ANGULAR SPIN ORDERING IN TYPE Z HEXAGONAL FERRITES

V. A. SIZOV, R. A. SIZOV, and I. I. YAMZIN

Institute of Crystallography, U.S.S.R. Academy of Sciences

Submitted April 30, 1967

Zh. Eksp. Teor. Fiz. 55, 1186–1190 (October, 1968)

The diffraction of neutrons by single crystals of a hexagonal ferrite $(Sr_{0.8}Ba_{0.2})_3Zn_2Fe_{24}O_{41}$ was investigated at 293°K. An angular magnetic structure was observed, arising as a result of the antiparallel ordering of the projections of the total magnetic moments of the blocks, into which the unit cell of the crystal breaks up as a result of localization of the Zn^{2+} ions in definite tetrahedral positions.

1. CERTAIN FEATURES OF THE STRUCTURE OF TYPE Z FERRITES

FERRITES belonging to the structure type Z[1,2] have a hexagonal unit cell with very large c/a ratio (c = 52.3, a = 5.9 Å). The space group is $P6_3/mmc$. The unit cell contains two formal units $Me^1_3Me^2_2Me^3_{24}O_{41}$ (Me^1—large divalent cation, most frequently Ba^{2+}; Me^2—divalent cation of moderate dimensions, for example, Zn^{2+}; Me^3—trivalent ions of iron or elements that substitute for iron or elements that substitute for iron isomorphically in the given structure). The simplest in composition and the most thoroughly investigated is the ferrite $Ba_3Zn_2Fe_{24}O_{41}$.

The atomic structure of a type-Z ferrite, as well as the structures of other hexagonal ferrites, are characterized by a close packing of layers of oxygen ions perpendicular to the C axis. In this structure it is possible to separate blocks B_1' and B_2', as shown in Fig. 1 (the zinc ions are statistically distributed over all tetrahedral positions in accordance with the model proposed by Brown[1]). The blocks include oxygen layers containing barium ions: a single layer in block B_1' and a double one in block B_2'.

A comparison of the structure of the Z-type ferrite with the structures of other hexagonal ferrites shows that the block B_1' constitutes half the unit cell of the type M ferrite, while block B_2' amounts to one third of the cell of the type Y ferrite. The blocks alternate along the C axis with sequence B_1'–B_2'–B_1'–B_2'...

If we disregard the perturbations of the magnetic structure, due to certain cation substitutions, then the spins in the hexagonal ferrites based on barium are collinear, being parallel to the hexagonal C axis in the type-M structure and perpendicular to it in the type-Y structure.[3] Inasmuch as the Z structure is derived from the M and Y structures, it reveals a tendency to both types of the spin ordering. However, the tendency to orient the spins along the C axis turns out to be stronger and the type-Z barium ferrite is characterized on the whole by a uniaxial magnetic structure: the spin-ordering axis coincides with the C axis (see Fig. 1).

Following substitution of strontium for barium in the hexagonal ferrite $Ba_2Zn_2Fe_{12}O_{22}$(Y), we observed a new type of magnetic structure, characterized by a helical ordering of the total moments of the blocks B_2'.[4,5] We consider the cause of the formation of this magnetic structure to be the arrangement of the zinc ions in definite locations in the unit cell (tetrahedral positions 6c) with formation of layers of nonmagnetic Zn^{2+} ions, which apparently greatly weakens the exchange-coupling energy between the blocks and leads to a complicated spin ordering. The result obtained with a strontium-substituted ferrite of type Y gives grounds for expecting that the proposed mechanism of substitution and redistribution of the nonmagnetic ions can influence in similar manner the exchange interaction and change the spin ordering in ferrites of other structural types, in particular type Z.

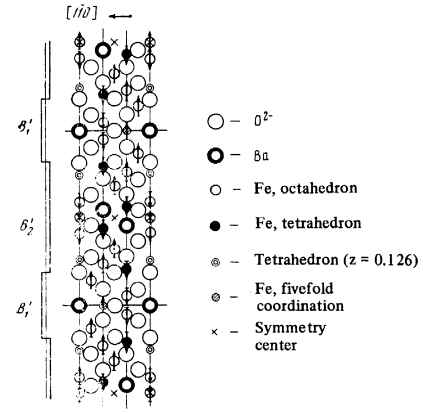

FIG. 1. Unit cell of hexagonal ferrite with type-Z structure.

This paper is devoted to an investigation of the magnetic structure of the hexagonal ferrite $(Sr_{0.8}Ba_{0.2})_3Zn_2Fe_{24}O_{41}$, which differs from the ordinary type-Z barium ferrite in that the greater part of the barium is replaced by strontium.

The crystals of the investigated ferrite were grown by the method of spontaneous crystallization from a solution in a $NaFeO_2$ melt. An x-ray diffraction determination of the parameters of the unit cell has shown that c = 52.26 Å and a = 5.87 Å. No impurities of other phases were observed in the obtained crystals.

2. NEUTRON DIFFRACTION INVESTIGATION

The neutron diffraction investigation was carried out at 293°K on single-crystal samples in the form of a prism measuring 1 × 2 × 4 mm, at points separated by 10 minutes of angle with simultaneous displacement of the sample and the counter in a ratio 1 : 2. The intensity of the 00*l* reflections and its dependence on the magnitude (up

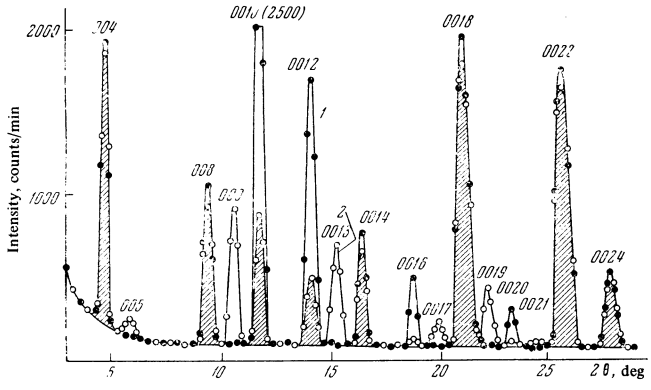

FIG. 2. Neutron diffraction patterns of $(Sr_{0.8}\ Ba_{0.2})_3 Zn_2 Fe_{24} O_{41}$ as a function of the field $H \perp \epsilon$: 1–H = 2000 Oe, 2–H = 0; T = 293°K.

to 20 000 Oe) and direction of the magnetic field **H** were measured.

Figure 2 shows the patterns of neutron diffraction from the investigated ferrite, taken at H = 0 and H = 2,000 Oe ($\mathbf{H} \perp \boldsymbol{\varepsilon}$, where $\boldsymbol{\varepsilon}$ is the scattering vector). The shaded sections correspond to the nuclear reflexes with l = 2n, allowed by the space group $P6_3/mmc$. However, the diffraction pattern (Fig. 2, pattern 1) contains, besides these reflections, also the "forbidden" reflections with l = 2n + 1. Whereas the reflections with even l contain practically no magnetic contributions, the "forbidden" reflections are due exclusively to magnetic scattering.

Superposition of even a small magnetic field perpendicular to the scattering vector $\boldsymbol{\varepsilon}$ greatly decreases the intensities of the "forbidden" reflections; their total vanishing is observed at H = 2000 Oe (Fig. 2, pattern 2). The intensities of the structure reflections increase simultaneously with decreasing intensity of the "forbidden" reflections (l = 2n). Figure 3 shows the dependence of the intensity of the reflections 009 and 0010 on the intensity of the magnetic field $\mathbf{H} \perp \boldsymbol{\varepsilon}$. The intensity of the reflection 0010 increases in parallel with the decrease of the intensity of the reflection 009; in fields above 2000 Oe, the diffraction pattern contains only the reflections with l = 2n, which contain both magnetic and nuclear contributions.

A magnetic field applied parallel to $\boldsymbol{\varepsilon}$ decreases the intensity of the "forbidden" reflections, which vanish completely when H ~ 18 000 Oe.

3. DISCUSSION OF RESULTS

A comparison was made of the calculated and experimental intensities of the nuclear reflections in the case of a statistical distribution of the Zn^{2+} ions and in the case when they are localized in one of the tetrahedral positions. For the given structure, the most probable

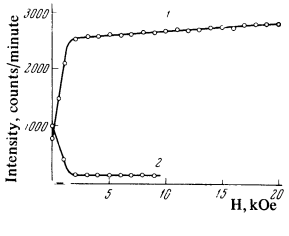

FIG. 3. Intensity of reflections of the investigated ferrite against the field $\mathbf{H} \perp \epsilon$: 1–0010 reflection, 2–009 reflection; T = 293°K.

Calculated and measured intensities of the reflections of the 00l zone at 293°K.

hkl	Calculation F^2	Calculation I_{calc}	I_{exp}	hkl	Calculation F^2	Calculation I_{calc}	I_{exp}
004	49,4	362	430	0018	201,6	448	605
005	88	223	38	0019	28,1	35,5	97
006	0	0	0	0020	1,08	3,5	15
007	0	0	0	0021	0,1	0	0
008	56,2	267	295	0022	334,9	478	420
009	132,2	262	262	0023	42,2	42,8	40
0010	67,2	256	247	0024	72,2	126	110
0011	5,2	10,2	0	0025	0,16	0	0
0012	43,1	163	122	0026	15,2	26,1	30
0013	121	183	195	0027	54,7	45,6	42
0014	44,9	138	152				
0015	7,2	11,1	0				
0016	0,1	0	15				
0017	25	35,3	53				

F^2 –structure factor.

location of the Zn^{2+} ions are the positions 4f (z = 0.126). Such a localization of the zinc leads, as can be seen from Fig. 1, to the formation in the structure of layers of nonmagnetic ions, which apparently can lead to a local weakening of the exchange bonds and as a result to a breakdown of the structure into different blocks B_1' and B_2'. Within the confines of each block, strong exchange interaction is retained, causing a collinear ordering of the magnetic moments. Under this assumption, the "forbidden" magnetic reflections observed under diffraction pattern, which become manifest only in reflections of the 00l series, can be connected with the antiparallel ordering of the projections of the magnetic moments of the ions on the basal plane.

The arrows of Fig. 4 indicate the total moments of the blocks B_1' and B_2'. We propose that the spins are collinearly ordered within each block. The simplest scheme that makes it possible to explain the observed picture of neutron diffraction is shown in Fig. 4a. On the basis of this model, satisfactory agreement between the calculated and experimental values was obtained for the reflection intensity. However, arguing against this model is the appreciable difference of the angles between the different pairs of the total moments of the blocks B_1' and B_2'. On the basis of the model of Fig. 4b, it is impossible to explain the existence of a resultant moment along the C axis, observed in both magnetic and neutron-diffraction investigations. The model of Fig. 4c explains in the best manner the results of the neutron diffraction and magnetic measurements.

On the basis of the last model it is easy to explain the existence of a collinear component, obtained from the components of the spin magnetic moments along the C axis. Comparison of the calculated and experimental

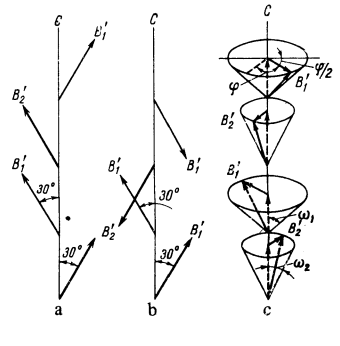

FIG. 4. Models of spin ordering in the investigated ferrite; $\varphi = 90°$, $\omega_1 = 45°$, $\omega_2 = 25°$.

values of the intensity has made it possible to establish that the angles ω_1 and ω_2 between the C axis and the total moments of the blocks B_1' and B_2' are respectively 45 and 25°. The angles φ between the components of the moments of the blocks B_1' and B_2' on the basal plane are close to 90°. The calculated and experimental intensities are compared for this model in the table (the reliability factor R = 21.1%). In the calculation of the intensities of the diffraction maxima, we used the atom coordinates as given by Braun.[1] It was also assumed that the spin 3d density is distributed in the lattice of the investigated crystal symmetrically with respect to the coupled nuclei.

[1] P. B. Braun, Philips Res. Rep. **12**, 491 (1957).
[2] E. W. Gorter, Proc. IEE, Suppl. **104B**, 252 (1957).
[3] J. H. Goedkoop, J. Hvoslef, and M. Zivadinovic, Acta Cryst. **12**, 476 (1959).
[4] V. A. Sizov, R. A. Sizov, and I. I. Yamzin, ZhETF Pis. Red. **6**, 690 (1967) [JETP Lett. **6**, 176 (1967)].
[5] V. A. Sizov, R. A. Sizov, and I. I. Yamzin, Zh. Eksp. Teor. Fiz. **53**, 1256 (1967) [Sov. Phys.-JETP **26**, 736 (1968)].

Translated by J. G. Adashko
132