

DELOCALIZATION OF THE MAGNETIC MOMENT OF  $\text{Fe}^{3+}$  IONS IN TYPE Y  
HEXAGONAL FERRITE AT  $293^\circ\text{K}$

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The spatial distribution of the magnetic moment in type Y hexagonal ferrite  $\text{Ba}_{0.4}\text{Sr}_{1.6}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$  is investigated by neutron diffraction at  $293^\circ\text{K}$ . The anomalous ratio of the intensities in spiral reflection pairs  $00l^\pm$  is explained by a shift of the magnetic moment density along the z axis from the position of the fixed nuclei. The maximum shift of the magnetic moment along the z axis is  $0.4 \pm 0.1 \text{ \AA}$ . Investigation of the  $h0l$  reflections shows that the moments are ordered in spiral chains. According to the accepted model, the magnetic moments, by shifting in the basal plane, arrange themselves along a helical line with radius equal to the magnitude of the shift in the basal plane  $\Delta x$ . The intensities in the observed diffraction pattern can be calculated on the basis of this model. The character and magnitude of the shifts of the center of gravity of the magnetic moments in the basal plane are established. The maximum value of  $\Delta x$  was  $0.7 \pm 0.1 \text{ \AA}$ . It is shown that in this case practically all of the magnetic moment associated with the  $\text{Fe}^{3+}$  ion is delocalized.

## 1. INTRODUCTION

THE aim of this investigation was to establish the spatial arrangement of the magnetic moment of  $\text{Fe}^{3+}$  ions in the lattice of the type Y hexagonal ferrite  $\text{Ba}_{0.4}\text{Sr}_{1.6}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$  at  $293^\circ\text{K}$ . According to Braun,<sup>[1]</sup> ferrites of this type crystallize in space group  $R\bar{3}m$  with hexagonal parameters  $a = 5.9 \text{ \AA}$ ,  $c = 43.6 \text{ \AA}$ . A description of the atomic and magnetic structure of this compound can be found in [2], where it is shown that there is a complicated spiral structure which combines collinearity of the atomic magnetic moments in a portion (block) of the elementary cell with spiral ordering of the magnetic axes of the blocks along the z axis. A similar ordering arises as a result of the local disposition of Zn ions on the faces of the blocks with formation here of nonmagnetic sheets. The model of the magnetic structure proposed in [2] is based on an investigation of the  $00l$  reflections with the assumption that only the orientation of the magnetic moment changes in the spherically symmetric magnetic moment density localized on fixed nuclei. However, our results have shown that a similar "pure" orientational or helicoidal model cannot explain the anomalous intensity ratios observed in the  $00l^\pm$  reflection pairs. This model also cannot explain the intensities of the  $10l^\pm$  satellite reflections.

It was found that these difficulties could be resolved if one used a model in which the  $\text{Fe}^{3+}$  magnetic moment can change, besides its orientation, its spatial relation to the fixed nuclei without any significant change in its spatial shape and density.

## 2. EXPERIMENT

The samples used for the neutron diffraction investigations were monocrystals of composition  $\text{Ba}_{0.4}\text{Sr}_{1.6}\text{Zn}_2\text{Y}$ , grown by the method of spontaneous crystallization from a flux. Phase analysis of these crystals was carried out in a URS-50 IM x-ray diffrac-

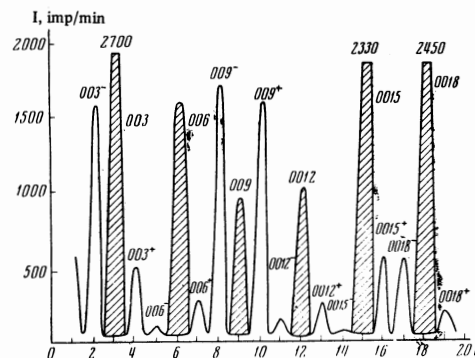


FIG. 1. Neutron diffraction pattern from the ferrite  $\text{Ba}_{0.4}\text{Sr}_{1.6}\text{Zn}_2\text{Y}$  at  $293^\circ\text{K}$ . Reflection  $00l$ . Periodicity of  $l$ -layer lines in reciprocal space is  $1/c$ , where  $c$  is the period of the ferrite cell along the z axis.

tometer. The parameters of the elementary cell were:  $c = 43.48 \text{ \AA}$ ,  $a = 5.9 \text{ \AA}$ . The content of strontium in the type Y structure,  $11.6 \pm 0.1$  in the chemical formula, was determined with an x-ray microanalyzer. In all, five samples from one melt were selected for investigation.

The neutron diffraction patterns were taken in the neutron diffractometer of the Solid State Physics Institute of the U.S.S.R. Academy of Sciences set up at the reactor of the Institute for Theoretical and Experimental Physics of the State Atomic Energy Commission. The wavelength of the neutron radiation was  $1.18 \text{ \AA}$ . The patterns were taken at a temperature of  $293^\circ\text{K}$ . The nuclear contributions were separated by heating above the Curie point, which is  $420^\circ\text{K}$  for this ferrite.<sup>[3]</sup>

Figure 1 shows the neutron diffraction pattern at  $293^\circ\text{K}$  for reflections of the  $00l$  series. The cross hatching indicates the nuclear contributions. The other reflections are the magnetic doublets  $00l^\pm$ , which prove the existence of a spiral magnetic structure in this compound.

The diffraction patterns from the basal planes ( $00l$ )

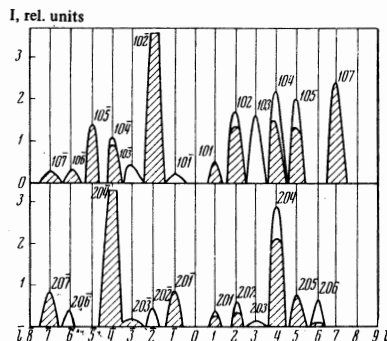


FIG. 2. Diffraction pattern from planes (h0l) of type Y ferrite at 293°K.

were taken at 293°K from five samples of one melt. The intensity ratios  $I_{00l^-}/I_{00l^+}$  were practically identical for all five samples. The data of this investigation permits refinement, and in some cases correction of values of the intensities of the 00l reflections given in [2]. The inaccuracies in [2], however, do not affect the basic conclusions about the model of block spirals, the existence of which is confirmed by the data of the present paper. From the arrangement of the 00l reflections, the period of the spiral for this ferrite was found to be  $43.5 \pm 1.0 \text{ \AA}$ , which agrees with the data of [2] for the same ferrite at 293°K.

The anomalous differences in the intensities of reflections from the 00l pairs are clearly seen in Fig. 1. It is particularly noticeable in the 006<sup>±</sup>, 0012<sup>±</sup>, 0015<sup>±</sup>, and 0018<sup>±</sup> doublets.

The diffraction pattern from the (h0l) planes are in Fig. 2. Indexing of the magnetic contributions can be accomplished on the basis of a "pure" orientational (helical) model for the magnetic structure. Since the direction of propagation of the spiral coincides with the z axis of the hexaferrite and the period of the spiral structure  $\tau$  is 43.5 Å, i.e., the period c of the elementary cell, the satellite reflections 00l<sup>±</sup> take positions of forbidden reflections: 002, 004, 005, 007, 008, 0010, 0012, etc. The satellite reflections h0l<sup>±</sup> (h ≠ 0) appear in the form of magnetic contributions in the structural reflections, the magnetic contribution in each reflection being determined by a pair of satellites from nearest neighbors. However, the helicoidal model cannot explain the observed values of the magnetic contributions.

The model that can not only index the observed magnetic reflections but also explain their intensities has been given the name of the magnetic chain spiral. The essence of this model is that the magnetic moments of the Fe<sup>3+</sup> ions in each block are shifted along the magnetic axis of the block in the basal plane. Since the orientation of the magnetic axes changes from block to block in accordance with spiral ordering, the magnetic moments, by shifting, arrange themselves along a spatial spiral line. Thus the densities of the moments form a spatial spiral chain analogous to the spiral chains of biological molecules packed in a crystalline lattice.

### 3. INDEXING OF MAGNETIC REFLECTIONS ON THE BASIS OF THE MAGNETIC CHAIN SPIRAL MODEL

The spiral magnetic chain in the case of a type Y ferrite is a broken spiral, i.e., it is a system of mag-

netic moments arranged along a continuous spiral branch. According to the theory of diffraction by chain molecules (cf. [4]) we should observe magnetic reflections from layer lines of index t with the general selection rule

$$t = qn + mp, \quad (1)$$

where q is the number of turns of the continuous spiral line fitting into the period of the broken spiral, t and n are the translational and angular parameters of the broken spiral, m is a parameter that determines the series of points in reciprocal space with period  $c^* = 1/c'$ , where c' is the distance between neighboring scattering points along the translation axis, and p is the number of points fitting in q rotations of the continuous spiral.

According to the conditions for diffraction by spiral chains, the intensity of reflections in layer lines of index t is determined by the square of the Bessel function of n-th order. Since the period of the spiral ordering equals the period c of the elementary cell of the type Y ferrite, the periods of the broken and continuous spirals coincide, and, consequently, so do the indexes l of the ferrite lattice with the indexes t of the layer lines of the broken spiral chain.

In the case of the Y ferrite, the magnetic contributions are observed at the intersections of layer lines of index t(l) with the lines of index h (0, 1, 2, ...) that are parallel to the z axis of the ferrite cell; these points are the locations of the structural reflections h0l. This phenomenon can be understood if the magnetic chains in this ferrite are folded into the crystalline lattice. The radial coordinate then determines the shift of the magnetic moment density, not from a single axis as in chain spiral molecules, but from the positions of the fixed Fe<sup>3+</sup> nuclei, which are arranged in the elementary cell of the ferrite in accordance with space group R $\bar{3}m$  and the coordinates found in [1].

The expressions for the magnetic structure factor  $F_{ht}$  will in this case represent the packet in reciprocal space of transformants of the functions that describe the spiral chain structure in the crystal lattice of the Y hexaferrite. The general form of the magnetic structure factor is

$$F_{ht} = \sum_v f_{j_n}(2\pi R \Delta x_v) \exp(i\varphi_v) \exp(2\pi i \mathbf{B}_H \mathbf{r}_v) \exp(i\alpha_v), \quad (2)$$

where  $\varphi_v$  and  $\alpha_v$  are phase angles pertaining respectively to the spiral chain and the orientation of the magnetic moment of the v-th ion,  $\Delta x$  is the radial coordinate of the magnetic moment density, equal to the shift of the center of gravity of the magnetic moment from the positions of the fixed nuclei,  $\mathbf{B}_H$  is the reciprocal space vector for the crystal lattice of the Y ferrite,

$$R = (4\lambda^{-2} \sin^2 \theta - t^2 / c^2)^{1/2},$$

$j_n(x)$  is the Bessel function of n-th order, and  $f_v$  is the magnetic scattering amplitude.

It can be seen from (2) that  $F_{ht}$  will differ from zero only at the places of intersection of the layer lines of index t with the lines of index h that are parallel to z, since only in this case are R and  $\mathbf{B}_H$  different from zero. Starting from the model of the magnetic spiral chain described above it can be stated that the 00l<sup>±</sup> re-

reflections arise as a result of helicoidal splitting of reflections of the meridional line with  $h = 0$ . The basic or "parent" sites can be selected according to the rule (1) for  $n = 0$ . The selection rule in this case becomes  $t = mp$ . Consequently, in the absence of helicoidal ordering of the magnetic moments, the magnetic contributions in the meridian would be arranged in the layer lines with indexes  $t$  equal to  $0, \pm 3, \pm 6, \pm 9$ , etc., in accordance with the values  $m = 0, \pm 1, \pm 2, \dots$ . The reflections located in lines with  $h \neq 0$  are conveniently indexed with the corresponding values of  $t$  and  $h$ . For example, reflections in the line  $h = 1$  will have indexes 1t.

#### 4. DETERMINATION OF THE SPATIAL DISLOCATION PARAMETERS OF THE Fe<sup>3+</sup> MAGNETIC MOMENT

In the experimental section of this paper, we noted that the ratio of intensities in the pairs of magnetic doublets  $00l^\pm$  was anomalous. On the basis of the model with dislocation of the magnetic moments of the ions along the  $z$  axis of the hexagonal cell of the ferrite, we calculated values of the ratio  $I_{00l^-}/I_{00l^+}$  that agreed closely with the experimental ones. The best agreement

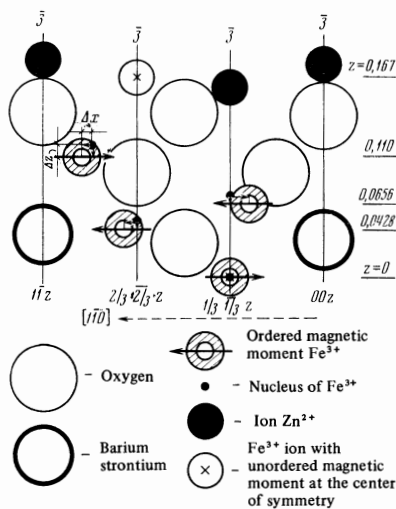


FIG. 3. Independent grouping of the elementary cell of type Y ferrite. The heavy arrows indicate the orientation of the Fe<sup>3+</sup> magnetic moments according to [6]. The light arrows determine the direction and magnitude of the shift of the Fe<sup>3+</sup> magnetic moments relative to the fixed nuclei. The form of the magnetic moment presented in the figure is an average over the moment densities in a multi-domain, unmagnetized crystal.

was obtained by assuming that the magnetic moment densities are shifted from the nonmagnetic Zn layers toward the origin (Fig. 3). The shift of the center of gravity of the Fe<sup>3+</sup> magnetic moment is a maximum for the ions in the 18h positions located close to the nonmagnetic layer, and zero for the Fe<sup>3+</sup> ion at the origin. The calculated values of  $\Delta z$  for different ionic positions are

Position:	18h (0,11)	6c (0.0656)	6c (0.0428)	3a (0)
$\Delta z$ , Å:	$0.4 \pm 0.1$	$0.3 \pm 0.1$	$0.2 \pm 0.1$	$0 \pm 0.1$

Here (and below) the coordinates of Fe<sup>3+</sup> along the  $z$  axis as found in [11] are given in parentheses.

The experimental and calculated intensities of the  $00l^\pm$  reflections obtained with the above values of  $\Delta z$  are presented in Table I. The calculated values of  $I_{00l^\pm}$  were determined from

$$I_{00l^\pm} = \frac{10^{23} F_{00l^\pm}^2 q^2}{\sin 2\theta} \exp \left[ -1.31 \frac{\sin^2 \theta}{\lambda^2} \right],$$

$$q^2 = \frac{1}{2} \left( \frac{1 + \cos^2 \delta}{2} \right),$$

where  $\delta$  is the angle between the normal to the plane of rotation of the magnetic moment and the scattering vector  $\epsilon$ . The important differences observed in the measured and calculated values of the intensities of the reflections 003 and 009 are due to extinction effects. Hence the experimental and calculated data are presented in the form of the corresponding ratios  $I_{00l^-}/I_{00l^+}$  (see Table I), which significantly reduces the extinction "interference."

In analyzing the magnetic contributions in the  $00l^\pm$  it was found that the magnetic moment of the Fe<sup>3+</sup> ion in the 3b positions was "disconnected" from the magnetic ordering, since these ions are located at the center of the nonmagnetic layer and lack magnetically active neighbors, which have been replaced by Zn ions.

Equation (2) was used to calculate the intensities of the magnetic reflections of the 1t series. The parameters of the angular periodicity of the chain spiral were obtained from the selection rule  $t = n + 3m$ . Since the shifts  $\Delta x$  in this case were not greater than 0.7 Å, and the functions  $j_n(\Delta x)$  of second order and higher were nearly zero, it sufficed to use only the one Bessel function with the least  $n$  in the calculations for each layer line. Table II gives the values of  $\Delta x$  for different crystallographic positions. The table also gives the phase angles  $\varphi$  of the magnetic chain spiral and the orientational phase angles  $\alpha$  of the mutual ordering of the magnetic moments.

In Table III are the measured and calculated values of the reflections of the 1t series, based on the param-

Table I. Measured and calculated values of the intensities of  $00l$  and their ratios for the ferrite Ba<sub>0.4</sub>Sr<sub>1.6</sub>Zn<sub>2</sub>Y at 293° K.

$00l$	Measurement			Theory				
	$I_{00l^-}$	$I_{00l^+}$	$I_{00l^-}/I_{00l^+}$	$F_{00l^-}^2$	$F_{00l^+}^2$	$I_{00l^-}$	$I_{00l^+}$	$I_{00l^-}/I_{00l^+}$
003	115	35	3.0	282.0	136.0	235.0	68.0	3.45
006	5	18	0.28	20.0	71.9	7.0	20.0	0.35
009	123	113	1.09	1225	1090	274.0	201.0	1.36
0012	8	17	0.47	100.0	144.0	16.4	20.0	0.82
0015	2	40	0.05	0.5	174.0	0.07	19.2	0.004
0018	39	13	3.0	180.0	65.6	20.0	6.4	3.1

**Table II.** Basic parameters of the delocalization of the Fe<sup>3+</sup> magnetic moment in the basal plane.

Position of Fe <sup>3+</sup> ions in the ferrite lattice	Shift parameter Δx, Å	Phase angle φ	Phase angle α	Position of Fe <sup>3+</sup> ions in the ferrite lattice	Shift parameter Δx, Å	Phase angle φ	Phase angle α
3a (0)	0	0	0	6c (0,0656)	0.7±0.1	π	π
6c (0.0428)	0.4±0.1	0	π	18h (0,11)	0.3±0.1	0	0

**Table III.** Measured and calculated values of the magnetic contributions in the reflections ht and h $\bar{t}$  and their ratios for the ferrite Ba<sub>0.4</sub>Sr<sub>1.6</sub>Zn<sub>2</sub>Y at 293° K.

ht	Measurement			Theory				
	I <sub>ht</sub>	I <sub>h<math>\bar{t}</math></sub>	I <sub>ht</sub> /I <sub>h<math>\bar{t}</math></sub>	F <sup>2</sup> <sub>ht</sub>	F <sup>2</sup> <sub>h<math>\bar{t}</math></sub>	I <sub>ht</sub>	I <sub>h<math>\bar{t}</math></sub>	I <sub>ht</sub> /I <sub>h<math>\bar{t}</math></sub>
10	0	—	—	2.9	—	0.7	—	—
11	0	2.0	—	1.4	4.8	0.4	1.4	0.28
12	3.0	1.0	3.0	10.0	2.0	3.0	0.6	5.0
13	36.0	8.0	4.5	225.0	28.0	76.0	9.3	8.2
14	15.0	1.0	15.0	25.0	2.2	9.2	0.5	18.4
15	7.0	0	—	13.0	0.4	5.0	0	—
16	0	0	—	2.6	4.8	0.6	1.8	0.33
17	1.0	0	—	2.6	0.1	0.6	0	—
18	0	0	—	1.4	0	0.3	0	—

eters in Table II. The quantity I<sub>ht</sub> was calculated from

$$I_{ht} = \frac{10^{23} F_M^2 q^2}{\sin 2\theta} e^{-2w}, \quad q^2 = \frac{1 + \cos^2 \delta}{2}$$

(e<sup>-2w</sup> is the temperature factor). The differences between the measured and calculated values of I<sub>13</sub> in Table III are attributed to extinction effects. In these calculations the values of the magnetic form factor of Fe<sup>3+</sup> were taken from [5].

In Fig. 3 the independent grouping of the elementary cell of a type Y ferrite is drawn to scale. One sees the general character of the shift of density of the ordered magnetic moments from the nuclei. The ionic radius of Fe<sup>3+</sup> was used as the magnitude of the outer radius of the fixed magnetic moment.

An investigation of the nuclear contributions to the structural reflections convinced us that the ions were located in positions within 0.1 Å of those found in [1].

## 5. CONCLUSION

The theoretical basis for delocalization of the magnetic moment in antiferromagnets of the α-Fe<sub>2</sub>O<sub>3</sub> type was provided by Gufan and Dzyaloshinskii, [7] who attributed the existence of a delocalized weak ferromagnetic moment density to spin-spin interaction between different ions. The data of the present investigation confirms the theoretical conclusions, practically all of the Fe<sup>3+</sup> magnetic moment being displaced in our case.

We have assumed that the magnetic moment, though delocalized, was still spherically symmetrical to a first

approximation. Although this is probably a simplification of the actual situation, it is justifiable if the agreement between the measured and calculated intensities is accepted as satisfactory.

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