
4			218	232
6			394	366
1	1	40	648	606
4			550	542
2	2	40	523	474
4			201	225
5			448	465
3	3	40	549	545
1	0	41	499	453
2			317	293
4			276	250
5			352	338
7			349	347
2	1	41	426	416
3			431	426
5			375	372
3	2	41	449	413
4			254	214
0	0	42	588	585
2			491	460
3			503	509
4			402	421
6			381	435
1	1	42	539	519
4			482	481
2	2	42	516	527
3	3	42	447	460
1	0	43	906	878
5			770	799
7			578	646
2	1	43	879	867
3			808	817
3	2	43	811	771
0	0	44	242	215
3			231	241
1	1	44	273	255
4			216	225
2	2	44	215	192
2	0	45	741	747
4			678	679
0	0	46	466	529
1			427	428
2			200	179
3			320	324
5			399	440
6			399	490
1	1	46	360	346
2			471	452
3			407	404
2	2	46	464	517
1	0	47	288	268
2			713	730
4			635	678
5			265	274
2	1	47	327	286
0	0	48	629	634
3			320	328
6			440	517
1	1	48	357	340
2	0	49	634	713
4			606	679
0	0	50	1195	1364
1			339	369
2			638	689
3			250	221
4			570	637
5			255	281
2	0	51	213	237
4			205	206
3	0	52	420	421
2	0	53	420	503
1	0	54	374	444
2			277	317

The two-dimensional data were used initially in the refinement. Using the full-matrix least-squares program of Busing *et al.* (1962), as translated to extended ALGOL by Gallaher and Kay (1964), convergence was achieved in 6 cycles using unit weight. The number of observed reflections per variable is about 15. In the last cycle, individual isotropic temperature factors were varied. The value of R was $11.7\,^0/_0$ for 395 observed reflections. The final parameters are given in the right columns of Table 1. As seen in the table, the temperature factors of all iron atoms are within a narrow range of 0.36 to 0.44, and that of oxygen from 0.52 to 0.75. Two exceptions are noted, however. They are: $B\,[\mathrm{Fe}(2)] = 1.30$ and $B\,[\mathrm{O}(1)] = 0.07$. This iron atom is in five-fold coordination, and O(1) atoms are equatorially bonded to Fe(2). When this paper was presented at the Austin meeting of the American Crystallographic Assocation on March 1966, Dr. David Harker pointed out that the Fe(2) atom might be disordered. At about the same time, two of us (A.J.P. and W.D.T.) had calculated the two-dimensional Fourier map and found that the Fe(2) peak was elongated along the *c* axis, supporting Dr. Harker's suggestion.

When the three-dimensional scan data became available, the refinement was initiated with the coordinates obtained from the two-dimensional refinement. Also the Fe(2) atom was moved 0.2 Å away from the horizontal mirror plane (from equipoint 2*b* to 4*e*, thus making them half atoms), the *R* factor dropped immediately, and the temperature factors of Fe(2) and O(1) also became very reasonable. The final *R* value for the 900 observed reflections was 5.9%. The parameters from the last cycle are given in the right columns of Table 1. The corresponding bond lengths, calculated from the three-dimensional refinement, are listed in Table 2. The observed and calculated structure factors are in Table 3.

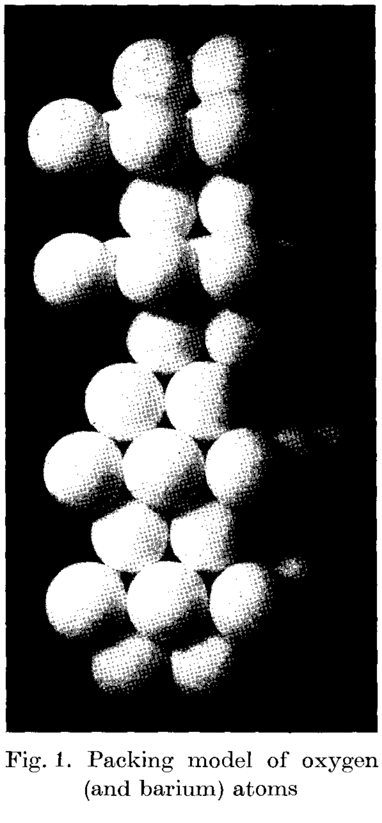

Fig. 1. Packing model of oxygen (and barium) atoms

Description of the structure

The structure of barium ferrite can be derived from that of magnetite. It might be visualized as composed of four double layers of oxygens, plus two single layers, in which $\frac{1}{4}$ of the oxygens are replaced by barium atoms. The latter two layers are interleaved between the first and the second, and the third and fourth double layers, delineating the magnetite block (the second and the third). These two layers are located at the horizontal mirror planes at $\frac{1}{4}c$ and $\frac{3}{4}c$. Figure 1 shows a packing model of oxygen (and barium) atoms. The iron atoms are in the octahedral and tetrahedral holes as in magnetite*, except for one set of iron atoms which are coordinated to five oxygens. Thus the unit cell contains eighteen octahedral, two trigonal bipyramidal, and four tetrahedral iron atoms. They are illustrated in Fig. 2. The packing of the oxygen atoms in the middle two double layers are cubic, and in the plates above and below the magnetite block, starting from the barium-containing layers, it is hexagonal close packing. Thus the notation, *BAB'ABCAC'AC*, can be used to denote the layer sequence along the c axis, where the primed letters indicate Ba-substituted layers.

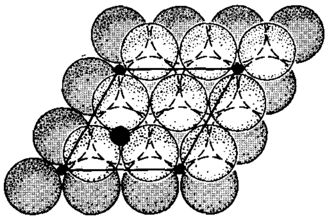

Fig. 2*a*. Bottom: *C* layer (belonging to the unit cell below). Top: *B* layer. Smaller solid circles are octahedral Fe atoms, and the larger tetrahedral iron

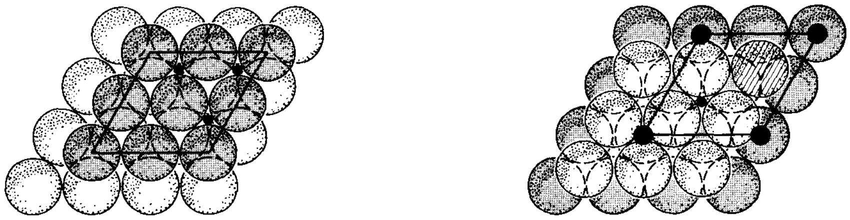

Fig. 2*b* Fig. 2*c*

Fig. 2*b*. Bottom: *B* layer (the same *B* as in Fig. 2*a*). Top: *A* layer

Fig. 2*c*. Bottom: *A* layer (the same *A* as in Fig. 2*b*). Top: *B'* layer. The small solid circles at the unit-cell corners are 5-fold Fe atoms

Fig. 2. A portion of layer stacking in $BaFe_{12}O_{19}$ showing 6-, 5-, and 4-fold coordinations of iron atoms in projection along the c axis

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* No distinction is made here to distinguish between normal and inverse spinel, for no divalent iron is involved. Thus "magnetite" structure, as used here, refers to the degree of filling of octahedral and tetrahedral interstices only.

There are two remarkable structural features in barium ferrite; namely the five-fold coordination of Fe(2) and the sharing of Fe(4) octahedral faces. These unusual coordinations can be seen clearly in the polyhedral model of Fig. 3. For the sake of clarity, however, four octahedra, at 0 0 0, 0 0 $\frac{1}{2}$, 1 1 $\frac{1}{2}$, and 1 1 1, are omitted from the drawing. Both of these unusual configurations are brought about by the mirror planes at $\frac{1}{4}c$ and $\frac{3}{4}c$. In the Fe_2O_9 coordination group, there are two Fe(4) atoms, three O(3) atoms in the shared face, and six O(5) atoms in layers of three, above and below the Fe(4) atoms. The theoretical and observed distances between the octahedral centers are shown in Table 4. The per cent shortening of 0.71 and 0.58 are given by Pauling (1960, p. 560). The last column shows the percentage distortion due to cation-cation repulsion from the

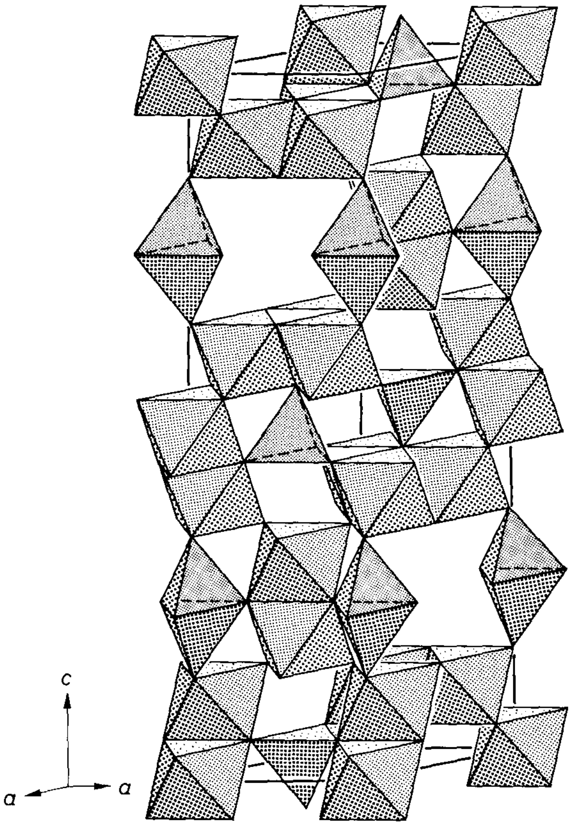

Fig. 3. Polyhedral model of $BaFe_{12}O_{19}$

Table 4. Fe—Fe *distances for octahedra sharing various elements*

Shared element	Theoretical distance	Observed distance	Distortion
Corner*	$4.00 \times 1.00 = 4.00$ Å	$4.00 \times 1.00 = 4.00$ Å	0%
Edge	$4.00 \times 0.71 = 2.84$	$4.00 \times 0.74 = 2.97$	4%
Face	$4.00 \times 0.58 = 2.32$	$4.00 \times 0.69 = 2.77$	19%

* Not observed in $BaFe_{12}O_{19}$.

undistorted polyhedra. Since no octahedra share corners in barium ferrite, the theoretical Fe—Fe distance is obtained by using Pauling's octahedral radii or $r(Fe^{3+}) = 0.60$ Å and $r(O^{2-}) = 1.40$ Å. The compensating distortion increases almost five times as polyhedra goes from edge-sharing to face-sharing. This trend is also found to be the case in hexagonal barium titanate (BURBANK and EVANS, 1948).

The O—O distances are all reasonable, except one short distance of 2.625 Å and one long distance of 3.225 Å. The shortest distance is exhibited by the O(3)—O(3) in the shared face, and the longest between the O(3) atoms not sharing the face. Looked at differently, the six oxygen atoms surrounding the central barium atom are not arranged as a regular hexagon, but rather as a truncated triangle, with short edges alternating with long edges, reminiscent of the Kekule's structure of benzene. On the average, the intralayer (same layer) O—O distances are slightly longer than the interlayer (between the layers above and below) distances, as exhibited in many close-packed structures. The charges surrounding the anions have been calculated and are listed in Table 5. It is noted that the charge surrounding the O(2) and O(4) are in excess of 10%, respectively. These two oxygen atoms make up the layers sandwiching the plane at $c = \frac{1}{2}$.

The disposition of Fe(2) atom can be described in two different ways. On the one hand, if the disorder of the iron atom is disregarded for the time being, the coordination is that of a trigonal bipyramid, with the Fe—O distance of 1.893 Å (equatorial) and 2.316 Å (apical). The trigonal bipyramidal coordination of Fe^{3+} is a unique feature of the *M* phase, not found in other hexagonal ferrites. Its bonding is usually designated as d^3sp with some dsp^3 hybrids. However, the lengthening of the apical Fe—O distances, indicating a localized ionic character, might considerably affect the nature of this hybrid bond.

On the other hand, as pointed out in the structure-determination section, the Fe(2) atom is split into two half-atoms with the Fe—Fe

Table 5. *Electrostatic-valency table*

Anion	Balancing cations	$\frac{\text{Charges of cation}}{\text{Coordination number}}$	$\frac{\text{Total charges}}{\text{surrounding anion}}$
O(1)	Fe(2)	$\frac{3}{5}$	2.10
	Fe(5)	$\frac{3}{6}$	
	Fe(5)	$\frac{3}{6}$	
	Fe(5)	$\frac{3}{6}$	
O(2)	Fe(3)	$\frac{3}{4}$	2.25
	Fe(5)	$\frac{3}{6}$	
	Fe(5)	$\frac{3}{6}$	
	Fe(5)	$\frac{3}{6}$	
O(3)	Ba	$\frac{2}{12}$	1.93
	Ba	$\frac{2}{12}$	
	Fe(2)	$\frac{3}{5}$	
	Fe(4)	$\frac{3}{6}$	
	Fe(4)	$\frac{3}{6}$	
O(4)	Fe(1)	$\frac{3}{6}$	2.25
	Fe(3)	$\frac{3}{4}$	
	Fe(5)	$\frac{3}{6}$	
	Fe(5)	$\frac{3}{6}$	
O(5)	Ba	$\frac{2}{12}$	1.67
	Fe(4)	$\frac{3}{6}$	
	Fe(5)	$\frac{3}{6}$	
	Fe(5)	$\frac{3}{6}$	

distance of 0.312 Å. Considered in this way, we have a case of two tetrahedra sharing a face, a clear violation of Pauling's third rule. Therefore the Fe(2) atom is either oscillating along the *c* axis or is statistically distributed on two sites displaced 0.156 Å from the central position on the mirror plane.

Since the magnetic properties of barium ferrite are of some interest, a speculation on its plausible magnetic structure is therefore in order. A theoretical value of $20\mu_B$ per formula unit can be obtained, for instance if Fe(1), Fe(2), and Fe(4) are coupled ferromagnetically, giving $+4\mu_B$, and between Fe(3) and Fe(5), giving $-20\mu_B$. But this spin arrangement would make the linear Fe(1)—O—Fe(2) coupling ferromagnetic, in violation of the superexchange interaction. Thus, a possibility arises that $\frac{1}{2}$ of Fe(3) and Fe(4), and $\frac{1}{6}$ of Fe(5) might couple ferromagnetically with Fe(2), still giving the net moment of $20\mu_B$, though the magnetic cell would then be doubled in this spin configuration.

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