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# Non-collinear magnetic order in a Sc-substituted barium hexaferrite

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## Abstract

A combined magnetic, neutron diffraction and field-dependent <sup>57</sup>Fe Mössbauer study of Sc-substituted Ba-hexaferrite in powder form is reported, and the findings are compared with the data for BaFe<sub>12</sub>O<sub>19</sub>. The five cation sublattice with collinear ferrimagnetic structure of uniaxial (Gorter) type for BaFe<sub>12</sub>O<sub>19</sub>, persists also for BaFe<sub>10.4</sub>Sc<sub>1.6</sub>O<sub>19</sub> at room temperature and below down to 130–190 K, depending on the applied field. Below room temperature, BaFe<sub>10.4</sub>Sc<sub>1.6</sub>O<sub>19</sub> undergoes a magnetic transition as indicated by the magnetization and Mössbauer spectroscopic measurements. The neutron diffraction results are compatible with a gradual transformation below 190 K into a complex canted structure with spins pointing out of the axial direction. The complex magnetic order at 10 K can be described in terms of an incommensurate complex block-type conical structure.

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For more than four decades BaFe<sub>12</sub>O<sub>19</sub> and related isostructural (M-type) hexaferrites derived by single or double cation substitution for Fe<sup>3+</sup> with preservation of the formal valence have attracted a significant interest from both scientific and application points of view. The M-type hexaferrites crystallize in P<sub>6</sub><sub>3</sub>/mmc space group. There are two formula units in a hexagonal unit cell. The nominally 24 Fe<sup>3+</sup> ions in the unit cell are distributed among five distinct sites: 12k, 2a, 4f<sub>2</sub>—octahedral, 4f<sub>1</sub>—tetrahedral, 4e—bipyramidal (half empty). At room temperature the magnetic structure is well described by the block-type ferrimagnetic model of Gorter [1] with three spin up sites (2a, 4e, 12k) and two spin down sites (4f<sub>1</sub> and 4f<sub>2</sub>), all aligned along the hexagonal *c*-axis which is the easy magnetization direction. The magnetic interactions may be tuned by suitable substitutions resulting in remarkable magnetic properties utilized extensively for permanent magnets, microwave devices and perpendicular recording

media [2]. In the latter context, the demand for a higher recording density invoked the current interest in fabricating the fine particles of substituted BaFe<sub>12</sub>O<sub>19</sub>. Concerning microwave applications such as absorbing media, the substitution of iron by non-magnetic scandium ions is known to reduce substantially the ferrimagnetic resonance frequency of BaFe<sub>12</sub>O<sub>19</sub>. This effect might be attributed to the modification of the exchange interactions, leading to the existence, at low temperatures, of a specific non-collinear magnetic structure named block helicoid and considered by Alesko-Ozhevskij et al. [3,4]. In an attempt to elucidate the magnetic structure evolution accompanying the magnetic anisotropy change, we undertook a combined magnetic, neutron diffraction and magnetic field-dependent <sup>57</sup>Fe Mössbauer study on the composition of BaFe<sub>10.4</sub>Sc<sub>1.6</sub>O<sub>19</sub>.

Single-phase powder material of micron-sized grains of BaFe<sub>10.4</sub>Sc<sub>1.6</sub>O<sub>19</sub> prepared by the ceramic route was kindly provided by Nedkov [5]. During preparation, the composition and phase purity of both the final and intermediate products were controlled by DTA, TG and X-ray phase

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analysis. The homogeneity of the final polycrystalline material was checked by SAED and its single-phase purity was confirmed by our neutron diffraction data.

Magnetization measurements were carried out using a Quantum Design MPMS-5S SQUID magnetometer. Some magnetization data were collected also for  $\text{BaFe}_{12}\text{O}_{19}$  by using a reference sample prepared by crushing a single crystal into fine powder. Fig. 1 shows the field-dependent magnetization at several temperatures. It clearly illustrates the increase of the high-field anisotropy at 5 K when Sc is substituted for Fe. On the other hand, the anisotropy is not significant at 300 K. It hints at a temperature induced magnetic transition for the Sc-substituted sample. It is supported more clearly by the inset of Fig. 1, which displays the magnetization as a function of the temperature at an applied field of 1 kOe. There is a clear downturn at about 190 K with decreasing temperature. This is to be compared with the monotonic increase of the magnetization at the same temperature for  $\text{BaFe}_{12}\text{O}_{19}$ . The transition temperature strongly decreases with increasing applied field, it is about 130 K for 5 T.

$^{57}\text{Fe}$  Mössbauer measurements were performed between 4.2 K and room temperature and in external magnetic fields applied parallel to the direction of the  $\gamma$ -beam. At 4.2 K a typical six-line spectrum characteristic of  $\text{Fe}^{3+}$  ions was obtained as shown in Fig. 2. The line broadening is caused by a different transfer hyperfine field contributions of the five iron sublattice sites and the Sc replacement. Reliable separation of the different iron sublattice sites is not feasible without applied magnetic fields. The external magnetic field influences the Mössbauer spectrum via the intensities of the 2–5 lines (corresponding to  $\Delta m = 0$  nuclear transitions, the relative intensities are given by  $I_{2-5} = 4 \sin^2 \theta / (1 + \cos^2 \theta)$ , where  $\theta$  is the angle between the magnetic moment and magnetic field,  $B_{\text{ext}}$ , applied

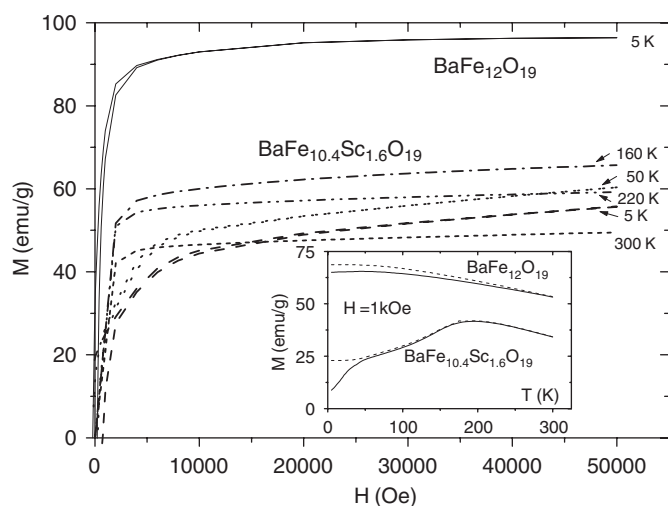


Fig. 1. Magnetization vs. magnetic field for  $\text{BaFe}_{12}\text{O}_{19}$  and  $\text{BaFe}_{10.4}\text{Sc}_{1.6}\text{O}_{19}$  measured at the temperatures indicated. Inset: temperature dependence of magnetization measured at a field of 1 kOe after zero-field cooling (solid lines) and field-cooling (dotted lines) at 1 kOe.

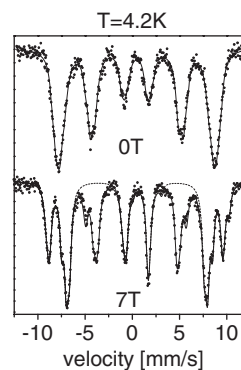


Fig. 2. Mössbauer spectra of  $\text{BaFe}_{10.4}\text{Sc}_{1.6}\text{O}_{19}$  measured at 4.2 K in 0 and 7 T external magnetic field applied parallel to the  $\gamma$ -direction. The broken line is the calculated curve for disappearing 2–5 lines.

parallel to the  $\gamma$ -beam direction) and via the absolute values of the hyperfine fields increasing for iron magnetic moments that are antiparallel to the direction of the magnetic field, meanwhile decreasing for the parallel orientation.

According to Fig. 2 in external magnetic field  $B_{\text{ext}} = 7$  T, the spectrum clearly shows a non-collinear magnetic structure since the 2–5 lines are not absent. A broken line in figure shows the calculated curve for  $I_{2-5} = 0$ . Also, it is obvious that the outer lines have increased hyperfine field corresponding to the antiparallel coupled iron magnetic moments. The relative occupancy of the antiparallel vs. parallel magnetic moments is 0.31:0.69—in excellent agreement with the neutron data (Table 1). Similar, non-collinear behaviour was observed at 80 K whereas at and above 160 K the magnetic structure was found to be collinear ferrimagnetic at  $B_{\text{ext}} = 7$  T.

In order to clarify the nature of magnetic transition seen around 190 K, the neutron diffraction measurements were performed using a PSD diffractometer ( $\lambda = 1.0577 \text{ \AA}$ ) in Budapest [6] and the 3T2 diffractometer ( $\lambda = 1.2251 \text{ \AA}$ ) at LLB, Saclay, [7] at ambient temperature and at 10 K. The Rietveld method [8] was applied to refine simultaneously the positional and thermal parameters and magnetic moment components. Careful inspection of both, the room temperature and 10 K diffraction patterns did not reveal any indication of changes in crystallographic symmetry and hence the refinements of crystal structure occurs in  $\text{P6}_3/\text{mmc}$  space group. The occupation of Sc at the five cation positions was obtained as summarized in Table 1.

For the magnetic contribution to the scattering at 300 K the model of a Gorter-type collinear ferrimagnetic structure, with three cation sites (2a, 4e, 12k) parallel, and two sites ( $4f_1$ ,  $4f_2$ ) of antiparallel spin alignment with respect to the hexagonal axis, characteristic for  $\text{BaFe}_{12}\text{O}_{19}$ , produced satisfactory results in terms of the conventional agreement factors.

At 10 K magnetic satellite reflections appeared, indicating the presence of an incommensurate, non-collinear magnetic structure. The reflection at  $2\Theta = 9.6^\circ$  could be

Table 1

Refined occupancy factors for the five cation sublattices (2a, 4f<sub>2</sub>, 12k—octahedral, 4f<sub>1</sub>—tetrahedral, 4e—bipyramidal) from neutron diffraction data

Cation position	Atomic occupancy	
	n <sub>Fe</sub>	n <sub>Sc</sub>
M1–2a	0.76	0.24
M2–4e × 1/2	1.00	0.00
M3–4f <sub>1</sub>	1.91	0.09
M4–4f <sub>2</sub>	1.34	0.66
M5–12k	5.44	0.56

indexed as (0 0 3 +  $k$ ) with  $k = 0.24$ , where  $k$  is the magnetic propagation vector ( $k = c/\text{magnetic periodicity length}$ ). The neutron diffraction pattern at 10 K could be well fitted, as it is illustrated in Fig. 3, by a block-type, conical magnetic ordering, based on a model introduced by Aleshko-Ozhevskii et al. [3,4]. Inside the blocks, the magnetic moments are ordered ferrimagnetically, but their directions are declined from the hexagonal axis. The borders, between the blocks, are formed by the mirror planes of s.g. P6<sub>3</sub>/mmc perpendicular to the hexagonal axis, and there is an antiphase coupling between the subsequent blocks. The obtained periodicity length was around 98 Å, and the Rietveld refinement revealed a cone angle of about 40°.

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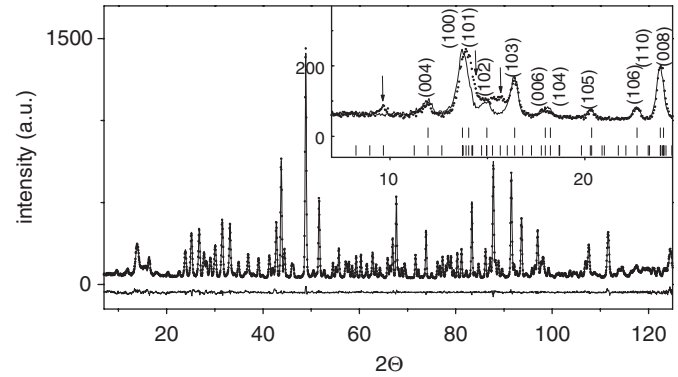


Fig. 3. Neutron diffraction pattern ( $\lambda = 1.2251$  Å) of BaFe<sub>10.4</sub>Sc<sub>1.6</sub>O<sub>19</sub> at 10 K and its Rietveld-refinement in the conical block-type magnetic structure in s.g. P6<sub>3</sub>/mmc ( $a = 5.9240$  Å  $c = 23.5395$  Å). The inset shows the low angle part both at 10 K (dots) and 300 K (solid line), the arrows indicate the extra magnetic reflections at 10 K.

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