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Noncollinear Magnetic Structures in Hexagonal Ferrites of the $Ba_{3-x}Sr_{3-x}Zn_2Fe_{24}O_{41}$ *(Z) System*

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Single crystals are investigated at temperatures from 78°K up to the Curie point for values x = 2.4; 2.0; 1.5; 0. The neutron diffraction pattern is explained on the basis of angular magnetic structures which combine spin collinearity within certain blocks of the unit cell and noncollinearity of their summary magnetic moments. Noncollinearity is observed in crystals in which a significant part of the ions are replaced by strontium. With increase of strontium concentration and lowering of temperature, a deviation of the spins from the hexagonal axis occurs and the angle between directions of the summary magnetic moments of the blocks increases. Moreover, spin modulation at temperatures below 110–120°K arises. The noncollinearity is ascribed to violation in the exchange interaction scheme on localization of zinc ions in crystallographic positions at the block boundaries.

RECENTLY, neutron-diffraction investigations have revealed new types of magnetic structures in a number of hexagonal ferrites with very simple crystal structure, types M and Y. These are the block angular structure[1,2], the block flat-spiral structure[3], and the block conical ferromagnetic helical structure[1]. It is natural to expect new types of magnetic order to appear also in more complicated hexagonal ferrites, for example of type Z.

I. ATOMIC STRUCTURE AND MAGNETIC PROPERTIES OF TYPE-Z FERRITES

The compound having the chemical formula $Ba_3Zn_2Fe_{24}O_{41}$ (Ba_3Z for short) has a complicated unit cell containing 140 atoms (two formula units). The space group ($P6_3/mmc$) and the ion coordinates were determined by x-ray diffraction in[4]. The unit-cell parameters are a = 5.9 Å and 52.3 Å. It is possible to separate in the cell four four-layer "spinel" blocks (S_4), which have been so named because the oxygen layers in them form a dense cubic packing and the metal ions lie between them in the same positions as in spinel ferrites. The S_4 blocks are joined in the Z structure with one another by means of alternating single (B_1) and binary (B_2) barium links—oxygen layers in which each fourth ion of oxygen is replaced by a barium ion.

Comparing the values of the magnetization in the barium ferrites of type Z, for which Me^{2+} = Co, Zn, Ni, and Mg, and the variants of the possible ordering of the moments of Fe^{3+} on the basis of the premises of Anderson's theory of indirect exchange[5], it was possible to show[6,7] that the ferromagnetic sublattices in these compounds form a ferromagnetic structure. In most considered cases, the magnetic moments were parallel to the c axis, and the ions Me^{2+} were distributed statistically over many crystallographic positions. However, in the case when Zn^{2+} was replaced by a cobalt ion[7,8], a complex picture of magnetic anisotropy was observed, with deviation of the spins from the c axis to the basal plane via the easy-magnetization cone. The main influencing factors in this case were the amount of cobalt introduced and the temperature. The collinearity of the spins within the unit cell was conserved in all cases.

The type-Z structure has a certain similarity, with respect to the structure of the atomic cell, to the hexagonal type-Y ferrite. On the basis of magnetic investigations[9] performed on the ferrites of the system $Ba_{2-x}Sr_xZn_2Fe_{12}O_{22}$(Y), it was proposed that a helical magnetic structure exists in this case. A neutron-diffraction investigation[3] has confirmed this hypothesis. The observed anomalies in the type-Z ferrites[10,11] and the initial attempt at a neutron-diffraction investigation[12] of the crystal $Ba_{0.6}Sr_{2.4}Zn_2Fe_{24}O_{41}$ gave grounds for expecting interesting results in the investigation of a system of strontium-substituted ferrites of this type.

II. NEUTRON-DIFFRACTION INVESTIGATION

1. Samples and Measurement Procedure

For the diffraction investigations we used single crystals of the system $Ba_{3-x}Sr_xZn_2Fe_{24}O_{41}$ with x = 0, 1.5, 2, and 2.4. The single crystals were grown by the method of spontaneous crystallization from the solution in the melt and took the form of flat hexagonal prisms measuring 2—5 mm in the basal plane and 0.5—2 mm in thickness. When all the barium was replaced with strontium, no type-Z crystals were observed in the melt. Both x-ray diffraction and neutron diffraction have shown that the samples were single-phase. Their composition was verified by the method of x-ray microchemical analysis. When the barium ions were replaced by strontium, no noticeable change in the unit-cell parameters was observed in comparison with Ba_3Z. An unpolarized neutron beam of wavelength 1.165 Å was used. We investigated the series of basal reflections 00l up to l = 22, and also the series of nonbasal reflections h00, hh0 and h0l. Since the space group of the crystal structure Z does not forbid any reflections in these nonbasal series, and since the magnetic scattering in them appeared only in allowed places, the greatest interest attached to the basal series, whose results were used for a quantitative calculation of the models.

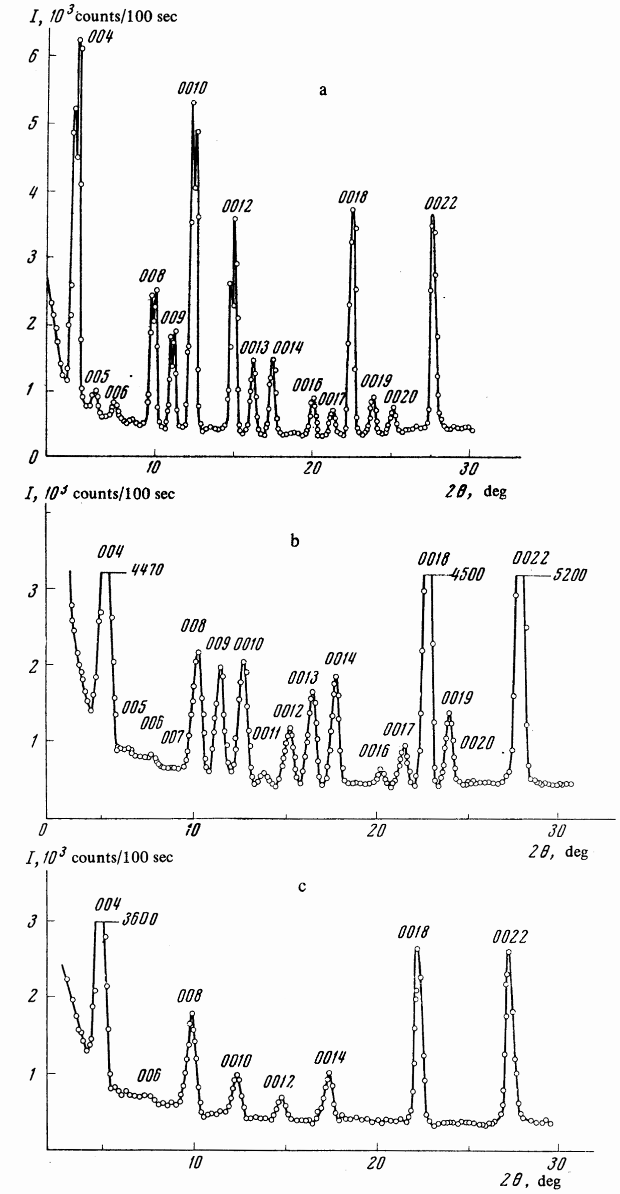

FIG. 1. Neutron diffraction patterns obtained from a series of basal planes for the single crystal $Ba_{0.6}Sr_{2.4}Z$: a) 105°K, b) 293°K, c) 570°K.

2. Experimental Results

A. The ferrite $Ba_{0.6}Sr_{2.4}Z$. Figure 1 shows the diffraction patterns for the series of basal planes at 105°K, room temperature, and a temperature above the Curie point. From the comparison of the patterns we see that at room temperature (Fig. 1b), reflections of considerable intensity appear in places forbidden by the space group (odd l) and are connected with magnetic scattering. In addition, practically all the reflections with even l have, in addition to the nuclear component (Fig. 1c), also appreciable magnetic contributions. When the temperature is decreased to 105°K, noticeable changes occur in the diffraction pattern (Fig. 1a). Whereas the superstructure (forbidden) reflections remain practically the same as before, the intensities of the magnetic contributions to the structure peaks increase strongly.

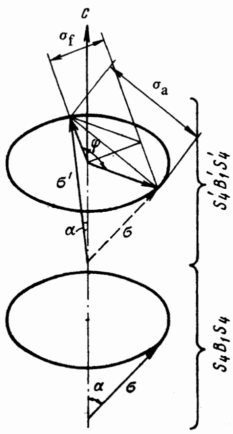

FIG. 2

FIG. 3

FIG. 2. Model of block angular magnetic structure for ferrites of the $Ba_{3-x}Sr_xZ$ system. The figure shows the relative direction of the summary magnetic moments (σ) in the neighboring blocks $S_4B_1S_4$, and also the appearance of the ferromagnetic (σ_f) and antiferromagnetic (σ_a) components formed by the projections of these moments in the basal plane.

FIG. 3. Temperature dependence of the intensity of the reflections (relative units) for the $Ba_{0.6}Sr_{2.4}Z$: 1–reflection 0010, 2–reflection 009.

Such a behavior of the magnetic contributions could not be explained on the basis of the models previously proposed[12] for this hexagonal ferrite. The models in question were connected with the assumption that there are no magnetic contributions in the structure reflections and could explain in principle the appearance of magnetic reflections only at forbidden locations.

On the basis of our experimental data, and also the magnetic-measurement data[11], we tried an appreciable number of noncollinear models that might be able to explain the diffraction pattern as applied to the Z structure. The best agreement between the calculated and experimental results was obtained for the case of the block angular model (Fig. 2), at which the unit cell is subdivided into two identical blocks with respect to the link B_2. In the two spinel blocks located between the links B_2, the spins retain the mutual collinear orientation in accordance with the Gorter-Neel scheme. However, the total magnetic moment σ of such a block makes an angle α with the c axis. The moment σ' of the neighboring block $S_4'B_1'S_4'$ is located on the generatrix of a similar cone, but shifted in phase, so that the projections of σ and σ' on the basal plane from an angle φ. If the direction of the rotation of the moments is not ordered on going from one magnetic block to the other along the c axis, then we deal with the case of an angular model that should ensure, as a result of the presence of the ferromagnetic and antiferromagnetic components in the basal plane, the appearance of magnetic contributions to the reflections with even and odd l. In the case of ordered rotation through an angle φ, one could expect the occurrence of the diffraction pattern for the block conical helix, similar to that observed in[1]. Table I lists for this composition the calculated and experimental results for the intensity at temperatures 570, 293, and 105°K, and also the values of the angles α and φ_1 and the convergence

Table I. Calculated and experimental intensities of the 00*l* series, and also parameters of angular magnetic structure for the ferrite $Ba_{0.6}$, $Sr_{2.4}$

00*l*	*T* = 570° K		*T* = 293° K *		*T* = 105° K **	
	I_{calc}	I_{calc}	I_{calc}	I_{exp}	I_{exp}	I_{exp}
004	305.2	383.7	395.4	409.1	720.3	961.5
005	0	0	18.4	14.0	17.0	14.2
006	2.0	0	15.7	16.3	18.7	10.7
007	0	0	1.6	0	1.5	5.0
008	191.6	202.3	186.2	211.8	515.0	426.0
009	0	0	220.8	195.5	251.7	271.0
0010	185.3	133.3	232.0	205.2	840.1	827.1
0011	0	0	3.6	11.2	3.3	5.3
0012	52.8	50.0	124.4	94.7	525.0	581.0
0013	0	0	165.9	136.5	172.7	199.1
0014	128.5	109.5	146.4	148.6	324.3	245.4
0015	0	0	3.0	0	2.7	0
0016	0.4	0	4.0	19.5	15.7	60.4
0017	0	0	54.3	57.4	51.0	42.7
0018	303.8	290.4	400.6	413.0	754.7	672.0
0019	0	0	89.8	101.3	86.6	64.0
0020	4.8	6.7	2.5	0	29.0	32.0
0021	0	0	13.8	17.7	12.6	12.8
0022	317.0	311.8	441.7	460.6	722.5	633.0
	R = 0.12		*R* = 0.09		*R* = 0.16	

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*Assumed values of phase angles: $\varphi = 120°$, $\alpha = 30°$.

**Phase angles $\varphi = 45°$, $\alpha = 45°$.

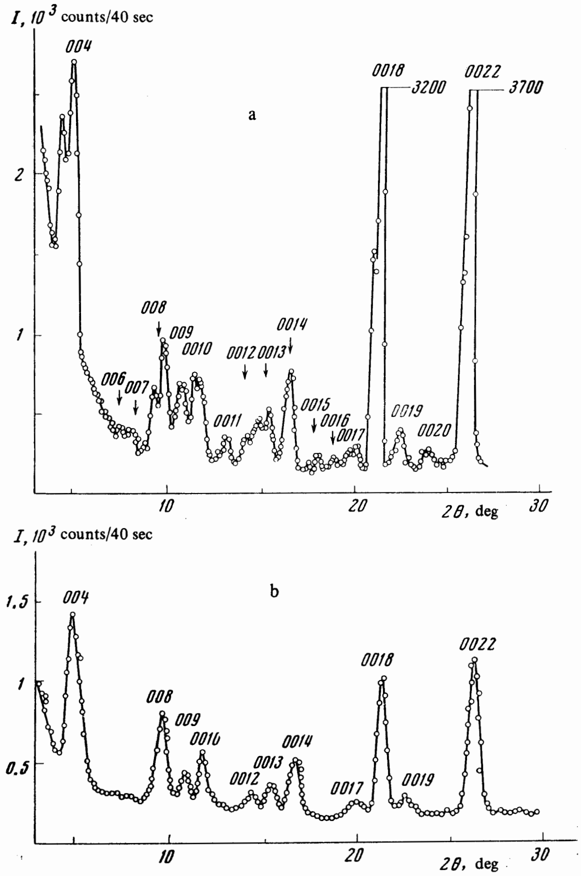

FIG. 4. Neutron-diffraction patterns from series of basal planes for the ferrite $BaSr_2Z$: a—at 78°K; b—at 293°K.

factor R. By I_{calc} and I_{exp} we denote respectively the calculated and experimental values of the intensities, normalized in the units of the structure factor (10^{-24} cm²). The thermal Debye-Waller factor was not introduced in the calculations on the basis of the experience gained in our previous investigations of hexagonal ferrites.

The temperature measurements carried out for the reflections 009 and 0010 at 105°K have shown that the magnetic contributions to the peak intensities decrease smoothly for this composition upon heating. The reflection 009 practically merges with the background at a temperature ~400°K. The intensity of the reflection 0010 becomes close to the value of the nuclear contribution at ~480°K. These data (Fig. 3) offer evidence of a smooth decrease of the angles φ and α with temperature, leading to a changeover from the described model to the ordinary-cone models, and then to the axial collinear model.

At 105°K (Fig. 1a) the neutron-diffraction pattern reveals a splitting of the upper part of the reflections that have considerable magnetic contributions. This splitting occurs for both allowed and forbidden reflections. Thus, with decreasing temperature, the spin configuration in the structure becomes more complicated and periodic modulation appears in the direction of the c axis. It is difficult to say anything definite concerning this modulation, owing to the mutual overlap of the superstructures. However, from the magnitude of the splitting we can estimate the period of the modulation, which turned out to be ~600 Å for the given composition.

B. The ferrite $BaSr_2Z$. The neutron-diffraction patterns for the single crystal of this composition (Fig. 4) recall in many respects the diffraction patterns for $Ba_{0.6}Sr_{2.4}Z$. An appreciable decrease of the intensity of the magnetic scattering in comparison with the nuclear scattering is observed in this case. The magnetic peaks broaden noticeably at 293°K, and at 78°K a number of reflections undergo appreciable broadening, distortion of the form, and overlap of the intensities. The character of the splitting is the same as in the preceding case, but the anomalies in the distribution of the intensities over the superstructure satellite peaks and the magnitude of the splitting are larger. An estimate of the average modulation period yielded ~250 Å in the c-axis direction. The appreciable broadening of the peaks is attributed by the authors both to the very fact of the splitting of the peaks and to phenomena caused by the possible inhomogeneity of the concentration of the strontium ions in the crystal. One should expect here the appearance of a set of magnetic reflections with different values of the splitting; superposition of these reflections leads to an uncertainty in the period of the modulation and to additional broadening. We present below the values of the convergence factors and of the phase angles of the magnetic structure for the $BaSr_2Z$ composition at 293 and 78°K:

	$T = 293°$ K	$T = 78°$ K
α, deg:	12	20
φ, deg:	150	120
R	0,16	0.17

At 570°K, the convergence factor is equal to 0.15.

C. The ferrites $Ba_{1.5}Sr_{1.5}Z$ and Ba_3Z. The diffraction patterns from the series of basal planes for Ba_3Z at room temperature and liquid-nitrogen temperature were similar to the neutron-diffraction pattern shown in Fig. 1c. For $Ba_{1.5}Sr_{1.5}Z$ at 78°K, we observed a certain increase of the background for the places with odd l and a broadening of the peaks, which indicates, in our opinion, the creation of superstructure peaks due to the noncollinearity in the magnetic structure. The relatively small values of the contributions of the magnetic scattering to the diffraction pattern from the series of basal planes indicate that the deviations from the axial collinear model, which is similar to the case of Ba_3Z, are small. An estimate of the angle α for this case yielded a value ~5°. The convergence factor for Ba_3Z was 0.08 at 293°K and 0.13 at 78°K.

III. CHOICE OF MODEL. CATION DISTRIBUTION. DISCUSSION OF RESULTS

In the calculation of the intensities we used the ion coordinates taken from[4] and the atomic-scattering amplitudes taken from[13]. We used the usual scheme of structure calculations, with corrections introduced for the primary and secondary extinctions by the Hamilton method. Since we did not have independently determined values of the mosaic parameters, in each concrete case we selected the values of the mosaic-block thickness and the angle scatter of the mosaic blocks until satisfactory convergence was obtained. The obtained values were close to those used in[1,2]. In the calculations of the magnetic structure amplitudes, we used the values of the form factors of Fe^{3+} from[14].

The nuclear scattering patterns for the ferrites of the system under consideration are not very sensitive to changes in the locations of the zinc and strontium ions in the crystallographic positions of the unit cell, in view of the low concentration of these ions and in view of the fact that the scattering amplitudes for zinc and strontium are of the same order of magnitude as the amplitudes for oxygen and iron, which determine in the main the intensity of the scattering. In the calculations for strontium we therefore assumed a statistical distribution over the barium positions, with coordinates $z = 0.02735$ and $z = 0.2500$.

Table II. Coefficient of occupation of the crystallographic positions 2a and $4f_2$ by zinc ions

Composition	K	
	$2a$	$4f_2$
Ba_3Z	0.1	0.1
$BaSr_2Z$	0.6	0.4
$Ba_{0,6}Sr_{2,1}Z$	0.8	0.5

The determination of the zinc-ion positions is aided by a deciphering of the magnetic diffraction patterns. The statistical distribution of the zinc over many crystallographic positions, or over positions with large multiplicity, should not introduce noticeable distortions into the mechanism of the exchange bonds between the magnetic ions. In these cases one should expect the Gorter axial model to remain in force. Since violation of the axial ordering of the spins and the occurrence of noncollinearity are observed, one must assume that the nonmagnetic zinc ions are concentrated in one or several crystallographic positions of the iron ions with small multiplicity, leading to a change in the scheme of the exchange interactions, and in final analysis to the occurrence of a noncollinear block magnetic structure. In the unit cell of the Z structure there is a large number of tetrahedral and octahedral positions of the aforementioned type. This gives rise to a considerable number of variants of subdividing the unit cell into magnetic blocks. The theoretical model should explain the occurrence of reflections at locations with odd l, due to the antiferromagnetic scattering component. In the case of subdivision of the unit cell into several blocks, for example with respect to the links B_1 and B_2, there are several variants of antiferromagnetic orientation of the projections of the total magnetic moments of blocks S_4 on the basal plane, namely $(+-+-)$, $(++--)$ etc. In a number of cases, the spin configurations become non-centrally-symmetrical with respect to the crystallographic centers. These circumstances make it necessary to carry out the calculation over all the atoms of the unit cell, and not over its quadrant having atoms with independent coordinates, and also to take into account the imaginary part of the structure amplitude in non-centrally-symmetrical cases.

Calculations performed with the BESM-6 computer with allowance for the foregoing considerations have shown that the only model that can explain the diffraction pattern satisfactorily is the model shown in Fig. 2. This result testifies in favor of the assumption that the preferable placement of the zinc ions is in the link B_2 over the crystallographic positions 2a and $4f_2$ with coordinates $z = 0$ and $z = 0.0359$. The magnetic structure is in this case non-centrally-symmetrical with respect to the crystal-symmetry center, which is located in the position 2a. Table II gives the values that were used in the calculations for the coefficient K of occupation of these positions by the zinc ions. The remaining Zn^{2+} ions were statistically distributed over all the octahedral positions. Since the unit cell cannot have a chemical composition with fractional amounts of the ions contained in it, this leads to the appearance in the crystal of a set of cells with different substitution concentrations, and consequently with different cation placements. Neutron diffraction will reveal a pattern of scattering from a certain average structure, although the spin configurations in these cells may differ.

In this investigation we observed a new type of magnetic structure, which combines ferrimagnetic collinearity of the spins within the limits of definite blocks of the unit cell with noncollinearity of the summary magnetic moments of these blocks. When half of the barium ions are replaced by strontium, the magnetic moment of the entire unit cell becomes inclined to the hexagonal axis. The angle between them increases with increasing concentration of the strontium ions introduced into the structure and decreases with increasing temperature. In addition, the appearance of spin modulation is observed in strontium-substituted compositions at temperatures below 110–120°K. The period of the modulation decreases with decreasing values of the concentration and temperature. The reason for the occurrence of noncollinear structures of the type under consideration is apparently the appreciable increase of the concentration of the zinc ions in the link B_2. This leads to the occurrence of a nonmagnetic layer in the unit cell, the weakening of the exchange bonds in this region, the subdivision of the unit cell into two weakly coupled magnetic blocks, and to violation of the axial collinear model.

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84