Magnetic structure and localization of Co^{2+} and Fe^{2+} ions in hexagonal ferrites

V. F. Belov, T. A. Khimich, M. N. Shipko, I. S. Zheludev,
E. V. Korneev, and N. S. Ovanesyan
Crystallography Institute of USSR Academy of Sciences

(Submitted December 19, 1972)
Zh. Eksp. Teor. Fiz. **64**, 2160-2172 (June 1973)

An investigation was made of Co-substituted hexagonal ferrites with the M, W, and Y structures. The localization of the Co^{2+} and Ti^{4+} ions in substituted M-type ferrites was determined. It was found that the nuclei of the Fe^{3+} ions, characterized by the fivefold coordination (sublattice e), were subject to strong electric-field gradients. The crystallographic anisotropy was affected mainly by the iron ions in the e sublattice in pure hexagonal barium and strontium ferrites. In the case of the Co-substituted ferrites the nature of the magnetic ordering and the magnetic anisotropy were strongly affected by the Co^{2+} ions. It was established that the replacement of the Fe^{2+} with the Co^{2+} ions in the hexagonal W-type ferrites altered the magnetic structure. The magnetic anisotropy of the W hexagonal ferrites was primarily due to the spin-orbit interaction. The magnetic structure and the localization of the Zn^{2+} and Co^{2+} ions in the substituted Y-type hexagonal ferrites was investigated. The Mössbauer effect was used to determine the sublattice magnetizations of these compounds and a comparison was made with the results of the magnetic measurements. It was concluded that a random canted spin structure appeared in zinc-rich samples.

1. INTRODUCTION

Hexagonal ferrites have complex crystal structures and interesting magnetic properties. Considerable success has recently been achieved in investigations of these compounds but many points are still not clear. For example, the microscopic nature of the magnetic anisotropy and the cation distribution in hexagonal substitutional ferrites are not yet known. Little work has been done on the magnetic structure. Moreover, only a few Mössbauer-effect investigations have been made of hexagonal ferrites.[1-7]

It was our aim to determine the magnetic structure and cation distribution in hexagonal ferrites with the M, W, and Y structures by the Mössbauer spectroscopy method.

We employed an electrodynamic Mössbauer spectrometer with a Co^{57} source in a Pd matrix. An analysis of the Mössbauer spectra was carried out on a BÉSM-4 computer by the least-squares method. The minimization was performed by the sufficiently effective local Newton-Raphson method with a parabolic interpolation to the minimum. The investigated hexagonal ferrites were prepared from the melt.[8]

2. CATION DISTRIBUTION AND MAGNETIC STRUCTURE OF HEXAGONAL FERRITES WITH M STRUCTURES

One formula unit of type M barium ferrite contains twelve iron ions. Six of the Fe^{3+} ions, with upward-directed spins, occupy octahedral sites (sublattice a), one ion is located in a different octahedral site (upward spin, sublattice b), two ions are at tetrahedral sites (downward spin, sublattice c), two ions occupy a third type of octahedral site (downward spin, sublattice d), and one iron ion is located at a site with fivefold coordination (downward spin, sublattice e). These structural data were used in the interpretation of the Mössbauer spectra. We employed the same notation for the sublattices and the associated spectra.

The Mössbauer spectra of $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ were similar to the spectra of these compounds reported in [2,9] and represented superpositions of five sextets of the iron ions located in five different magnetic sublattices. However, at room temperature the b-sublattice spectrum coincided with the d spectrum and only four sextets could be distinguished. An analysis of the intensities of the sextet components representing the iron ions located at different positions indicated that the replacement of Fe^{3+} with Co^{2+} and Ti^{4+} in $SrFe_{12}O_{19}$ reduced the intensities of the a-sublattice components. This indicated that the Co^{2+} and Ti^{4+} ions occupied octahedral positions in the a sublattice. In the case of $BaCo_2Ti_2Fe_8O_{19}$ we observed a strong reduction in the iron ion population of the a sublattice, relative to that in pure barium ferrite.

Table I lists the chemical isomeric shift δ, quadrupole splitting Δ, and local magnetic field H_l deduced from the Mössbauer spectra. All the sublattices of $BaFe_{12}O_{19}$ exhibited a considerable quadrupole splitting. The highest value of Δ was obtained for the Fe^{57} nuclei located in the e sublattice. The replacement of Ba^{2+} in $BaFe_{12}O_{19}$ with the smaller Sr^{2+} ions reduced the quadrupole splitting in all the sublattices, except e. This indicated an increase in the symmetry of the local environment of the Fe^{3+} ions located in the a, c, and d sublattices. The value of Δ for the e sublattice in $SrFe_{12}O_{19}$ and, consequently, the electric-field gradients increased somewhat because of the substitution. The anisotropy constant K_1 did not vary greatly with the composition (for $BaFe_{12}O_{19}$ this constant was $K_1 = 3.3 \times 10^6$ erg/cm^3 and for $SrFe_{12}O_{19}$ it was $K_1 = 3.6 \times 10^6$ erg/cm^3).

The replacement of some of the Fe^{3+} ions with Co^{2+} and Ti^{4+} in strontium ferrite ($SrCo_{0.42}Ti_{0.42}Fe_{11.16}O_{19}$) had the greatest effect on the local symmetry of the environment of the Fe^{3+} ions located in the e sublattice. It is evident from Table I that the value of Δ for the e sublattice decreased considerably. At the same time the magnetic anisotropy constant K_1 fell from 3.6×10^6 to

TABLE I

Sub-lat-tice	δ, mm/sec	Δ, mm/sec	H_L, kOe	Sub-lat-tice	δ, mm/sec	Δ, mm/sec	H_L, kOe	Sub-lat-tice	δ, mm/sec	Δ, mm/sec	H_L, kOe
$BaFe_{12}O_{19}$				$SrFe_{12}O_{19}$				$Sr(Co, Ti)_{0,42}Fe_{11,16}O_{19}$			
a	0,43	0,3	408	*a*	0,49	0,19	402	*a*	0,36	0,22	403
c	0,34	0,11	493	*c*	0,3	0,05	486	*c*	0,24	0,01	477
d	0,46	0,21	516	*d*	0,41	0,15	506	*d*	0,34	0,1	493
e	0,22	1,1	397	*e*	0,23	1,14	406	*e*	0,05	0,90	388
								Error	±0,03	±0,03	±5

TABLE II

Ferrite	Sublattice magnetization σ					σ_m	σ_m
	a	*c*	*d*	*b*	*e*	G.cm³ • g⁻¹	
$BaFe_{12}O_{19}$	129	51,8	54,4	27	20,9	70,7	72
$SrFe_{12}O_{19}$	127	51,2	53,2	26,6	21,3	70,5	
$Sr(Co, Ti)_{0,42}Fe_{11,16}O_{19}$	115	50,1	51,8	25,9	20,4	59,9	60
$BaCo_2Ti_2Fe_8O_{19}$	19,7	11,2	7,5	26,5	19,7	47,2	47
$BaSc_{1,5}Fe_{10,5}O_{19}$	92	36,8	40,8	13,6	12,9	40,9	60

TABLE III

Crystallo-graphic position	Tetrahedron	Trigonal bipyramid	Octahedron	Sublattice
$12K_3(S)$			6↑	*a*
$4f_3(S)$			2↑	*b*
$4e_1(S)$	2↓			c_1
$2d(R)$		1↑		*e*
$4f_5(R)$			2↓	*d*
$6g(S)$			3↑	a_1
$4f_2(S)$	2↓			c_2

1.8×10^6 erg/cm³. In the case of $BaCo_2Ti_2Fe_8O_{19}$ the quadrupole splitting of all the sublattices (except e) became negative. This indicated a change in the direction of easy magnetization. In fact, at room temperature the magnetic ion spins in this compound were located in the basal plane and not aligned along the c axis as in the case of $BaFe_{12}O_{19}$.[8]

The correlation between the constant K_1 and the quadrupole splitting indicated that the magnetic anisotropy of the investigated compounds was governed primarily by the spin-orbit interaction. In barium ferrite all the sublattices (and particularly a and e) made a considerable contribution to the magnetic anisotropy. In the Co-substituted hexagonal ferrites the magnetic anisotropy was due to the iron ions located in the e sublattice and to the Co^{2+} ions.

The replacement of barium with strontium had hardly any effect on the nuclei of the iron ions. However, in the case of $Sr(Co,Ti)_{0.42}Fe_{11.16}O_{19}$ and $BaCo_2Ti_2Fe_8O_{19}$ the local magnetic fields at the Fe^{57} nuclei located in the e, d, and c sublattices were weaker than the H_l^e, H_l^d, and H_l^c fields in $SrFe_{12}O_{19}$ and $BeFe_{12}O_{19}$.

The reduction in the magnetic fields at the Fe^{57} nuclei located in the e, d, and c sublattices could be due to a change in the indirect interaction. The strongest interactions in the d and e sublattices were those of the de and ad type. The localization of the Co^{2+} and Ti^{4+} ions in the a sublattice reduced the exchange interactions of the ad and ac types, which—in its turn—weakened the magnetic fields at the Fe^{57} nuclei. Some of the iron ions, whose immediate cation environment included the nonmagnetic titanium ions, became paramagnetic and made no contribution to the ferrite magnetization. Calculations indicated that in the case of $BaCo_2Ti_2Fe_8O_{19}$ more than hand the Fe^{3+} ions located in the d, a, and c sublattices exhibited no magnetic hyperfine splitting.

It should be pointed out that the magnetic fields at the iron ion nuclei characterized by the fivefold coordination (sublattice e) were much weaker than in the other sublattices. This could be due to a considerable transfer of the spin density from the Fe^{3+} ions to the surrounding oxygen atoms, which should give rise to a strong exchange interaction between these ions and the iron ions in the d sublattice. In view of this the sublattice e should strongly influence the exchange interaction between the other sublattices. This hypothesis was confirmed by measurements carried out on $BaS_{1.5}Fe_{10.5}O_{19}$, in which the nonmagnetic Sc^{3+} ions were localized in the b, e, and a sublattices. Even small amounts of scandium reduced considerably the magnetic fields in all the sublattices.

Measurements of the magnetic fields at the nuclei allowed us to determine the sublattice magnetizations σ. We could compare the magnetizations deduced directly from the magnetic measurements σ_m with the magnetizations σ_M obtained from the Mössbauer-effect measurements of the magnetic fields at the nuclei. This comparison is made in Table II.

We can see from Table II that the Mössbauer results are in good agreement with the magnetic measurements and this is true for all the compounds with the exception of $BaSc_{1.5}Fe_{10.5}O_{19}$. It follows that the hypothesis of a collinear distribution of spins in these ferrites is correct. The discrepancies between the magnetizations σ_M and σ_m for $BaSc_{1.5}Fe_{10.5}O_{19}$ indicate a deviation from the collinear model.

3. MAGNETIC STRUCTURE AND LOCALIZATION OF Fe^{2+} AND Co^{2+} IONS IN HEXAGONAL FERRITES WITH W STRUCTURES

According to the neutron-diffraction investigations,[8,10] there are seven magnetic sublattices in $BaFe_{2-x}Fe_{16}O_{27}$. The number of ions in these sublattices and the directions of the magnetic moments are given in Table III. Arrows directed up or down represent in a conventional manner the directions of the magnetic moments of the iron ions located at inequivalent crystallographic sites. The resultant magnetic moment in the collinear model should be directed upward.

Figure 1 shows the Mössbauer spectra of $BaCo^{2+}Fe^{2+}Fe^{3+}_{16}O_{27}$ obtained at room and liquid nitrogen temperatures. At room temperature the spectrum has 21 lines and represents a superposition of seven sextets of the Fe^{3+} ions located at different crystallographic sites (Table III).

The components of the spectra were identified by investigating the ferrite Co_1W in an external magnetic field H = 17 kOe normal to the direction of propagation of the γ rays. Figure 2 shows the Mössbauer spectrum of Co_1W, recorded using a Co^{57} source in a chromium matrix and an external field H = 17 kOe. The external field shifted the d, c_1, and c_2 lines in the direction of higher velocities, i.e., in the direction of higher hyperfine fields. This indicated that the directions of the magnetic moments of the Fe^{3+} ions, corresponding to these lines, were opposite to the direction of the resultant magnetization of the ferrite. In the W structure these ions (Table III) were located in the d, c_1, and c_2 sublattices. The highest value of the hyperfine field was observed

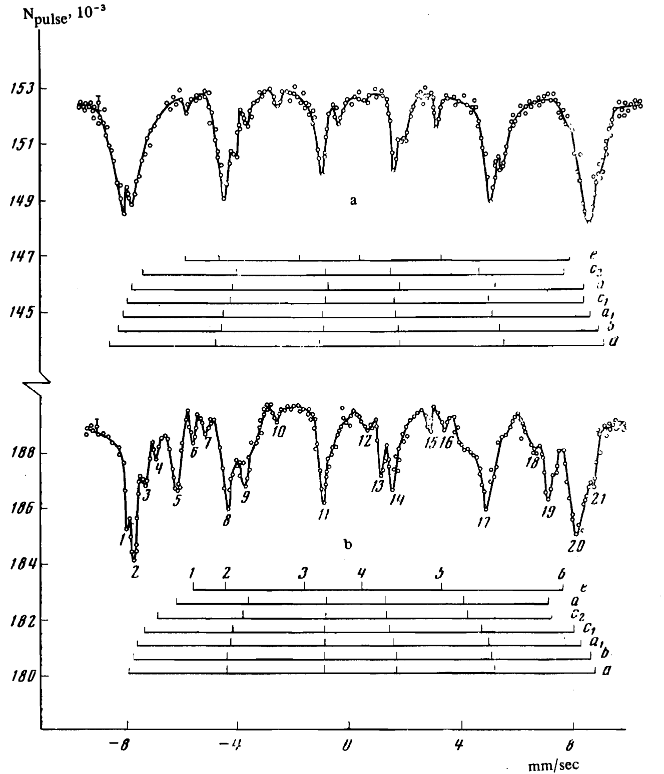

FIG. 1. Mössbauer spectra of the hexagonal ferrite BaCo^{2+}Fe^{2+}Fe$^{3+}_{16}$O$_{27}$: a—at liquid nitrogen temperature; b—at room temperature. The a, a$_1$, e, c$_1$, c$_2$, b, d sextets are due to the iron ions in the sublattices listed in Table III.

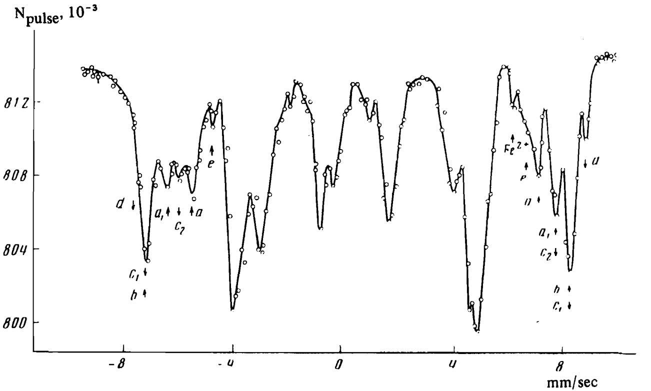

FIG. 2. Mössbauer spectrum of BaCoFeFe$_{16}$O$_{27}$ measured in an external magnetic field H = 17 kOe using a Co^{57} source in chromium. The arrows represent the directions of the magnetic moments of the iron ions in seven sublattices.

for the d sublattice (R block) in the W structure (differing from the M structure by spinel blocks). Hence, we could attribute the outer d lines to the d sublattice. The c$_1$ and c$_2$ lines were due to the c$_1$ and c$_2$ sublattices. The components b, e, and a shifted toward weaker fields when an external field was applied. Consequently, they were attributed to the Fe^{3+} ions located in the b, e, and a sublattices (Table III). An analysis of the intensities of the components b, e, and a and a comparison with the results of an investigation by the NMR method demonstrated that the smallest value of H_l was observed for the e sublattice (fivefold coordination). This interpretation of the spectrum was in good agreement with the NMR data on Fe$_2$W.

An increase in the concentration of the Co^{2+} ions (corresponding to an increase of x from 1 to 1.75) altered strongly the hyperfine splitting pattern. The spectrum of a sample with x = 1.75 (Fig. 3) had 16 components, i.e., the number of lines was less than in the spectrum of a sample with x = 1. This was due to the overlap of the components of the spectra representing inequivalent positions of the Fe^{3+} ions. It should be noted that the same increase in the concentration of cobalt reduced strongly the intensities of the components representing the Fe^{3+} ions located in the a octahedral sublattice. This reduction in the intensity was due to a reduction in the iron ion population of the a sublattice.

Since the iron ions in the BaCo$_x$Fe$_{2-x}$F$_{16}$O$_{27}$ system were replaced with the Co^{2+} ions, we concluded that the observed reduction in the intensities of the a-sublattice lines was due to the localization of cobalt at the 12K$_3$ positions (Table III). In fact, neutron-diffraction investigations demonstrated that most of the cobalt ions occupied the 12K$_3$ positions in the ferrites grown from the melt. The rest of the Co^{2+} ions were distributed at random between other positions in the spinel blocks.

The spectrum of a sample of Co$_1$W differed from that of Fe$_2$W by the presence of additional lines (7, 15) evidently due to Fe^{2+}. This was supported by the Mössbauer spectra of the samples in which the Fe^{2+} ions were replaced almost completely with the Co^{2+} ions. A comparison of Figs. 1 and 3b indicated that the lines 7 and 15 (Fig. 3b) of the Fe^{2+} ions were not observed in the spectra of BaCo$^{2+}_{1.75}$Fe$^{2+}_{0.25}$Fe$^{3+}_{16}$O$_{27}$.

Thus, the presence of the Fe^{2+} lines in the spectrum of Co$_1$W indicated that the Fe^{2+} ions in the investigated samples were localized at one crystallographic position (in one sublattice). If the Fe^{2+} ions were located in several sublattices the spectra would have had a series of sextets due to the inequivalent positions of these ions. The question then arose as to where these Fe^{2+} ions were localized.

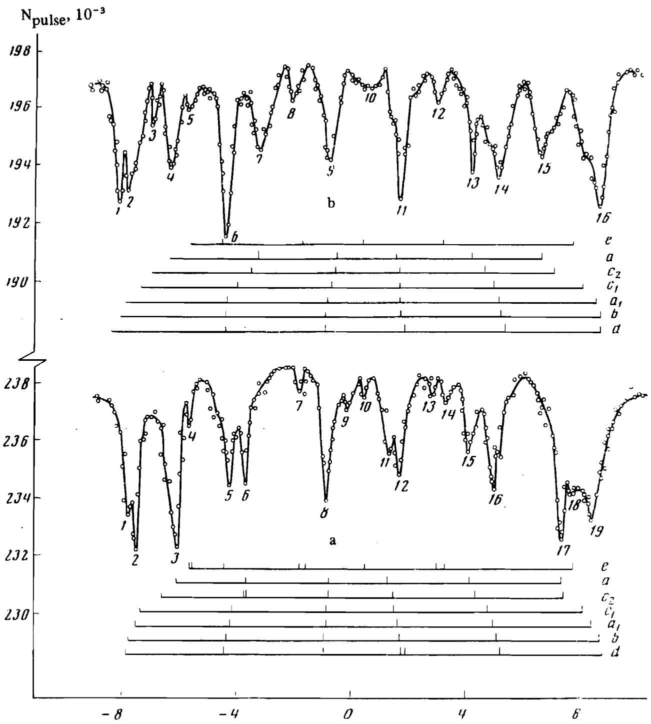

FIG. 3. Mössbauer spectra of: a—BaFe$^{2+}_2$Fe$^{3+}_{16}$O$_{27}$; b—BaCo$^{2+}_{1.75}$Fe$^{2+}_{0.25}$Fe$^{3+}_{16}$O$_{27}$.

It should be pointed out that x-ray structure investigations of Fe_2W ferrites failed to establish the positions of the divalent iron ions because of the similarity of the scattering factors of the Fe^{2+} and Fe^{3+} ions. Braun[11] applied the condition of electrical neutrality and assumed that the Fe^{2+} ions were located in spinel block but he did not specify their crystallographic positions. Measurements of the Mössbauer spectra of Co_1W in a magnetic field indicated that the direction of the magnetic moments of the Fe^{2+} ions coincided with the direction of the net magnetization of the ferrite. An analysis of the intensities of the components in the spectra showed that the Fe^{2+} ions were localized in the a sublattice.

Table IV lists the isomeric ehcmical shifts δ, the magnetic fields at the Fe^{57} nuclei (H_l), and the quadrupole splittings Δ in the investigated samples. In pure hexagonal ferrite Fe_2W the greatest quadrupole splitting (0.85 mm/sec) was exhibited by the Fe^{3+} ions characterized by a fivefold coordination (sublattice e). In contrast to the hexagonal ferrites with the M structure, the values of Δ were small for all the other sublattices. Special atomic positions (2d positions in the e sublattice, Table III) were found in the crystal lattice of the hexagonal ferrite Fe_2W. These positions were the nodes of chains of the exchange interactions. The Fe^{3+} ions located at these positions were coupled by the exchange interactions of the iron ions in the d and a sublattices. The orientation of the magnetic moments of the iron ions in the e sublattice evidently had a strong influence on the orientation of the magnetic moments in the other sublattices. Since the trigonal axis of the fivefold coordination of the Fe^{3+} ions in Fe_2W was the principal symmetry axis of the tensor of the electric-field gradient and it coincided with the hexagonal c axis, the strong spin-orbit interaction oriented the magnetic moments of the iron ions in the e sublattice along the c axis. This was not in conflict with the results of neutron-diffraction and magnetic measurements.[8]

The quadrupole splitting was greatest for the Fe^{3+} ions located in the a and e sublattices. The introduction of Co^{2+} ions into Fe_2W resulted in large changes in the quadrupole splitting of the iron ions in the c_2 and a sublattices, relative to the splitting in pure Fe_2W. The replacement of half the Fe^{2+} ions with Co^{2+} in the c_2 sublattice reversed the sign of the quadrupole splitting. This change in the splitting could be due to a change in the magnetic structure of the ferrite, i.e., due to deviations of the magnetic moments of the iron ions from the hexagonal axis. One should also allow for the possibility of local distortions of the crystal lattice. However, such distortions could not result in the observed large changes (particularly the reversal of the sign) of the quadrupole splitting. The negative sign of the quadrupole splitting in the c_2 sublattice of Co_1W could be explained by the presence of the Co^{2+} ions in the a sublattice. The nearest sphere of the cation environment of a Co^{2+} ion included two iron ions in the d sublattice, one ion in the e sublattice, and three ions in the c_2 sublattice. Consequently, the strong exchange interactions of the Co^{2+} ions in Co_1W with their nearest neighbors deflected the magnetic moments of these neighbors away from the c axis. These deviations altered the angle between the direction of the magnetic field at the Fe^{57} nuclei and the symmetry axis of the electric-field gradient, i.e., they altered the quadrupole splitting.

It is evident from Table IV that the replacement of half the Fe^{2+} ions in Fe_2W with the Co^{2+} ions altered only the quadrupole splitting of the Fe^{3+} ions located in the nearest sphere of the cation environment of a cobalt ion. Obviously, the direction of the magnetic moments of the iron ions in the c_2 sublattice did not coincide with the direction of the hexagonal axis but made some angle with the latter.

TABLE IV

Sublattice	δ, mm/sec	Δ, mm/sec	H_L, kOe	Sublattice	δ, mm/sec	Δ, mm/sec	H_L, kOe
Fe_2W; $T=300°$ K				$Co_{1,75}W$; $T=300°$ K			
d	0,45	0,08	517	d	0,4	—0,14	526
b	0,45	0,08	510	b	0,44	—0,02	517
a_1	0,42	0,05	496	a_1	0,44	—0,01	506
c_1	0,37	0,06	478	c_1	0,40	—0,04	476
c_2	0,38	0,05	434	c_2	0,37	—0,23	433
a	0,46	0,22	414	a	0,40	—0,14	401
e	0,25	0,85	409	e	0,26	0,87	413
Co_1W; $T=300°$ K				Co_1W, $T=82°$ K			
d	0,49	0,02	517	d	0,46	—0,03	546
b	0,47	0,04	508	b	0,49	—0,04	529
a_1	0,42	0,01	491	a_1	0,43	—0,01	516
c_1	0,40	0,06	474	c_1	0,40	—0,02	503
c_2	0,34	0,02	436	c_2	0,39	—0,07	466
a	0,45	0,12	411	a	0,56	—0,09	500
e	0,32	0,83	408	e	0,25	0,97	429

It should be noted that the Co^{2+} ions formed a second type of node of chains of the exchange interactions (position $12K_3$, sublattice a). In the Co_1W ferrite these positions made a considerable contribution to the magnetic anisotropy because of the freezing of the orbital moments of the Co^{2+} ions by the inhomogeneous crystal field.

Thus, the main contribution to the magnetic anisotropy of Co_1W was made by the Co^{2+} ions and by the Fe^{3+} ions in the e sublattice. Even greater changes, relative to Fe_2W, were observed in the quadrupole splitting of the ferrite $Co_{1.75}W$. In this case, the quadrupole splitting was reversed in sign for all the Fe^{3+} ions, except those in the e sublattice. According to neutron-diffraction investigations,[8] the magnetic moments of the ions in this sample were oriented in the basal plane. The quadrupole splitting Δ in the e sublattice of the ferrite $Co_{1.75}W$ was equal, within the limits of the experimental error, to the corresponding splitting in Co_1W and Fe_2W. This could indicate a constancy of the angle θ between the magnetic moment of the Fe^{3+} ions and the axis of the tensor of the electric-field gradient. However, this was in conflict with the results of neutron-diffraction studies. In view of the absence of x-ray structure data on changes in the distorted fivefold coordina-

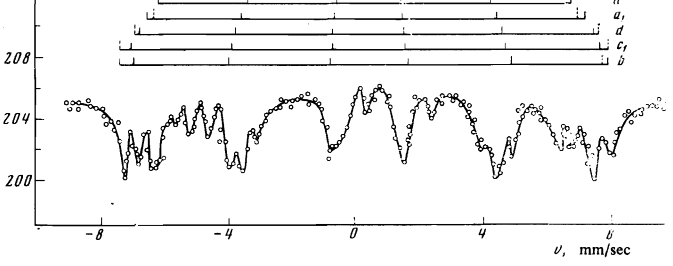

FIG. 4. Mössbauer spectrum of the hexagonal ferrite $Ba_2Co_{1.75}Zn_{0.25}Fe_{12}O_{22}$. The dashed lines in the upper part of the figure represent the positions of the sextet components in an external magnetic field H = 17 kOe and the continuous lines represent their positions in the absence of a field (H = 0).

tion with the value of x in the system $Co_xFe_{2-x}W$, the orientation of the axis of the electric-field gradient tensor could not be determined and the direction of the magnetic moment of the Fe^{3+} ions in the e sublattice of $Co_{1.75}W$ could not be found relative to the crystallographic axes. Therefore, up to now it has been difficult to explain the results obtained.

Measurements on the hexagonal ferrite Co_1W were carried out at liquid nitrogen temperature. It is evident from Table IV that the quadrupole splitting in all the sublattices was negative, except in the e sublattice. This change in the sign of the quadrupole splitting in all the sublattices was evidence of a change in the direction in the magnetic moments of the iron ions.

4. MÖSSBAUER SPECTROSCOPY OF HEXAGONAL FERRITES WITH Y STRUCTURES

According to the structure data,[8,11,12] the crystal lattices of the hexagonal ferrites with a common chemical formula $Ba_2Zn^{2+}_{2-x}Co^{2+}_xFe^{3+}_{12}O_{22}$ (type **Y** structure) consist of spinel (S) and tetragonal (T) blocks. One formula unit of these ferrites includes seven inequivalent positions of the metal ions. The number of ions at different positions in the S and T blocks and the relative directions of their magnetic moments are given in Table V. The results of structure investigations carried out in[8,11,12] were used at the starting point in the analysis of the complex Mössbauer spectra of the hexagonal type-**Y** ferrites.

Figure 4 shows, by way of example, the spectrum of the hexagonal ferrite $Ba_2Zn_{0.25}Co_{1.75}Fe_{12}O_{22}$. The presence of seven different positions of the iron ions made it necessary to resolve this spectrum into seven sextets of the iron ions in the a, a_1, b, c_1, c_2, d, and f sublattices (Table V). The positions of these sextet lines were identified by continuous lines in the schematic representation given in the upper part of Fig. 4. The components of the spectra were identified by measurements in an external magnetic field H = 17 kOe. These measurements established the shifts of the lines for five magnetic sublattices a, d, b, c_1, and c_2. The positions of the sextet components in an external magnetic field were represented by dashed lines in the schematic representation given in the upper part of Fig. 4. The lines corresponding to the sextets a and b shifted in the direction of lower hyperfine fields at the Fe^{57} nuclei. Consequently, the directions of the magnetic moments of the iron ions corresponding to these sextets were parallel to the resultant magnetization and could be attributed to the a and b sublattices. A definite shift of the components in the direction of higher values of H_l was observed for the sextets c_1 and c_2. These sextets were due to the Fe^{3+} ions, whose magnetic moments were antiparallel to the resultant magnetization and, consequently, were located in the c_1 and c_2 sublattices. Unfortunately, it was not possible to establish the direction of the shifts of the a_1 and f lines because of the poor resolution. We simply assumed that they were due to the Fe^{3+} ions in the a_1 and f sublattices.

TABLE V

Sublattice	Position	Octahedron	Tetrahedron
a	$18h(S)$	3←	
a_1	$18h(T)$	3←	
b	$3b(S)$	1←	
c_1	$6c(S)$		2→
c_2	$6c(T)$		2→
d	$6c(T)$	2→	
f	$3a(T)$	1←	

Figure 5 shows the dependences of the relative intensities of the outer components of the six sextets a, a_1, b, c_1, c_2, and d in $Ba_2Zn_{2-x}Co_xFe_{12}O_{22}$ on the cobalt concentration. The replacement of the Zn^{2+} ions with Co^{2+} increased the relative intensity of the components of the c_1 and c_2 sextets and, consequently, increased the iron ion populations of the c_1 and c_2 sublattices. Obviously, the replacement of the Zn^{2+} ions with Co^{2+} resulted in a transfer of the iron ions from the sublattices where cobalt was localized to the sublattices where zinc atoms were located. Consequently, we could assume that the Zn^{2+} ions were localized in the tetrahedral sublattices c_1 and c_2. This was in agreement with the results of neutron-diffraction investigations of the $Zn_{2-x}Co_xY$ ferrites.[13] An increase in the concentration of Co in $Co_xZn_{2-x}Y$ reduced the intensities of the lines corresponding to the a, a_1, and b sublattices. This could be due to the localization of the Co^{2+} ions in these sublattices.

The saturation magnetic moment n calculated per formula unit by the application of the Gorter model, making allowance for the distribution of the Zn^{2+} and Co^{2+} ions between the magnetic sublattices found in our investigation, was in good agreement with the experimental value of n deduced from the specific saturation magnetization. For example, in the case of total localization of the Co^{2+} ions in the a and a_1 sublattices of $Zn_{0.25}Co_{1.75}Y$ the magnetic moment was 10.54 μ_B. This value was almost identical with the experimental value $n = 10.6\ \mu_B$.

The parameters of the Mössbauer spectra of the investigated ferrites are collected in Table VI. Slight quadrupole shifts were observed for all the magnetic sublattices in the $Co_xZn_{2-x}Y$ ferrites. The smallest values of Δ in Zn_2Y obtained for the c, d, and a sublattices were -0.01 ± 0.02 mm/sec. The shifts were somewhat larger for the c_2 and f sublattices. A characteristic feature of the spectra of Zn_2Y was the negative sign of the quadrupole shifts of all the sublattices. Replacement of the Zn^{2+} ions with Co^{2+} did not alter significantly the quadrupole shifts. In the case of pure Zn_2Y, these shifts were small and negative. The negative sign and the almost identical values of the quadrupole splitting of these compounds indicated that the direction of the magnetic moment was the same for all

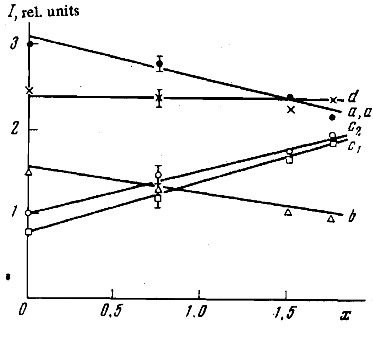

FIG. 5. Dependences of the relative intensities of the outer components of the a, a_1, b, c_1, c_2, and d sextets of the $Ba_2Co_xZn_{2-x}Fe_{12}O_{22}$ ferrites on the cobalt concentration. The intensities of the components of the a and a_1 sublattices are identical.

TABLE VI

Parameter	Sublattice							Error
	b	*c*₁	*d*	*a*	*a*₁	*c*₂	*f*	
Zn_2Y								
H_L, kOe*	388(388)	375(366)	355(351)	338(335)	310(310)	290(279)	267(260)	±8 kOe
δ, mm/sec	0.41	0.41	0.41	0.42	0.43	0.38	0.38	±0.03 mm/sec
Δ, mm/sec	—0.02	—0.01	—0.01	—0.01	—0.02	—0.07	—0.09	±0.03 mm/sec
$Zn_{1,25}Co_{0,75}Y$								
H_L, kOe	435	421	406	381	362	346	311	±8 kOe
δ, mm/sec	0.41	0.39	0.41	0,42	0.42	0.4	0.36	±0.03 mm/sec
Δ, mm/sec	—0,07	—0.01	—0,06	—0.025	—0,07	—0.12	—0,10	±0.03 mm/sec
$Zn_{0,5}Co_{1,5}Y$								
H_L, kOe	466	450	436	418	395	377	344	±5 kOe
mm/sec	0,43	0.4	0.46	0.4	0.46	0.50	0,45	±0.02 mm/sec
mm/sec	—0,06	—0,04	—0.01	—0,06	—0,06	—0.02	—0,05	±0,02 mm/sec
$Zn_{0,25}Co_{1.75}Y$								
H_L, kOe	473	455	441	424	401	379	357	±5 kOe
mm/sec	0,42	0,43	0.44	0,44	0,425	0,46	0,45	±0.02 mm/sec
mm/sec	—0,06	—0.03	—0,02	—0.02	—0,05	—0,02	—0,01	±0.02 mm/sec

*The values in parentheses are the field H_L, in kOe, taken from [6].

compounds at room temperature and that these compounds had an easy magnetization plane. This was in agreement with the results of neutron-diffraction investigations which showed that at room temperature these ferrites exhibited a collinear ordering of spins oriented in the basal plane.[13]

Replacement of the nonmagnetic Zn^{2+} ions with the magnetic Co^{2+} altered considerably the magnetic fields at the Fe^{57} nuclei. In the case of the Zn_2Y ferrite the hyperfine fields at the Fe^{57} nuclei were (267–388) ± 8 kOe for the seven sublattices. The introduction of the Co^{2+} ions expanded this range. For example, in the case of $Co_{1.75}Zn_{0.25}Y$ the lowest value of the local magnetic field $H_l = 357 \pm 8$ kOe was obtained for the f sublattice. The highest field (473 ± 5 kOe) was found at the nuclei of the iron ions in the b sublattice.

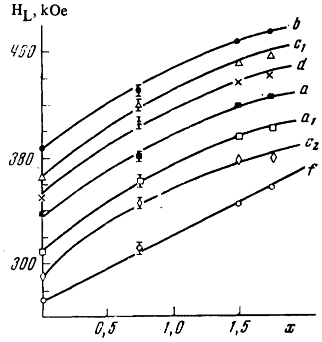

FIG. 6. Dependences of the magnetic fields at the Fe^{57} nuclei in the a, a_1, b, c_1, c_2, d, and f sublattices on the concentration of coblat in $Ba_2Zn_{2-x}Co_xFe_{12}O_{22}$.

Figure 6 shows the dependences of the magnetic fields at the Fe^{57} nuclei in seven magnetic sublattices on the concentration of Co. The local magnetic fields at the nuclei increased on the replacement of Zn^{2+} with Co^{2+}. This increase in H_l was in agreement with the rise of the Curie temperature. The largest change in H_l on transition from Zn_2Y to $Co_{1.75}Zn_{0.25}Y$ was observed for the f sublattice. This sublattice was characterized by the lowest value of the hyperfine field in pure Zn_2Y. This could be due to the weak indirect exchange interaction of the iron ions in the f sublattice with the ions in the other sublattices. The hyperfine field at the Fe^{57} nuclei was found to depend on the average value of the magnetic moment of an iron ion $\langle S_z \rangle$ which was affected by the exchange interaction.[14]

A random distribution of the Zn^{2+} ions between tetrahedra suppressed the strong exchange coupling (of the AB type) between the sublattices f and c_2, and between a_1 and c_2. The strongest was the weakening of the indirect exchange interaction of the f sublattice, which gave rise to a low value of the hyperfine field at the Fe^{57} nuclei (H_l^f). Replacement of the Zn^{2+} ions with Co^{2+} enhanced the exchange interaction and increased strongly the values of H_l^f.

Let us now compare the saturation magnetization of the Co-substituted hexagonal ferrites with the **Y** structure, determined directly by a magnetic method, with the magnetization deduced from the measurements of the magnetic fields at the nuclei carried out by the Mössbauer method. The magnetic measurements indicated that the replacement of the Zn^{2+} ions in $Co_xZn_{2-x}Y$ with Co^{2+} reduced the magnetization from 42 to 34 $G \cdot cm^3 \cdot g^{-1}$ when x was increased from 0 to 1.75. The magnetization deduced from the magnetic measurements on samples with $x \leq 1.5$ was considerably smaller than the magnetization calculated from the Mössbauer spectroscopic data. This difference was particularly strong at high concentrations of zinc. The large difference between the results of the magnetic and Mössbauer measurements has frequently been attributed to an ordered or random canted spin structure.

Measurements of the Mössbauer effect in $Ba_2Zn_2Fe_{12}O_{22}$ allowed Albanese, Asti, and Lamborizio[6] to suggest the existence of a canted magnetic structure in this compound at room temperature. It should be noted that the symmetry of the crystal structure of the Y ferrites allows a spin noncollinearity at those points in the lattice where the indirect exchange is weakened.[15] However, neutron-diffraction investigations showed that at room temperature the investigated ferrites did not exhibit an ordered canted magnetic structure.[13]

Evidently, the large discrepancies between the results of the magnetic and Mössbauer measurements were due to random canted configurations of spins in the zinc-rich samples.

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Translated by A. Tybulewicz
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