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NEUTRON DIFFRACTION STUDIES OF SOME HEXAGONAL FERRITES: $BaFe_{12}O_{19}$, $BaMg_2$–W AND $BaCo_2$–W

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Neutron diffraction studies on powder samples have been carried out on the $BaFe_{12}O_{19}$ (M-type), $BaMg_2Fe_{16}O_{27}$ and $BaCo_2Fe_{16}O_{27}$ (W-type) room-temperature ferrimagnetic hexagonal ferrites. From high temperature data, above the Curie temperature (≈ 450–$500\,^\circ$C), we first determine the Mg^{2+} and Co^{2+} location among the seven sublattices of the W-type structure; these M^{2+} cations lie essentially in the octahedral and tetrahedral sites of the spinel S-blocks. From low temperature (4.2 K) data, we confirm, for the three compounds, the collinear Gorter model; the spin configuration is along the hexagonal c axis in the $BaFe_{12}O_{19}$ and $BaMg_2$–W compounds whereas it is a quasi-planar one in the $BaCo_2$–W compound, the angle of the magnetic moments with the c axis being 68.5°. The magnetic moments on each site of the M- and W-type structures are given and we compare the spontaneous magnetizations with the saturation ones.

1. Introduction

Hexagonal ferrites are a large family of hexagonal or rhombohedral ferrimagnetic oxides with interesting applications as permanent magnets, magnetic recording media or microwave devices materials and a lot of studies have been already reported [1,2]. Their crystal structures can be described by the superposition of some fundamental structural blocks formed by a close packing of hexagonal or cubic stacked layers with Ba(Sr, Pb)O_3 and O_4 composition; in this framework the metallic cations are located in octahedral, tetrahedral and five-fold coordination interstices.

The M-type $BaFe_{12}O_{19}$ hexaferrite, isotype to the mineral magnetoplumbite [3] was studied for the first time by Townes et al. [4]. The crystal structure (space group: $P6_3/mmc$) can be symbolically described with the ...R*S*|RSR*S*|RS... sequence, where R is a three-oxygen layer block and S is a two-oxygen layer block; the * symbol means that the preceding block is turned 180° around the hexagonal c axis by the 6_3 symmetry axis and the vertical lines limit the elementary cell ($a \approx 5.9$ Å, $c \approx 23.2$ Å) which contains two chemical formula units ($Z = 2$). Recently, Obradors et al. [5] gave an accurate analysis of the structural and dynamic properties of this compound from single crystal X-ray diffraction data at room-temperature. We sum up in table 1 the crystallographic and magnetic characteristics of the M-type $BaFe_{12}O_{19}$ hexaferrite.

The W-type hexagonal ferrites, the chemical formula of which is Ba(Sr)$M_2^{2+}Fe_{16}O_{27}$ ($M^{2+} = Fe^{2+}, Mg^{2+}, Zn^{2+}, Co^{2+}, \ldots$) have been studied for the first time by Braun [6] with the $BaFe_2^{2+}Fe_{16}^{3+}O_{27}$ compound ($BaFe_2$–W). The crystal structure (S.G.: $P6_3/mmc$) can be described with the $\ldots R\bar{S}|SR^*\bar{S}^*S^*R\bar{S}|SR^*\ldots$ sequence; the – symbol means that the corresponding block is deduced from the inversion operation and the elementary cell ($a \approx 5.9$ Å, $c \approx 33.0$ Å) contains also two chemical formula units ($Z = 2$). Recently the crystal structure and the magnesium and cobalt locations were given: from single crystal X-ray diffraction data at room-temperature for

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Table 1
Crystallographic and magnetic characteristics of the M-type $BaFe_{12}O_{19}$ hexaferrite

Cation	Position	Coordination	Block	Nb. ions per f.u.	Magnetic moment direction *
Fe1	2a	octahedral	S	1	up
Fe2	$4e \times 1/2$ (2b)	pseudo-tetra (five-fold)	R	1	up
Fe3	$4f^{IV}$	tetrahedral	S	2	down
Fe4	$4f^{VI}$	octahedral	R	2	down
Fe5	12k	octahedral	R–S	6	up

* According to the Gorter model [9].

the $BaMg_2Fe_{16}O_{27}$ compound ($BaMg_2$–W) [7] and from single crystal X-ray/neutron diffraction data at 20°C/510°C for the $BaCo_2Fe_{16}O_{27}$ compound ($BaCo_2$–W) [8]. The crystallographic and magnetic characteristics of the W-type hexagonal ferrites are summarized in table 2.

All these compounds are ferrimagnetic at room-temperature [1,2]. The magnetic structure model was suggested for the first time by Gorter [9] from the application of the Kramers–Anderson indirect exchange theory; all the magnetic moments are ordered along the hexagonal *c* axis, according to the schemes given in tables 1 and 2. This current model is in good agreement with the magnetic measurements of some compounds; by means of neutron diffraction, it was roughly checked on the Ba(Sr, Pb)$Fe_{12}O_{19}$M-type hexaferrites [10,11], however, the spin on-collinearity was mentionned for the $BaFe_{12}O_{19}$ compound [12,13]. About the W-type compounds, a local spin reversal was put toward in order to explain the decreasing of the experimental saturation magnetization with regard to the Gorter theoretical one in $BaZn_2Fe_{16}O_{27}$ [14] whereas a spin reorientation as a function of temperature was described by several authors in $Ba(Sr)Zn_{2-x}Co_xFe_{16}O_{27}$ [15–19].

The recent progress in the single crystal structure determinations and in the cations location in these structures, associated to high resolution neutron diffraction experiments together with a new crystallographic and magnetic refinement program, led us to determine, at low temperature ($T = 4.2$ K), the magnetic structure of $BaFe_{12}O_{19}$, $BaMg_2Fe_{16}O_{27}$ and $BaCo_2Fe_{16}O_{27}$ by using powder samples.

2. Experiments

Single phase polycrystalline samples were prepared from high temperature solid state reactions

Table 2
Crystallographic and magnetic characteristics of the W-type hexagonal ferrites

Cation	Position	Coordination	Block	Nb. ions per f.u.	Magnetic moment direction *
Me1	$4f \times 1/2$ (2d)	pseudo-tetra (five-fold)	R	1	up
Me2	$4f^{VI}$	octahedral	S	2	up
Me3	6g	octahedral	S–S	3	up
Me4	4e	tetrahedral	S	2	down
Me5	$4f^{IV}$	tetrahedral	S	2	down
Me6	$4f^{VI}$	octahedral	R	2	down
Me7	12k	octahedral	R–S	6	up

* According to the Gorter model [9].

of stoichiometric $BaCO_3$, Fe_2O_3, $MgCO_3$ or CoO raw materials; the mixtures, obtained by an accurate homogenizing process under ethanol using an agate mortar, were pressed as pellets, sintered in air at 1250°C–1320°C during one or two days with some intermediate grindings and finally quenched in air [20]. The purity of the samples was tested with long exposure X-ray Guinier patterns using FeKα radiation. The lattice parameters were obtained by least squares refinements of interplanar distances: $a = 5.887(2)$ Å and $c = 23.192(6)$ Å for $BaFe_{12}O_{19}$, $a = 5.906(1)$ Å and $c = 32.915(8)$ Å for $BaMg_2$–W, $a = 5.904(1)$ Å and $c = 32.910(7)$ Å for $BaCo_2$–W.

The neutron diffraction experiments were performed with the D1B multidetector set-up (400 detectors, 0.10° θ step) of the Institut Laue–Langevin; the wavelength of the incident neutron beam was: $\lambda = 2.519$ Å.

The crystallographic and magnetic structure refinements were carried out in the centrosymmetric $P6_3/mmc$ space group by using the MXD program [21].

3. High temperature study

3.1. $BaFe_{12}O_{19}$

The Curie temperature of this barium hexaferrite is $T_c = (450 \pm 1)$°C [22], so, the paramagnetic diagram was recorded at $T = 470$°C. The knowledge of the nuclear structure of that compound at this temperature was not essential for the understanding of its physical properties, but the results of the structural refinement enable us to check the new MXD program in comparison with the Rietveld one [23,24]; we determined, too, the high temperature isotropic thermal parameters. The knowledge of these values is essential for the refinement of the substituted cations location in the M-type structure because of the strong correlation between population and thermal parameter on the same site; owing to these values we gave the locations of manganese and chromium in the $Ba(Sr)Fe_{12}O_{19}$ substituted series [25,26].

Inside the (4°–140°) 2θ range, the powder diffraction diagram of $BaFe_{12}O_{19}$ contains 37 independent intensities corresponding to 78 Bragg reflections. The refinements of the 12 positional and 11 isotropic thermal parameters were carried out by means of either MXD program or Rietveld method; the neutron nuclear scattering amplitudes were: $b(Ba) = 0.52$, $b(Fe) = 0.95$ and $b(O) = 0.575$ given in 10^{-12} cm [27]. The results are reported in table 3; they are in good agreement with those determined at room-temperature from single crystal X-ray diffraction data [5]. However, we will notice the difference between the two z positional parameter values of the pseudo-tetrahedral Fe2 cation: $z_{\text{Neut.}} = 0.261(1)$, $Z_{\text{R.X}} = 0.25733(4)$; The Fe2 cation is much more displaced from the BaO_3 mirror plane ($d_{\text{Neut.}} = 0.26$ Å as compared to $d_{\text{R.X.}} = 0.17$ Å) reinforcing in this way the tetrahedral character of this site. Such a deviation was already observed in the R-type hexagonal structures as determined from powder neutron diffraction data: $d = 0.38$ Å in $BaFe_4Ti_2O_{11}$ [28]; $d = 0.24$ Å and $d = 0.28$ Å in $BaFe_4Ti_2O_{11}$ and $BaFe_4Sn_2O_{11}$, respectively [29]. We could explain the increasing of this Fe2-mirror plane distance by the fact that the neutrons interact with the nucleus of the atom whereas the X-rays interact with all the electrons and consequently the z positional parameter value is in fact the inertia center of the electronic cloud one; this assumption would mean that the electronic cloud is distorted towards the three O_3 oxygen anions, located in the BaO_3 mirror plane, which mark out the shared face of the two tetrahedra (see figs. 2–4 in ref. [5]). However, we have not to forget the strong correlation between the z positional and the B thermal parameters as previously observed [5] in this site.

3.2. W-type compounds

As said previously, the refinements of the W-type crystal structure and the Mg^{2+} or Co^{2+} locations were given recently from single crystal X-ray/neutron diffraction data [7,8]. Because of the difference between the synthesis processes of single crystals and powder samples, the checking of the bivalent cations populations was necessary; thus, the powder neutron diffraction diagrams were performed in the paramagnetic phase for the $BaMg_2$–W and $BaCo_2$–W compounds. The loca-

Table 3
Final positional and isotropic thermal parameters * as determined from neutron diffraction data at $T = 470\,^\circ C$ for the $BaFe_{12}O_{19}$ compound

Site	Atom	Position	x	y	z	$B(Å^2)$
	Ba	2d	2/3	1/3	1 /4	2.4(10)
						1.0(8)
VI(S)	Fe1	2a	0	0	0	0.7(6)
						1.3(4)
V(R)	Fe2	4e×1/2	0	0	0.261(1)	0.2(5)
					0.261(1)	0.2(5)
IV(S)	Fe3	$4f^{IV}$	1/3	2/3	0.0264(5)	1.2(4)
					0.0270(4)	1.0(2)
VI(R)	Fe4	$4f^{IV}$	1/3	2/3	0.1897(5)	0.7(4)
					0.1908(3)	0.4(3)
VI(R–S)	Fe5	12k	0.1667(8)	0.3334	−0.1081(3)	0.7(2)
			0.1671(5)	0.3342	−0.1080(1)	1.2(1)
	O1	4e	0	0	0.1510(9)	1.9(8)
					0.1492(5)	0.5(5)
	O2	4f	1/3	2/3	−0.0558(8)	0.8(6)
					−0.0547(7)	0.8(4)
	O3	6h	0.183(2)	0.366	1/4	0.5(5)
			0.181(1)	0.362		0.7(3)
	O4	12k	0.157(1)	0.314	0.0520(3)	1.0(3)
			0.1559(8)	0.3118	0.0517(2)	0.7(2)
	O5	12k	0.503(1)	1.006	0.1494(4)	1.0(3)
			0.5013(8)	1.0026	0.1491(2)	1.0(2)

* There are two values for each refined parameter: the first and the second ones are respectively given by the MXD (a) and Rietveld (b) programs.

(a) MXD program: $a = b = 5.929(1)$ Å, $c = 23.413(1)$ Å,

$$wR(\mathrm{LSQ}) = \left[\Sigma w^2 (I_{\mathrm{obs}} - I_{\mathrm{cal}})^2 / \Sigma w^2 I_{\mathrm{obs}}^2\right]^{1/2} = 2.2\%,$$

$$\chi^2 = \Sigma w^2 (I_{\mathrm{obs}} - I_{\mathrm{cal}})^2 / (N - P) = 1.8,$$

N = number of independent observations, P = number of independant refined parameters,
w = weight $= 1/\sigma$.

(b) Rietveld program: $a = b = 5.9281(4)$ Å, $c = 23.407(1)$ Å,
$U = 12276(271)$, $V = -7030(424)$, $W = 2917(154)$

$$R = \Sigma | I_{\mathrm{obs}} - I_{\mathrm{cal}} | / \Sigma I_{\mathrm{obs}} = 3.0\%,$$

$$R_{\mathrm{p}} = \Sigma | Y_{\mathrm{obs}} - Y_{\mathrm{cal}} | / \Sigma Y_{\mathrm{obs}} = 5.2\%$$

$$R_{\mathrm{w}} = \left[\Sigma w^2 [Y_{\mathrm{obs}} - Y_{\mathrm{cal}}]^2 / \Sigma w^2 Y_{\mathrm{obs}}^2\right]^{1/2} = 6.9\%,$$

$$R_{\mathrm{E}} = \left[\Sigma w^2 Y_{\mathrm{obs}} / (N - P + C)\right]^{1/2} = 0.7\%$$

N = number of independent observations, P = number of refined parameters,
C = number of constraints, I = integrated intensity, $w = 1/\sigma$.

tion of the bivalent cation is always defined with the p_i population indicating the presence of this cation among the seven sublattices of the W-type structure. In this way, we can write: $Me_i = p_i M^{2+} + (1 - p_i) Fe^{3+}$ where Me_i is the resulting metallic cation, $M^{2+} = Mg^{2+}$ or Co^{2+} and $i = 1, \ldots, 7$.

3.2.1. $BaMg_2$–W

The Curie temperature of this compound is $T_c = (452 \pm 3)\,^\circ C$ [30], in good agreement with that one given by Albanese et al. [31], so, the paramagnetic diagram was recorded at $T = 510\,^\circ C$. Inside the (6°–86°) 2θ range, the powder diffraction pattern contains 23 independent intensities corresponding to 41 Bragg reflections. The refinements of 17 positional and 7 population parameters were carried out with the MXD program; the Mg neutron nuclear scattering amplitude was $b(\mathrm{Mg}) = 0.5210^{-12}$ cm [27] and the fixed values of the thermal parameters were those obtained from single crystal diffraction data refinement of $\mathrm{BaCo_2}$–W at $T = 550°\mathrm{C}$ [8]. The low number of observed intensities led us to perform several successive refinements, each one corresponding to a set of variables: positional parameters of Me cations or oxygen anions, or population parameters. We report in table 4 the different population parameters and we compare them to the corresponding ones obtained from single crystal X-ray refinements [7]. We notice the zero values of p_1, p_6 and p_7: there is no magnesium inside the R and R–S blocks. The comparison between the five first p_i values obtained from different technics, shows small disparities; the different heating treatments during the synthesis of the two samples (crystal and powder) could lead either to a difference in the two chemical compositions or, to a deviation in the $\mathrm{Mg^{2+}}$ population rates as it previously occurred in the $\mathrm{MgFe_2O_4}$ spinel compound [32]. We prefer to think that these disparities result from the great unreliability when refining populations with very low values, even if the standard deviations are quite small.

Table 4
Magnesium population parameters in the $\mathrm{BaMg_2}$–W compounds

	This work *	Single crystal refinements [7]	
		Isotropic	Anisotropic
p_1	0.00(2)	0.0082(17)	0.052(3)
p_2	0.086(7)	0.120(9)	0.107(7)
p_3	0.405(4)	0.379(8)	0.370(6)
p_4	0.148(6)	0.160(10)	0.148(8)
p_5	0.124(7)	0.101(9)	0.104(7)
$p_6 = p_7$	0	0	0
$p_{\mathrm{exp.}}$ [a]	1.93(4)	1.98(10)	1.88(8)

* $wR(\mathrm{LSQ}) = 1.3\%$, $\chi^2 = 0.8$.
[a] $p_{\mathrm{exp}} = p_1 + 2p_2 + 3p_3 + 2p_4 + 2p_5$ = number of $\mathrm{Mg^{2+}}$/f.u.

Table 5
Cobalt population parameters in the $\mathrm{BaCo_2}$–W compound

	This work *	Single crystal refinements [8]
p_2	0.096(9)	0.120(9)
p_3	0.441(7)	0.463(8)
p_4	0.108(9)	0.084(9)
p_5	0.067(6)	0.043(9)
$p_1 = p_6 = p_7$	0	0
$p_{\mathrm{exp.}}$ [a]	1.87(6)	1.88(7)

* $wR(\mathrm{LSQ}) = 2.8\%$, $\chi^2 = 1.2$.
[a] $p_{\mathrm{exp.}}$ = number of $\mathrm{Co^{2+}}$/f.u.

3.2.2. $\mathrm{BaCo_2}$–W

The Curie temperature of this compound is $T_c = (490 \pm 3)°\mathrm{C}$ [30]; inside the (6°–86°) 2θ range, the powder diffraction diagram, recorded at $T = 560°\mathrm{C}$, contains 26 independent intensities corresponding to 44 Bragg reflections. The refinements were carried out as upper described; the Co nuclear scattering amplitude was $b(\mathrm{Co}) = 0.52 \times 10^{-12}$ cm [27]. We report in table 5 the different population parameters and we compare them to the corresponding ones obtained from single crystal neutron diffraction refinements [8]. p_1, p_6 and p_7 are equal to zero: there is no cobalt in the R and R–S blocks; about the two sets of p_i values, we have the same remarks as upper described.

4. Low temperature study ($T = 4.2$ K)

4.1. Macroscopic theory

The comparison between the diffraction patterns taken at 4.2 K and above the Curie temperature shows that there are no other peaks than the nuclear ones. This means that the magnetic contribution obey the extinction rules of the $P6_3/mmc$ space group: the propagation vector is $\boldsymbol{k} = 0$; so, for the application of the macroscopic theory of Bertaut [33], we will consider this group which can be generated with the following elements: 6_3, 2_x, $\bar{1}$. In the M-type $\mathrm{BaFe_{12}O_{19}}$ structure, the Fe1 cation is on an inversion center (2a position with the $\bar{3}m$ local symmetry) and, in the W-type struc-

Table 6
Irreductible representations of the $P6_322$ group

	ε	6_3	2_x
A_1	$+1$	$+1$	$+1$
A_2	$+1$	$+1$	-1
B_1	$+1$	-1	$+1$
B_2	$+1$	-1	-1
E_1	$\begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix}$	$\begin{vmatrix} 1 & \bar{1} \\ 1 & 0 \end{vmatrix}$	$\begin{vmatrix} 1 & \bar{1} \\ 0 & \bar{1} \end{vmatrix}$
E_2	$\begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix}$	$\begin{vmatrix} 1 & \bar{1} \\ 1 & 0 \end{vmatrix}$	$\begin{vmatrix} \bar{1} & 1 \\ 0 & 1 \end{vmatrix}$

ture the Me3 cation is also on an inversion center (6g position with the local 2/m symmetry); consequently, all the moment configurations corresponding to an odd representation are forbiden and the inversion center character is fixed as $\chi(\bar{1}) = +1$. In this way, it is sufficient to consider the $P6_322$ group which is generated with the 6_3 and 2_x elements. This group, the order of which is $g = 12$, has 6 irreductible representations: 4 one-dimensional and 2 two-dimensional ones as shown in table 6.

We name $\boldsymbol{S}_i$ the axial spin vectors of all the cations located in the different crystallographic positions: 2a, 4e, 4f, 6g and 12k. The i index corresponds to the numeration of the atoms as occurred in the International Tables [34]; for example, the $\boldsymbol{S}_i$ spin vectors of the Me3 cation situated in the (6g) position are:

$\boldsymbol{S}_1(1/2, 0, 0)$, $\boldsymbol{S}_2(0, 1/2, 0)$, $\boldsymbol{S}_3(1/2, 1/2, 0)$,
$\boldsymbol{S}_4(1/2, 0, 1/2)$, $\boldsymbol{S}_5(0, 1/2, 1/2)$,
$\boldsymbol{S}_6(1/2, 1/2, 1/2)$.

The projection operator method, applied to the $S_{i\alpha}(\alpha = x, y, u, z)$ components, leads to the basis vectors which are listed in table 7.

4.2. $BaFe_{12}O_{19}$

The absence of the (001) magnetic reflections indicates we are in presence of a collinear c axis magnetic arrangement belonging to the A_2 representation (see table 7) because of the ferrimagnetic behavior of this compound. Inside the (4°–140°)

Table 7
Basis vectors (*) for the different positions

	2a	4e	4f	6g	12k
A_1	– –	G_z –	G_z –	– $a_{1x} + a_{2y} + a_{3u}$	$G_{1z} + G_{2z} + G_{3z}$ $C_{1x} + C_{2y} + C_{3u}$
A_2	f_z –	F_z –	F_z –	$f_{1z} + f_{2z} + f_{3z}$ –	$F_{1z} + F_{2z} + F_{3z}$ $A_{1x} + A_{2y} + A_{3u}$
B_1	– –	A_z –	A_z –	– $f_{1x} + f_{2y} + f_{3u}$	$A_{1z} + A_{2z} + A_{3z}$ $F_{1x} + F_{2y} + F_{3u}$
B_2	a_z –	C_z –	C_z –	$a_{1z} + a_{2z} + a_{3z}$ –	$C_{1z} + C_{2z} + C_{3z}$ $G_{1x} + G_{2y} + G_{3u}$
E_1	$f_{x,y,u}$ (**)	$F_{x,y,u}$ (**)	$F_{x,y,u}$ (**)	$(f_1 + f_2 + f_3)_{x,y,u}$ (**)	$(F_1 + F_2 + F_3)_{x,y,u}$ (**)
E_2			(***)		

(*) (2a) position $\boldsymbol{f} = \boldsymbol{S}_1 + \boldsymbol{S}_2$ $\boldsymbol{a} = \boldsymbol{S}_1 - \boldsymbol{S}_2$
(4e) and (4f) positions $\boldsymbol{F} = \boldsymbol{S}_1 + \boldsymbol{S}_2 + \boldsymbol{S}_3 + \boldsymbol{S}_4$ $\boldsymbol{G} = \boldsymbol{S}_1 - \boldsymbol{S}_2 + \boldsymbol{S}_3 - \boldsymbol{S}_4$
$\boldsymbol{C} = \boldsymbol{S}_1 + \boldsymbol{S}_2 - \boldsymbol{S}_3 - \boldsymbol{S}_4$ $\boldsymbol{A} = \boldsymbol{S}_1 - \boldsymbol{S}_2 - \boldsymbol{S}_3 + \boldsymbol{S}_4$
(6g) position: $\boldsymbol{f}_i = \boldsymbol{S}_i + \boldsymbol{S}_{i+3}$ $\boldsymbol{a}_i = \boldsymbol{S}_i - \boldsymbol{S}_{i+3}$
(12k) position: $\boldsymbol{F}_i = \boldsymbol{S}_i + \boldsymbol{S}_{i+3} + \boldsymbol{S}_{i+6} + \boldsymbol{S}_{i+9}$
$\boldsymbol{G}_i = \boldsymbol{S}_i - \boldsymbol{S}_{i+3} + \boldsymbol{S}_{i+6} - \boldsymbol{S}_{i+9}$
$\boldsymbol{C}_i = \ldots$, $\boldsymbol{A}_i = \ldots$

(**) Non-existing or antiferromagnetic configurations ∥ to the c axis.

(***) Non-existing or antiferromagnetic configurations ∥ or ⊥ to the c axis.

2θ range, the diagram contains 40 independent intensities corresponding to 81 nuclear and magnetic Bragg reflections; the refinements of 11 positional parameters together with 5 magnetic moments, according to the Gorter model (see table 1), were carried out by means of MXD program. The magnetic form factor of the Fe^{3+} cation was the experimental one given by Brockhouse et al. [35] and the fixed value of the thermal parameters of all the ions was $B = 0.2$ Å^2 (generally used at this temperature). The first refinement cycles showed the z positional parameter of the Fe2 cation to be equal to $z = 0.25$ with a large standard deviation; this indication, which is not an accurate result, could be explained with the following assumption: at room temperature, the Fe2 cation in the R-block stays in a double-well quasi harmonic atomic potential with two minima at each side of the BaO_3 mirror plane and presents a fast diffusional motion between the two pseudotetrahedral sites corresponding to the (4e × 1/2) position: 0 0 z with $z \# 0.26$ [5]; at low temperature, this Fe2 cation is "frozen" on the mirror plane in the bipyramidal (five-fold) site corresponding to the (2b) position: 0 0 1/4. The freezing of this Fe2 cation from #80 K has been previously pointed out from Mössbauer spectroscopy study [36], but the authors did not give the final frozen position. About our results, we lay great stress on the hypothetical character of our conclusions; the low temperature (10 K) single crystal X-ray diffraction study we are carrying out at present will enable us to answer this question soon.

The results, with the Fe2 cation fixed in the 2b position, are given in tables 8 and 10. The magnetic symmetry of this structure leads to the Shubnikov group: $P6_3/mm'c'$.

4.3. W-type compounds

Each diagram was recorded inside the (5°–85°) 2θ range. The refinements were performed with the Me1 cation "frozen" in the (2d) position instead of the (4f × 1/2) one and by using the Fe^{3+} magnetic form factor applied to all the Me_i cations; the fixed value of the thermal parameter of all the ions was $B = 0.2$ Å^2. Because of the low number of observed intensities, several runs of cycles were carried out by refining either the positional parameters of the Me_i cations or the positional parameters of the O anions or the magnetic moments and by using the results of the precedent run as fixed values for the following one.

The absence of the (001) magnetic reflections in the $BaMg_2$–W diagram indicates, as precedently, a collinear c axis magnetic arrangement belonging to the A_2 representation. 26 independent intensities corresponding to 41 nuclear and magnetic Bragg reflections were used for the refinement of 16 positional parameters together with 7 magnetic moments according to the Gorter model (see table 2). The results are given in tables 9 and 10 and we report on table 11 the comparison between the

Table 8
Final positional parameters as determined (*) from neutron diffraction data at $T = 4.2$ K for the $BaFe_{12}O_{19}$ compound

Site	Atom	Position	x	y	z
	Ba	2d	2/3	1/3	1/4
VI(S)	Fe1	2a	0	0	0
V(R)	Fe2	2b	0	0	1/4
IV(S)	Fe3	$4f^{IV}$	1/3	2/3	0.0280(4)
VI(R)	Fe4	$4f^{VI}$	1/3	2/3	0.1897(4)
VI(R–S)	Fe5	12k	0.1666(8)	0.3332	−0.1083(2)
	O1	4e	0	0	0.1519(8)
	O2	4f	1/3	2/3	−0.0555(8)
	O3	6h	0.188(3)	0.376	1/4
	O4	12k	0.159(2)	0.318	0.0523(4)
	O5	12k	0.500(2)	1.000	0.1493(4)

* $a = b = 5.865(2)$ Å, $c = 23.099(5)$ Å, $wR(\text{LSQ}) = 3.6\%$, $\chi^2 = 7.0$.

Table 9
Final positional parameters (*) as determined from neutron diffraction data at $T = 4.2$ K for the $BaMg_2$–W and $BaCo_2$–W compounds

Site	Atom	Position	*x*	*y*	*z*
	Ba	2b	0	0	1/4
V(R)	Me1	2d	1/3	2/3	−1/4
VI(S)	Me2	$4f^{VI}$	1/3	2/3	−0.4254(4) −0.4268(3)
VI(S–S)	Me3	6g	1/2	0	0
IV(S)	Me4	4e	0	0	0.0558(4) 0.0552(6)
IV(S)	Me5	$4f^{IV}$	1/3	2/3	0.0933(3) 0.0926(4)
VI(R)	Me6	$4f^{VI}$	1/3	2/3	0.2082(2) 0.2072(4)
VI(R–S)	Me7	12k	−0.1638(3) −0.1643(5)	−0.3276 −0.3286	0.1495(1) 0.1506(1)
	O1	4e	0	0	0.116(1) 0.116(1)
	O2	4f	1/3	2/3	0.0317(9) 0.033(1)
	O3	4f	1/3	2/3	−0.327(1) −0.327(2)
	O4	6h	0.489(2) 0.488(4)	0.978 0.976	1/4
	O5	12k	0.503(2) 0.502(3)	1.006 1.004	0.1096(3) 0.1098(9)
	O6	12k	−0.175(1) −0.176(2)	−0.350 −0.352	0.0371(3) 0.035(1)
	O7	12k	0.164(1) 0.170(2)	0.328 0.340	0.1820(5) 0.1811(9)

(*) There are two values for each refined parameter: the first and the second ones correspond to the $BaMg_2$–W (a) and $BaCo_2$–W (b) compounds respectively.

(a) $a = b = 5.892(2)$ Å, $c = 32.85(1)$ Å, $wR(LSQ) = 2.1\%$, $\chi^2 = 1.1$.

(b) $a = b = 5.899(1)$ Å, $c = 32.846(5)$ Å, $wR(LSQ) = 3.4\%$, $\chi^2 = 2.5$.

Table 10
Experimental magnetic moments (μ_B) as determined from neutron diffraction data at 4.2 K

Site	$BaFe_{12}O_{19}$			$BaMg_2$–W		$BaCo_2$–W	
				(a)	(b)	(a)	(c)
V(R)	M(Fe2)	4.8(3)	M1	3.8(1)	3.8(1)	3.9(2)	3.9(2)
VI(S)	M(Fe1)	4.1(3)	M2	4.1(1)	4.5(2)	4.9(2)	5.1(3)
VI(S–S)	–	–	M3	3.0(1)	5.0(2)	4.1(1)	5.0(3)
IV(S)			M4	−4.1(2)	−4.8(3)	−4.7(1)	−4.9(2)
	M(Fe3)	−4.5(2)					
IV(S)			M5	−4.0(1)	−4.6(2)	−4.5(1)	−4.6(2)
VI(R)	M(Fe4)	−4.2(2)	M6	−5.0(1)	−5.0(1)	−4.2(2)	−4.2(2)
VI(R–S)	M(Fe5)	4.9(1)	M7	4.6(1)	4.6(1)	4.8(1)	−4.8(1)

(a) Magnetic moment of the resulting cation Me_i.

(b) Magnetic moment of the Fe_i^{3+} cation: $M(Fe_i^{3+}) = M_i/1 - p_i$; the p_i vales are those determined in this work (see table 4).

(c) Magnetic moment of the Fe_i^{3+} cation:

$$M\left(Fe_i^{3+}\right) = \left[M_i - p_i M\left(Co^{2+}_{H.S.}\right)\right]/(1 - p_i),$$

with $M(Co^{2+}_{H.S.}) = 3\mu_B$; the p_i values are those determined in this work (see table 5).

observed intensities and the nuclear and calculated ones. The Shubnikov group is P6$_3$/mm'c'.

The BaCo$_2$–W diagram shows the (001) magnetic reflections to be present: magnetic components exist in the basal plane. So, the first run of refinement was performed with the planar configuration belonging to the E$_1$ representation (table 7). This configuration is ferrimagnetic according

Table 11
Powder neutron diffraction patterns at $T = 4.2$ K; comparison between the observed and calculated intensities

BaMg$_2$–W					BaCo$_2$–W			
hkl	$I_{obs.}$	$I_{calc.}$	$I_{cal.}^{mag.}$	$I_{calc.}^{nucl.}$	$I_{obs.}$	$I_{calc.}$	$I_{cal.}^{magn.}$	$I_{cal.}^{nucl.}$
002	6	6	0	6	2	2	1	1
004	28	28	0	28	58	59	28	31
006	31	31	0	31	408	416	383	33
100	1374	1380	9	39	743	766	22	38
101			1238	4			706	1
102	377	396	392	4	335	299	289	10
103	163	163	78	85	175	175	116	59
104	234	233	132	101	229	236	164	72
008	16	16	0	16	232	230	223	7
105	38	37	23	14	40	40	29	11
106	138	138	50	88	141	145	59	86
107	29	32	23	9	40	42	32	10
0010	69	64	0	64	244	242	166	76
108	103	102	16	86	77	76	36	40
109	1739	1660	37	482	1414	1449	90	506
110			497	634			263	590
112			0	8	*	*		
114	1019	1018	30	37	1222	1193	29	46
1010			35	848			88	698
0012			0	68			264	68
116	3372	3433	97	1917	3636	3534	100	1689
1011			11	1408			83	1189
200	304	249	55	1			28	1
201			193	0			2	180
202	*	*					27	235
203	905	878	12	866	750	749	0	749
204	*	*			317	308	241	67
1012	2870	2130	6	342	1760	1687	9	257
118			13	616			4	591
205			1151	2			823	3
0014	297	247	0	247	469	456	160	296
206	1330	1323	14	1309	1413	1475	29	1446
1013	5	3	1	2	1	1	0	1
207	272	261	152	109	270	267	145	122
208	3148	3198	77	3121	2789	2811	145	2666
0016	0	0	0	0	*	*		
2011	2086	2124	140	408	1966	1792	133	413
210			14	64			20	22
211			876	30			449	41
212			241	100			160	86
1016			118	48			325	64
213			61	24			71	8
214	*	*			118	128	71	40
2012	*	*					14	3

* Unspecified because of the bad determination of the background.

to the Gorter model; because of the "Shirane theorem" [37], it is not possible to distinguish the different x, y or u modes, all the different magnetic Bragg reflections being at the same θ angle. For this reason the magnetic moments were arbitraryly fixed along the x direction. Because of the very bad results, an other run was performed with the same basal scheme, but a magnetic component along the c axis was allowed; we named α_i ($i = 1,\dots,7$) the azimuthal angle of each M_i magnetic moments. The results were quite good and all the α_i angles were inside the (63°–70°) range; so, for the last run, we fixed all the α_i to the same value α. 26 intensities corresponding to 41 nuclear and 122 magnetic bragg reflections were used for the refinement of 16 positional parameters together with 7 magnetic moments and with the α azimuthal angle. The cristallographic and magnetic results are given in tables 9 and 10, the final value of α being $(68.5 \pm 1.5)°$; the comparison between the observed and calculated intensities is reported on Table 11. The mixing of the two E_1 and A_2 representations leads to a strong decreasing of the magnetic symmetry which is P2/m.

5. Discussion

About the location of the M^{2+} cation in the W-type compounds, these results obtained from neutron diffraction on powder samples confirm the previous ones determined from single crystal X-ray/neutron diffraction [7,8]. However, we will notice some differences with others authors. For the BaMg$_2$–W compound, by using Mössbauer spectroscoopy, Albanese et al. pointed out that the Magnesium cations were mainly located in the (4f^{VI}) and (6g) positions corresponding to the octahedral sites of the S and S–S blocks [31]; our results are: 72% of Mg^{2+} lie in these (4f^{VI}) and (6g) positions whereas 28% are in the (4e) and (4f^{IV}) positions corresponding to the tetrahedral sites of the S blocks. By means of neutron diffraction on the $BaFe^{2+}_{0.25}Co^{2+}_{1.75}Fe_{16}O_{27}$ compound, Yamzin et al. put all the Co^{2+} cations in the (12k) position (octahedral site of the R-S blocks) [16]; by using Mössbauer technic, Albanese et al. conclude that 0.2 Co^{2+} enter this (12 k) position and 1.8 Co^{2+} are distributed among the (4f^{VI}) and (6g) positions (octahedral sites of the S and S–S blocks) [19]. We conclude from our results that there are 79% of Co^{2+} among the (4f^{VI}) and (6g) octahedral sites and 21% in the (4e) and (4f^{IV}) tetrahedral ones; there is no cobalt in the (12 k) octahedral site.

In table 12 we report the different values of the magnetization at 4.2 K for the three studied compounds: M_s is the spontaneous magnetization deduced from the experimental values of the different magnetic moments as determined from powder neutron diffraction data; M_0 is the saturation magnetization obtained on the same powder samples in magnetic fields up to 150 kOe [22,30]; M_s(th) is the theoretical magnetization according to the Gorter model by using $M(Fe^{3+}) = 5\mu_B$ and $M(Co^{2+}_{H.S}) = 3\mu_B$. The agreement between the three M_0, M_s and M_s(th) values is very good in the $BaFe_{12}O_{19}$ hexaferrite. About the BaMg$_2$–W compound, the experimental M_s value confirms the M_0 one, but they are together lower than the M_s(th) one; this discrepancy could be explained taking into account the weakening of the magnetic interactions due to the presence of the diamagnetic Mg^{2+} cation. This assumption was previously pointed out by Albanese et al. in the BaZn$_2$–W compound, and they conclude to a local spin reversal [14]; a similar conclusion (a random spin canting) was put toward in the study of the M-type $LaZnFe_{11}O_{19}$ compound [38,39]. Local spin reversal or random spin canting would come out, in terms of neutron diffraction, with a

Table 12
Spontaneous magnetization M_s, saturation magnetization M_0 and theoretical magnetization M_s (th) (*), expressed in μ_B/f.u. at 4.2 K, for the three studied compounds

	$BaFe_{12}O_{19}$	BaMg$_2$–W	BaCo$_2$–W
M_s	20.6±0.6	22.3±1.7	28.0±1.5
M_0	20.0±0.1 [22]	22.8±0.1 [30]	26.9±0.1 [30]
M_s(th)	20.0	25.8±0.3 (a)	27.7±0.2(a)
		25.3±0.5 (b)	27.2±0.2(d)
		25.7±0.3 (c)	

* According to the Gorter model, by using the M^{2+} population parameters as determined (a) in this work (see tables 4 and 5); (b) and (c) from isotropic and anisotropic single crystal refinements respectively (see table 6); (d) from single crystal refinement (see table 5).

decreasing of the observed magnetic moments on the assigned sublattices; because of the decreasing of the magnetization, these sublattices are obviously the spin up ones: 2d, 4f$^{\mathrm{VI}}$, 6g and 12k. In our case, the difference between M_s or M_0 and M_s(th) is small ($\approx 10\%$) and the weakening of some Fe_i^{3+} magnetic moments (see table 10) is not significant taking into account the observed ones in the $\mathrm{BaFe_{12}O_{19}}$ and $\mathrm{BaCo_2}$–W compounds; no confirmation of local spin reversal or random spin canting can be given. In the $\mathrm{BaCo_2}$–W compound, the spontaneous magnetization M_s, resulting from the quasi-planar spin arrangement, is borne out by the M_0 value; both are in good agreement with the M_s(th) one. This M_s(th) value, together with the $M(\mathrm{Fe_i})$ ones (table 10), calculated by using $M(\mathrm{Co}^{2+}) = 3\mu_B$, confirm the high spin state of the Co^{2+} cation, high spin state which was previously stated from crystallographic reasons [8].

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