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G. Albanese. RECENT ADVANCES IN HEXAGONAL FERRITES BY THE USE OF NUCLEAR SPECTROSCOPIC METHODS. Journal de Physique Colloques, 1977, 38 (C1), pp.C1-85-C1-94. 10.1051/jphyscol:1977117 . jpa-00216976

HAL Id: jpa-00216976
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Submitted on 4 Feb 2008

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RECENT ADVANCES IN HEXAGONAL FERRITES BY THE USE OF NUCLEAR SPECTROSCOPIC METHODS

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Résumé. — L'application des spectroscopies Mössbauer et RMN ainsi que de la diffraction neutronique à l'étude des ferrites hexagonaux permet de mieux connaître les corrélations entre la distribution des cations, l'aimantation des sous-réseaux et la configuration des spins. Dans le présent exposé on discute comparativement les résultats obtenus sur des ferrites hexagonaux de type M, Y, W et Z.

Abstract. — The application of the Mössbauer, NMR and neutron spectroscopies to the study of the hexagonal ferrites allows to give more insight into the correlations between the cation distribution, the sublattice magnetization and spin configuration. In the present paper a comparative discussion of the data obtained on M, Y, W and Z-type hexagonal ferrites is given.

1. **Introduction.** — In the fifties a large class of ferrimagnetic oxides with hexagonal crystal structure has been sintetized at the Philips laboratory [1]. They were called hexagonal ferrites in order to distinguish them from the ferrimagnetic oxides with spinel and garnet structure. The basic crystallographic and magnetic properties of the main hexagonal ferrites have been reviewed by J. Smit and H. P. J. Wijn in their classical book *Ferrites* [2].

The hexagonal ferrites can be prepared by standard ceramic techniques, firing stoichiometric amounts of the oxides MO (M = Ba, Sr, Pb, etc.), Fe_2O_3 and MeO (Me = Zn, Mg, Mn, Co, etc.). The chemical composition of the main Barium hexagonal ferrites can be represented in a ternary diagram having BaO, Fe_2O_3 and MeO as vertexes (Fig. 1). Along the line connecting BaO and Fe_2O_3 there is the point representing the well known composition $BaFe_{12}O_{19}$, the so-called M-type ferrite and along the line connecting Fe_2O_3 and MeO we find the spinel compound $S = Me_2F_4O_8$. Using intermediate amounts of the starting oxides we can obtain the stable and homogeneous compounds indicated in the diagram with the letters W, Z, Y, X and U. In some of these compounds the Ba ions can be substituted by Sr, Pb, Ca, La, etc. whilst the divalent metal ions Me can be replaced by a suitable combination of monovalent and trivalent ions. Moreover the substitution of Fe^{3+} ions with other trivalent cations such as Al^{3+}, Ga^{3+}, Sc^{3+}, In^{3+}, etc. is also possible. In this way we can obtain an extremely large number of compounds with considerably different magnetic properties. This fact makes the hexagonal ferrites attractive for different technical applications and interesting for basic studies on the magnetic interactions in insulators.

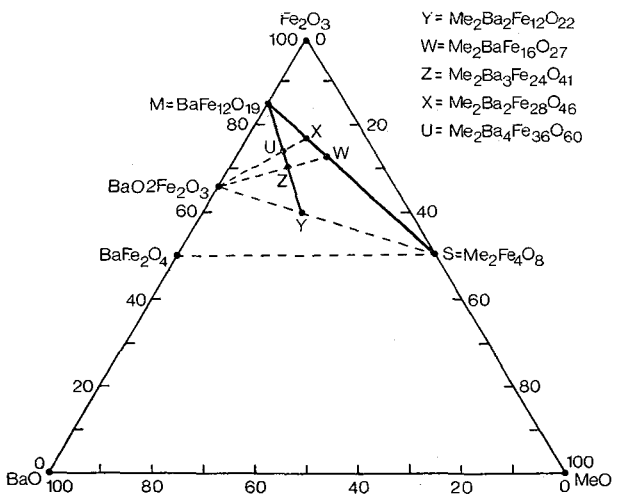

FIG. 1. — Ternary diagram showing the composition of the main barium hexagonal ferrites. The symbol Me represents a divalent cation.

The crystalline structure of the hexagonal ferrites is the result of a close packing of oxygen ion layers. The divalent and trivalent metallic cations are located in interstitial sites of the structure, while the heavy Ba or Sr ions enter substitutionaly the oxygen layers. All the known hexagonal ferrites have a crystalline structure which can be described as a superposition of three fundamental structural blocks : the so called S, R and T blocks (Fig. 2). The S block results from a cubic close packing of two oxygen layers giving rise to the typical spinel structure. The R and T blocks instead result from an hexagonal close packing of three and four oxygen layers respectively with part of the oxygen substituted by barium.

The metallic cations are distributed among several lattice sites, up to ten or more, different both from the crystallographic and the magnetic point of view and

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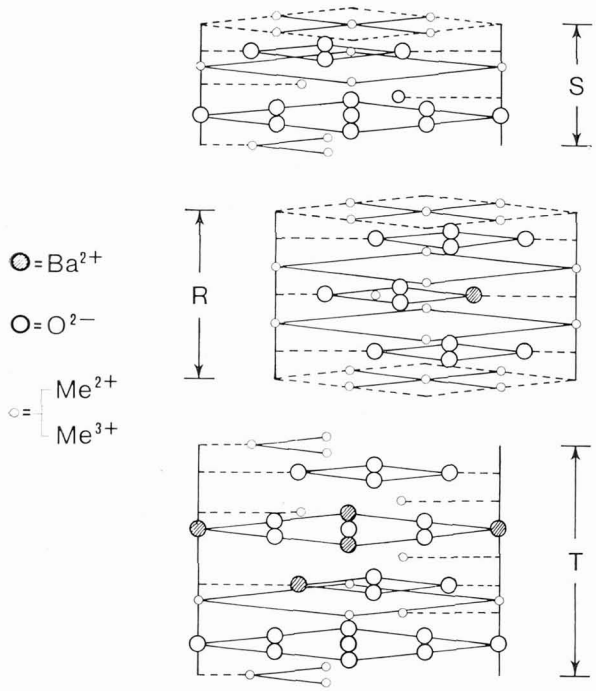

FIG. 2. — The three fundamental structural blocks S, R and T of the hexagonal ferrites.

therefore play different roles in determining the magnetic properties of the hexagonal ferrites. Thus it is evident that without any detailed data for each sublattice serious difficulties may arise when we try to interpret their magnetic behaviour in terms of intrinsic properties and basic interactions.

In the last ten years the application of Mössbauer, NMR and neutron diffraction techniques made it possible to get more insight into the correlations between the macroscopic magnetic parameters and the basic intrinsic properties of the hexagonal ferrites. In the following some significative results obtained by the application of nuclear spectroscopic methods to M-Y-W and Z-type ferrites will be reported and discussed.

2. **M-type hexagonal ferrites.** — The unit cell of the M-type Barium ferrite ($BaFe_{12}O_{19}$) is shown in figure 3. This structure can be built up from spinel blocks (S) interposed by the hexagonal R block which contains the Barium ions. The layer containing Barium is a mirror plane so that we can also look at this structure as an assembly of four-layer spinel blocks interposed by an hexagonal layer containing the Ba ions. The iron ions are distributed among five different lattice sites as reported in table I. Inside the R-block the iron ions in the octahedral $4f_{VI}$ sublattice have coordination figures which share a common face. This configuration is characterized by a potential energy higher than the one of octahedra sharing only a corener. Inside the R block we also find the 2b lattice sites where the iron is surrounded by five oxygen ions

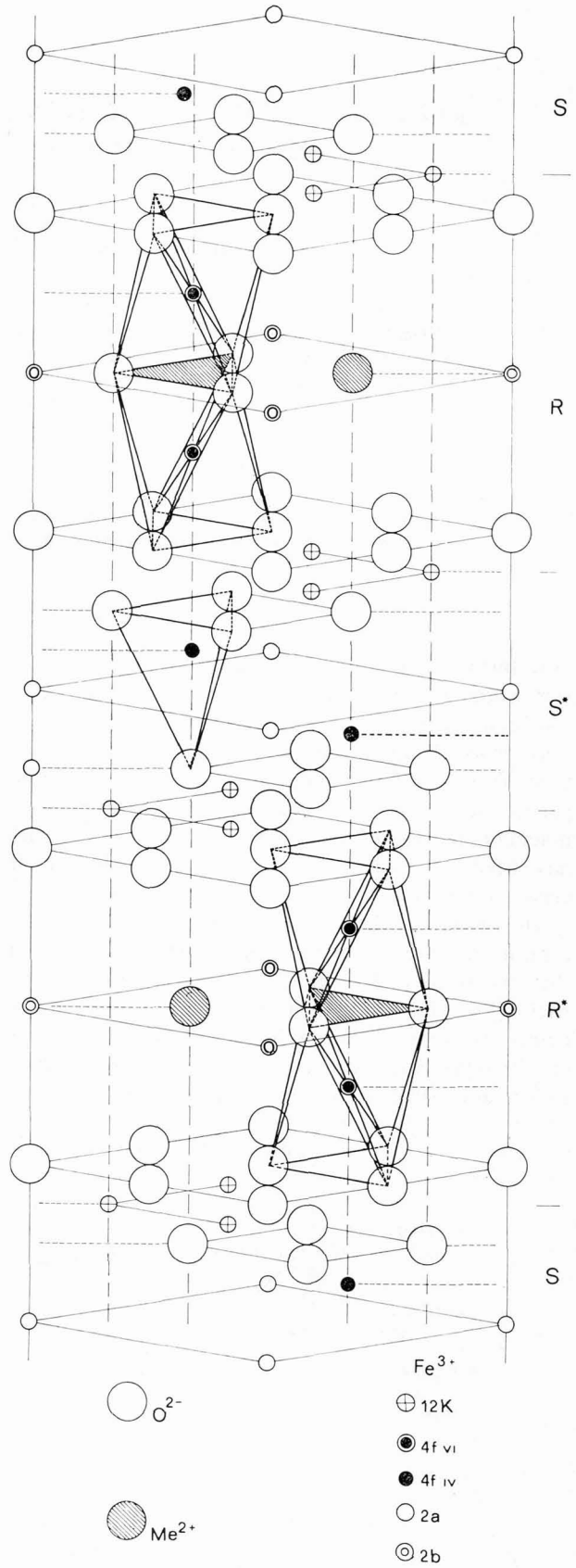

FIG. 3. — Unit cell of the M-type ferrites $MeFe_{12}O_{19}$ (Me=Ba, Sr etc.). The asterisk indicates a rotation of a block of the cell over 180° around the vertical *c*-axis. (ALBANESE, G. *et al.*, *Nuovo Cimento* **15B** (1973) 147.)

TABLE I

Number of ions per unit formula, coordination and spin orientation in the five iron sublattices of M-type structure.

Sublattice	Coordination	Block	Number of ions	Spin
12 K	octahedral	S-R	6	up
$4f_{IV}$	tetrahedral	S	2	down
$4f_{VI}$	octahedral	R	2	down
2a	octahedral	S	1	up
2b	fivefold	R	1	up

at the corners of a trigonal bipiramid. Six of the twelve iron ions per unit formula are located in the 12 K lattice sites at the boundary between S and R blocks.

In table I the spin orientation of the various iron sublattices is also reported according to the model proposed by Gorter [3]. This model gives a value of 20 μ_B for saturation magnetization at 0 K which agrees well with the experimental value. The temperature dependence of the saturation magnetization (σ) puts in evidence a nearly linear decrease of σ with increasing T (Fig. 4*c*). As regards the magnetic anisotropy the Barium M-type ferrite is a hard uniaxial material with an anisotropy field at room temperature (R. T.) of 17 kOe.

The ^{57}Fe Mössbauer absorption spectrum for $SrFe_{12}O_{19}$ and $BaFe_{12}O_{19}$ ferrites was interpreted for the first time by Van Wieringen and Rensen [4, 5] in 1966. Figure 4*a* shows the Mössbauer spectrum at R. T. for $BaFe_{12}O_{19}$. It can be decomposed into five sextets : the more intensive one (sextet I) was attributed to the iron ions in 12 K sublattice where 6 of the 12 iron ions per unit formula are located ; the sextet IV is assigned to the sublattice 2b in which the high quadrupole splitting give rise to a strongly asymmetric sextet ; sextets II and V were attributed to the sublattices $4f_{IV}$ and 2*a* respectively i. e. to the iron ions belonging to the spinel block ; sextet III was assigned to the sublattice $4f_{VI}$. From the Mössbauer spectra the temperature dependence of the hyperfine magnetic fields (H_{hf}) at ^{57}Fe nuclei in the five sublattices of Barium ferrite has been deduced (Fig. 4*b*). We can see that contrary to other sublattices the hyperfine magnetic field relative to the 12 K sublattice rapidly decreases with increasing temperature. From these data, taking into account both the proportionality between H_{hf} and the atomic magnetic moment as well as the cationic distribution and the spin order, it is possible to deduce the temperature dependence of the saturation magnetization (σ).

In figure 4*c* the calculated and measured values of σ for $BaFe_{12}O_{19}$ as a function of temperature are reported ; the values calculated from the hyperfine magnetic field values are in good agreement with the measured ones. Therefore the peculiar linear temperature

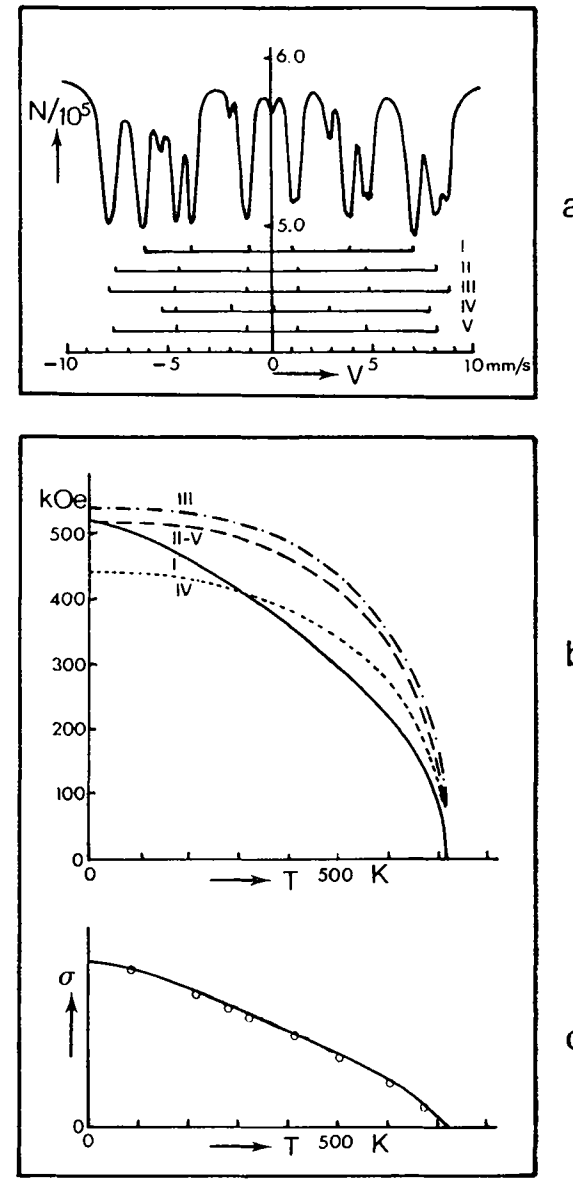

FIG. 4. — *a*) ^{57}Fe-Mössbauer spectrum for the compound $BaFe_{12}O_{19}$ at room temperature. *b*) Temperature depencene of the hyperfine magnetic fields relative to Fe^{3+} ions in various sublattices of $BaFe_{12}O_{19}$. *c*) Temperature dependence of the saturation magnetization of $BaFe_{12}O_{19}$ compound. The points refer to measured value while the line to the values calculated from the hyperfine magnetic fields data (VAN WIERINGEN, J. S., *Philips Tech. Rev.* **28** (1967) 33).

dependence of σ in $BaFe_{12}O_{19}$ can be explained as due to the rapid decrease of the magnetization of the sublattice 12 K. The rapid decrease of the magnetization of 12 K sublattice can be understood if we take into account that the 12 K sublattice is subjected to a strong interaction with the 2b spin-up sublattice in addition to the orienting interactions with $4f_{VI}$ (spin down) and $4f_{IV}$ (spin down) iron ions. The 12 K-2b interaction is the main responsible for the marked temperature decrease of the magnetization of 12 K ions. Moreover a detailed study of the temperature

dependence of the sublattice magnetization in Al and Ga substituted M-type ferrites [6] indicated that the magnetization of 12 K ions is, to some extent, also affected by the 12 K-2a interaction and by the intrasublattice interaction between the 12 K ions themselves.

In 1968-69 R. L. Streever [7, 8] reported an NMR study of $BaFe_{12}O_{19}$. In figure 5 the spin-echo spectra of

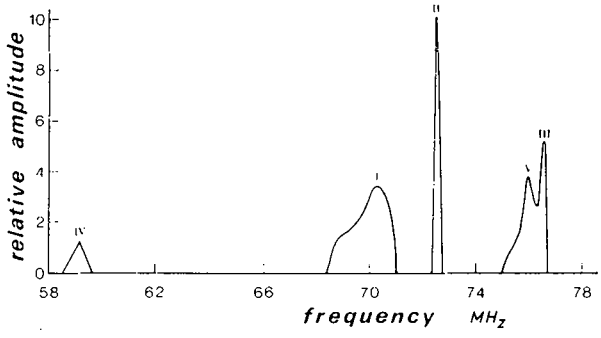

FIG. 5. — Zero field NMR (spin echo) spectrum for the single crystal powders of $BaFe_{12}O_{19}$ compound at 4.2 K (STREEVER, R. L., *Phys. Rev.* **186** (1969) 285).

Barium M-type ferrite at 4.2 K is shown. The peaks are due to the hyperfine magnetic fields at the ^{57}Fe nuclei of various sublattices. The resolution is remarkable and better than the one which can be obtained from Mössbauer measurements. Unfortunately at higher temperatures the signal to background ratio decreases and near R. T. the NMR technique becomes less effective. However the Mössbauer and N. M. R. low temperature data are in satisfactory agreement.

The knowledge of the temperature dependence of the sublattice magnetizations recently allowed Asti and Rinaldi [9] to determine the contribution of the various sublattices of Barium ferrite to the anisotropy constants. The temperature dependence of K_1 turns out to be essentially due to the contribution of single ion anisotropy from ferric ions located in 12 K and 2b lattice sites. Contrary to previous assumption, the 12 K contribution is not negligible and affects the temperature dependence of K_1 by nearly 50 %.

The successful application of the Mössbauer spectroscopy to the study of Ba and Sr M-type hexagonal ferrites induced Albanese, Asti and Batti to perform a Mössbauer study of Al and Ga substituted compound with composition $BaFe_{12-x}Al_xO_{19}$ and $SrFe_{12-x}Ga_xO_{19}$ [10, 11, 12]. The choice of Al^{3+} and Ga^{3+} as substituting ions was due to the fact that these ions, having different ionic radii, were expected to have different substitution rates in the various lattice sites. As a consequence the equilibrium of the superexchange interactions between the non-substituted Fe^{3+} ions in the two cases might be different and thus affect the magnetic behaviour of the substituted compounds in different ways.

In figure 6 we report the ^{57}Fe Mössbauer absorption spectra of the compound $SrFe_{12-x}Ga_xO_{19}$ for $x = 0.1$ at R. T. For $x = 1$ the iron nuclei in 12 K sublattice give rise to two distinct sextets (Ia and Ib)

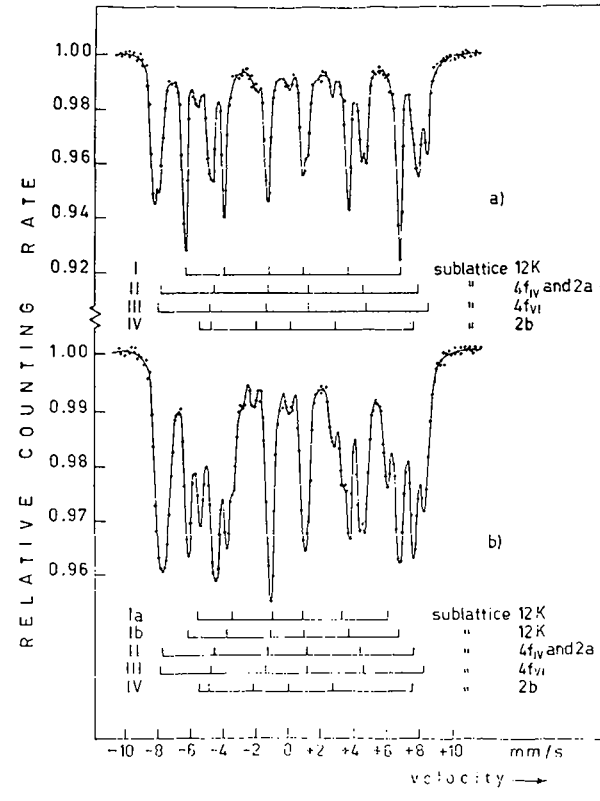

FIG. 6. — ^{57}Fe-Mössbauer spectra : *a*) for $SrFe_{12}O_{19}$; *b*) for $SrFe_{11}Ga_1O_{19}$. I, Ia, Ib sublattice 12 K ; II sublattice $4f_{IV}$ and 2a ; III sublattice $4f_{VI}$; IV sublattice 2b. (ALBANESE, G., *et al.*, *Nuovo Cimento* **58B** (1968) 467).

one of which (sextet Ia) has an H_{hf} lower than the one relative to sextet I in the case $x = 0$. With increasing x an increase of the line intensity for the sextet Ia with respect to the sextet Ib is observed. This fact clearly demonstrates that in Gallium substituted M-type strontium ferrite the iron ions in 12 K sublattice are magnetically non-equivalent. This unequivalence has been explained as due to the effects of the substitution of part of Fe^{3+} by Ga^{3+} ions in f_{VI} lattice sites. Indeed this fact leads to a local cancellation of the superexchange interactions between $4f_{VI}$ and 12 K sublattices. As a consequence part of the Fe^{3+} ions in 12 K sites shows a temperature dependence of the magnetization different from the one due to 12 K ions which have no nearest neighbours substituted by non-magnetic Ga ions.

Such an effect has not been detected for Al substituted Barium or Strontium ferrite ; this fact indicates that the different order of substitution of Aluminium gives rise to a different equilibrium in the superexchange interactions. However the measured sublattice magnetization and order of substitution does not satisfactorily

account for the decrease of saturation magnetization with increasing degree of substitution in Al and Ga substituted compounds. A good agreement between the data obtained by magnetic and Mössbauer measurements can be obtained only by assuming that in both cases a strong perturbation of the magnetic interactions occurs leading to the destruction of the collinear-order and to the formation of canted and block spin configurations.

Similar changes in the sublattice magnetization and in the equilibrium of the magnetic interactions among different sublattices were also obtained by Rensen *et al.* [13] by substituting Fe^{3+} with suitable amounts of divalent and tetravalent ions like, NiTi, ZnGe, etc. In these cases the Mössbauer spectra give evidence of the formation of new magnetic sublattices as in the case of Ga substituted ferrites. A Mössbauer study of CoTi substituted M-type ferrite has been also performed by V. F. Belov *et al.* [4].

As already pointed out the Fe^{3+} ions in the trigonal 2b site is one of the main responsible for the uniaxial anisotropy of Barium ferrite. Therefore a particular interest was devoted to the experimental determination of the degree of substitution of Fe^{3+} ions in site [15]. These data can be obtained from the measurement of the line intensities of Mössbauer spectra for the substituted ferrites at $T > T_c$. The low symmetry of the 2b-position gives rise to a quadrupole splitting of the Mössbauer line nearly five times as large as that measured for ^{57}Fe nuclei in the other lattice sites. Thus the Mössbauer peaks due to iron in the 2b position are clearly separated from the peaks due to other iron sublattices (Fig. 7). From this analysis it was seen that up to $x = 4$ the iron ions in 2b position are not substituted by Al and Ga. At higher X values, the entrance of Al and Ga in 2b sites appeared to be

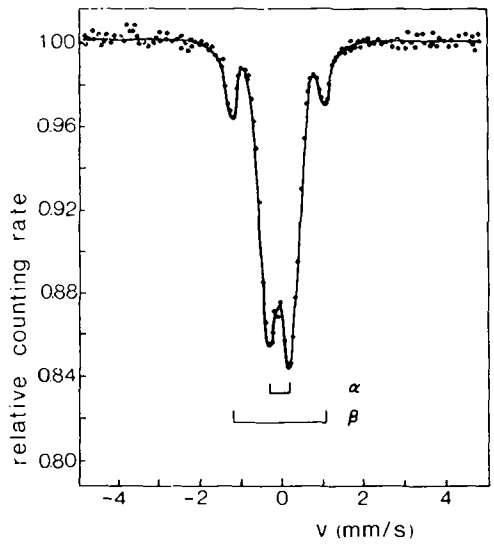

FIG. 7. — ^{57}Fe-Mössbauer spectrum for $BaFe_6Al_6O_{19}$ at 425 K. The quadrupole doublet β is due to the iron ions in 2*b* sublattice ; the doublet α to iron ions in the remanent lattice sites. (ALBANESE, G., *et al.*, *Nuovo Cimento* **58B** (1968) 480).

strongly influenced by the type of heavy cation (Ba or Sn) present in the structure.

Mössbauer studied have been also performed on As substituted Barium ferrite [16]. Contrary to Al and Ga, the As ions seem to have marked preference for the 2b sublattice.

The effect of substitution of iron by non-magnetic ions on the spin order of Barium M-type ferrite has been studied also by neutron diffraction. Among the earlier works, that of Bertaut *et al.* [17] on Al and Ga and Cr substituted barium ferrites is relevant.

Later one, with the availability of single crystal specimens, the researchers of the Institute of Crystallography of the Academy of Science of the Soviet Union were able to perform an interesting series of studies on Indium and Scandium substituted ferrites [18, 19]. We must remember that for M-type ferrites with collinear axial magnetic order the magnetic scattering does not contribute to the neutron diffraction spectrum from the basal planes, i. e. the spectrum displays only *nuclear peaks* OO*l* with *l*-even. In fact for the non-substituted $BaFe_{12}O_{19}$ the diffraction pattern does not reveal reflections with 1-old confirming the collinear magnetic order.

On the contrary in the diffraction spectrum for $BaFe_{12-x}In_xO_{19}$ with $X = 3$ and $X = 3.4$ [18] at low temperature, reflections with 1-odd appear (Fig. 8). Taking into account that the magnetic measu-

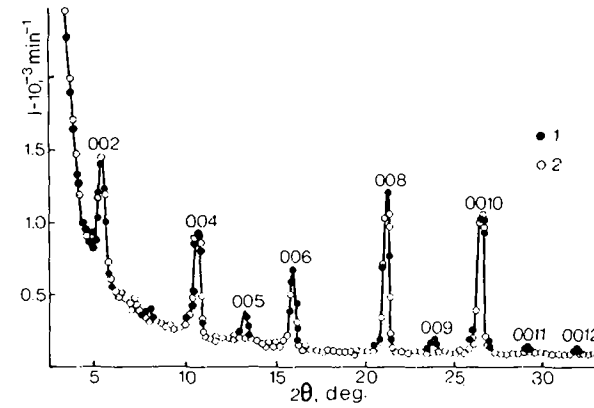

FIG. 8. — Neutron diffraction spectra from basal planes, of the $BaFe_{8.6}In_{3.4}O_{19}$ single crystal ; 2) at 300°, 1) at 78 K. (NAMTALISHVILI, M. I., *et al.*, *Sov. Phys. Sol. State* **13** (1972) 2137).

rements indicate that for this compound the easy magnetization axis lays along the *C*-axis, the neutron scattering data can be justified by assuming an angular block spin order as indicated in figure 9. The unit cell is divided into blocks O and O′ separated by the hexagonal layer containing the Ba ions. Inside each block the magnetic moments of the iron ions are supposed to be collinear but the direction of the resultant magnetization changes from block to block. The angle between the spin axis and the hexagonal axis is $\theta = 15°$ for $x = 3.4$ and $\theta = 10°$ for $x = 3$ at 78 K and varies with temperature. These results

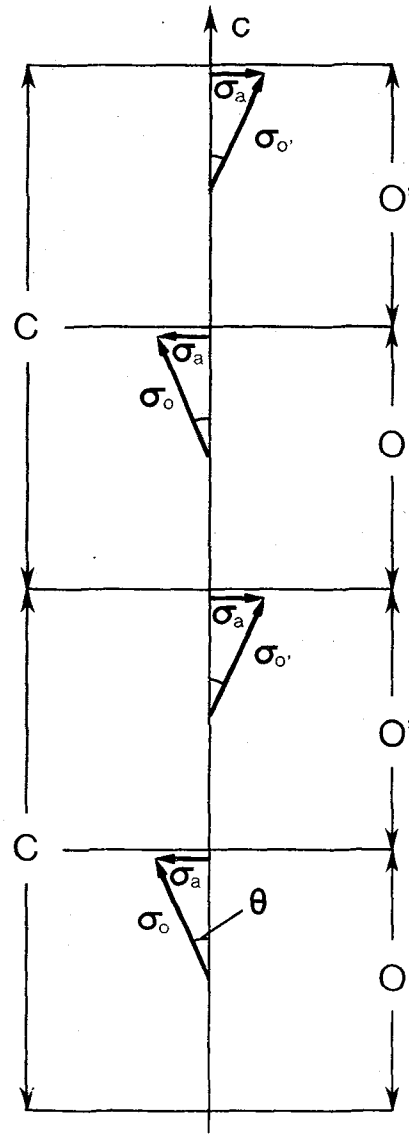

FIG. 9. — Scheme of the block angled spin order observed in $BaFe_{12-x}In_xO_{19}$.

have been explained by considering that the In ions substitute the Fe^{3+} ions preferentially in the trigonal 2b sites thus weakening the main exchange couplings in the hexagonal layers, i. e. in the layer which separates two adjacent spinel blocks. Then the antisimmetric exchange between ions located in the opposite sides of Ba-layer becomes significative and the axial model goes over to an angular block magnetic structure. The influence of the antisimmetric exchange on the spin order of the hexagonal ferrites has been discussed in some detail by Koroleva and Mitina [20, 21].

Another case of departure from axial order is the one of Scandium substituted ferrite $BaSc_xFe_{12-x}O_{19}$ [19]. In this case the neutron diffraction pattern also contains, in addition to the *l*-even reflections, superstructure doublets of magnetic origin typical for helical spin order. In figure 10 a part of the neutron diffraction spectra for $x = 1.8$ is shown. These results together with those obtained by magnetic measurements suggest that, as in the case of In substitued ferrite the unit cell may be divided into two magnetic blocks O and O′ separated by the layer containing Ba ions. However, in the case of Sc substituted ferrite the

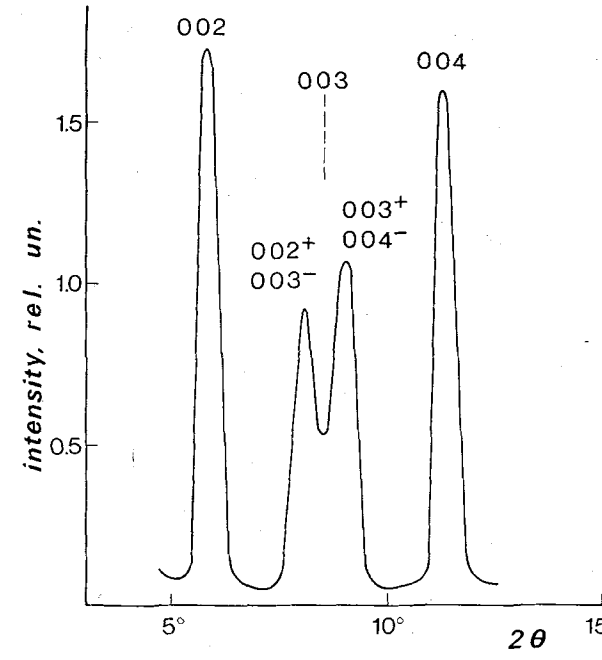

FIG. 10. — Neutron diffraction patterns in the region of the 003 reflection for $BaFe_{10.2}Sc_{1.8}O_{19}$ single crystal. (ALESHKO-OZHEVSKII, P., *et al.*, *Sov. Phys. JETP* **29** (1969) 655).

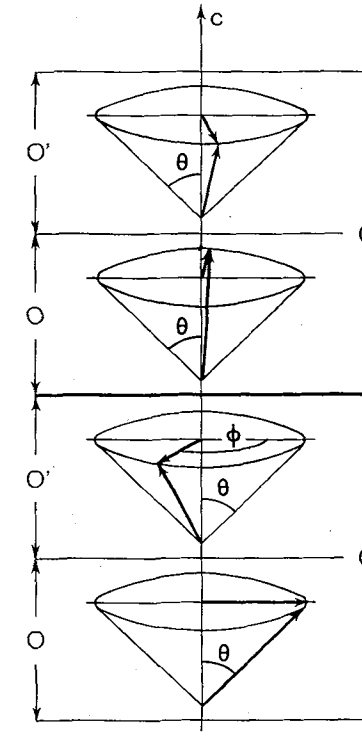

FIG. 11. — Scheme of block conical spiral-spin order observed in $BaFe_{12-x}Sc_xO_{19}$.

magnetic moments of the two blocks O and O′ form a conical helix generated by subsequent rotation of the spin axes around the *C*-axis (Fig. 11). The direction of the basal component of the total magnetic moment changes from block to block of an angle depending both on the scandium concentration and on temperature. The vertex angle of the cone was also found to depend upon the scandium concentration. The different magnetic order displayed by the In and Sc substituted ferrites can be probably due to the different distribution of In^{3+} and Sc^{3+} ions among 2b and $4f_{VI}$ lattice sites.

However a deeper understanding of the whole phenomenology in Sc and In substituted ferrites would require a better knowledge of the order of substitution as well as of the temperature dependence of the sublattice magnetization. These data which could be easily obtained from Mössbauer measurements, are not yet available in the literature. On the other hand neutron diffraction measurement could clarify the problem of the magnetic order involved in Al and Ga substituted ferrites.

3. **Y-type hexagonal ferrites.** — The Y-type hexagonal ferrites with composition $Ba_2Me_2Fe_{12}O_{22}$ (Me = Zn, Co, Mg, Mn, etc.) have a crystalline structure built up as a superposition of S and T blocks (Fig. 12). The unit cell is composed of the sequence STSTST including three formula units. The metallic cations are distributed among six sublattices as reported in table II where the basic spin orientation is also indicated. It is worth noting that inside the T block, three octahedral ions, belonging to $6c_{VI}$ and $3b_{VI}$ sublattices, lies on a vertical threefold axis, the central $3b_{VI}$ ion sharing two faces of its coordination figure with the adjacent $6c_{VI}$ ions. Such a configuration, as already pointed out, is responsible for a higher potential energy of the structure due to a stronger electrostatic repulsion between the cations ; therefore such sites are likely to be preferred by low charge ions. As a consequence a non-magnetic Me^{2+} ions with a marked preference for the octahedral coordination

TABLE II

Number of ions per unit formula, coordination and spin orientation for the various metallic sublattices of Y-structure

Sublattice	Coordination	Block	Number of ions	Spin
$6c_{IV}$	tetrahedral	S	2	down
$3a_{VI}$	octahedral	S	1	up
$18h_{VI}$	octahedral	S-T	6	up
$6c_{VI}$	octahedral	T	2	down
$6c_{IV}$	tetrahedral	T	2	down
$3b_{VI}$	octahedral	T	1	up

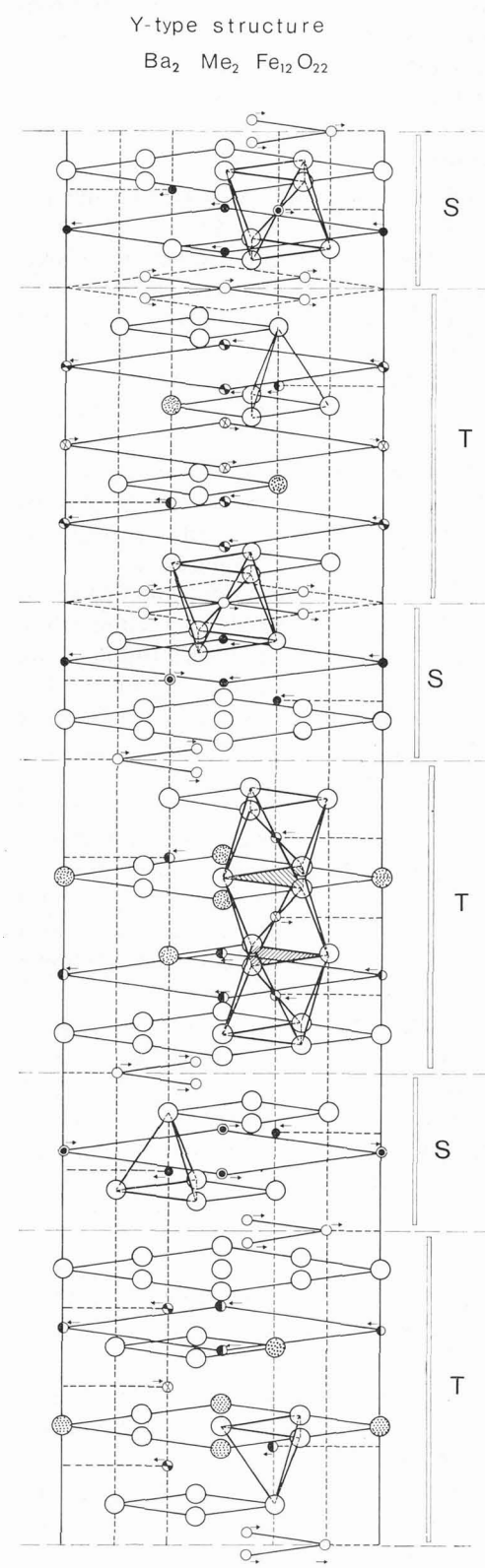

FIG. 12. — Unit cell of the Y-type ferrite. The anions O^{2-} (large empty circles), the divalent barium cations Ba^{2+} (large dotted circles). The metallic ions in the sublattices $3a_{VI}$(⊙), $6c_{VI}$(⊖), $3b_{VI}$(⊗), $18h_{VI}$(○), $6c_{IV}$(●) and $6c^{*}_{IV}$(◐) are indicated. The coordination figures of the metallic ions in the different lattice sites, together with their spin orientation, are put in evidence. (ALBANESE, G., *et al.*, *Appl. Phys.* 7 (1975) 277).

may cause drastic changes in the magnetic configuration with respect to the usual Gorter scheme ; indeed the occupation of either $6c_{VI}$ or $3b_{VI}$ by non-magnetic ions leeds to the cancellation of the antiferromagnetic b_{VI}-c^*_{IV} interaction which is the strongest one in the Y-structure.

Recently a magnetic and Mössbauer study of Mg_2-Y ($Ba_2Mg_2Fe_{12}O_{22}$) and Co_2-Y($Ba_2Co_2Fe_{12}O_{22}$) ferrites was performed [22]. A different behaviour of the sublattice magnetization for the two compounds has been evidenced. Moreover in the case of Mg_2-Y the observed anomalies in the magnetization curves can be explained assuming a non-collinear magnetic order. These differences in the magnetic behaviour of Mg_2-Y and Co_2Y are related to the occupation by Mg^{2+} and Co^{2+} of the octahedral sites inside the T block. In particular the presence of a non-magnetic ion such as Mg^{2+} in the $3b_{VI}$ sites in responsible for the deviation from the collinear order in Mg_2-Y ferrite. This site links the upper and lower part of the unit cell through the strong interaction with six ions $6c^*_{IV}$; furthermore the partial substitution of iron ions in $6c_{VI}$ sites results in the breaking of the inversion symmetry around $3b_{VI}$ sites. As a consequence antisymmetric interactions between couples of ions on opposite sides of $3b_{VI}$ sites like $6c_{VI}$ or $18h_{VI}$ ions, are allowed. In this case according to the fifth Morija rule [23] the antisymmetric exchange vector **D** must be parallel to the *C*-axis thus favouring the formation of angles between the moments lying in the basal plane. However for a rigorous definition of the magnetic order of Mg_2-Y ferrite, neutron diffraction measurements are necessary.

Modifications of the equilibrium inside the T block can also occur if localized lattice distortions and symmetry breakings are induced by the simultaneous presence in the oxygen planes of ions having different ionic radii such as Sr and Ba. An example is the case of the compound $Ba_{2-x}Sr_xZn_2Fe_{12}O_{22}$. In an early work by Enz [24] an anomalous behaviour of the torque and magnetization curves was observed for this ferrite. Enz interpreted his results by considering that due to the difference of ionic radii of Ba^{2+} and Sr^{2+} ions (Ba-1.43 Å, Sr-1.27 Å), the interaction $6c^*_{IV}$-$6c_{VI}$ is reinforced whereas the interaction $6c_{VI}$-$3b_{VI}$ is weakened. This results in the occurrence of an angle between the successive spinel bocks and thus in the formation of a helicoidal spin order.

The magnetic order in $Ba_{2-x}Sr_xZn_2Fe_{12}O_{22}$ has subsequently been investigated by Sizov and Yamzin [25]. They obtained neutron diffraction spectra typical for non-collinear spin configurations and interpreted their results by admitting a block helical spin order for this ferrite. The measured periods of the helix are multiples of 1/3 of the unit cell dimension and decrease with increasing strontium content. The authors correlate the formation of an helical block spin order to the distribution of non-magnetic Zn ions among the tetrahedral sites $6c^*_{IV}$ and $6c_{IV}$. In BaZn-Y ferrite the Zn ions should occupy the $6c^*_{IV}$ positions. On the contrary by substituting Ba with Sr, the local distortion may favour the entrance of Zn in $6c_{IV}$ sites. As a result the layer of tetrahedra preferentially occupied by zinc ions divides the cell into blocks. Within the blocks the equilibrium of superexchange interactions does not change and the spins. remain collinearly oriented. This interpretation seems to be supported by neutron diffraction measurements in $Ba_{0.4}Sr_{1.6}Co_2Fe_{12}O_{22}$ [25] which differs from the previous one in that all the zinc was replaced by cobalt. In this case no magnetic superstructure was observed in the diffraction spectra. However it seems that up to now some uncertainties remain concerning the localization of the layers representing the boundary between the magnetic blocks in the Y-type structures.

The Y-type ferrites have also been studied with NMR techniques. Streever *et al.* [26] measured the spin echo-NMR spectra for Mn^{55} in $Ba_2Zn_{2-y}Mn_{x+y}O_{22}$ ferrite in order to determine the relative amount of Mn^{3+} replacing Fe^{3+} and Mn^{2+} replacing Zn^{2+} in these compounds. The spectrum obtained at 4.2 K shows a broad line due to Mn^{3+} and two narrow lines that can be attributed to Mn^{2+} ions substituting Zn in the two different tetrahedral sublattices present in Y-structure. The obtained data about the Mn-distribution are consistent with the conclusion of an early Mössbauer work on $(MnZn)_2$-Y ferrite [27]. NMR measurements on ^{57}Fe have been performed also on Ni_2-Y and Co_2-Y ferrites [28]. However the spectra do not display distinct peaks and the obtained data are not conclusive.

4. **W-type hexagonal ferrites.** — The crystalline structure of the W-ferrites ($BaMe_2Fe_{16}O_{27}$) is similar to that of M-type ferrites. The only difference lies in the fact that the hexagonal R blocks are separated by two S blocks instead of one as in the M type ferrites. Generally speaking the phenomenology encountered in W-compounds is very close to the one discussed in section two. However the presence of both divalent and trivalent cations makes these ferrites interesting since their characteristics may in principle be varied as required by proper substitution of both trivalent and divalent cations. Moreover high saturation magnetizations can be obtained in these compounds due to the presence of four tetrahedral lattice sites (two in each S block) : indeed the iron ions with tetrahedral coordination have their magnetic moments opposite to the direction of the total magnetization. Therefore by substituting in these positions the iron with non-magnetic ions we may expect to increase the saturation magnetization at 0 K. An example of this situation is given by $BaZn_2Fe_{16}O_{27}$ (Zn_2-W) ferrite, since the non-magnetic Zn ions have a marked preference for the tetrahedral coordination ; in this case the theoretical evaluation of the saturation magnetization σ_0 gives a value of 40 μ_B. Recent magnetic measurements on

Zn_2-W ferrite [29] have given a value of 35 μ_B for σ_0 and at R. T. a value 13 % higher than that of $BaFe_{12}O_{19}$. The difference between the measured and the theoretical value of σ_0 may be ascribed to local spin reversal inside the octahedral sublattice of the S block. This is caused by the weakening of the tetrahedral-octahedral superexchange interactions due to the high concentration of Zn ions in tetrahedral sublattices. The Mössbauer data [30] confirm this interpretation and indicate also that for an other part of Fe^{3+} octahedral ions a remarkable decrease of the magnetic moment with increasing temperature occurs.

Mössbauer [31] and MNR [32] measurements have been also performed on the Mg_2-W compound. The temperature dependence of the sublattice magnetization obtained from Mössbauer spectra is in agreement with that measured by means of NMR technique. The cation distribution deduced from NMR and Mössbauer measurements, indicates that the Mg ions mainly occupy the octahedral sites inside the S-blocks.

As far as the effect of the substitution of iron by non-magnetic ions is concerned the situation is very similar to that already discussed in section 2 : the substitution of iron in some definite lattice sites may give rise to non-collinear magnetic structures. Antiphase block helical structures have been revealed by neutron diffraction measurements in Scandium substituted Ni_2-W ferrite with composition $BaNi_2Sc_2Fe_{14}O_{27}$ [33].

Neutron diffraction measurements have also been performed on Fe_2-W and $(FeCo)_2$-W compounds [34, 35].

5. **Z-type hexagonal ferrites.** — The Z-type ferrites ($Ba_3Me_2Fe_{24}O_{41}$) present a more complex crystalline structure than that of M, Y and W compounds. The unit cell is built up by all the three foundamental structural blocks S, R and T and the divalent and trivalent metallic cations are distributed among ten different lattice sites. Nevertheless detailed studies of their intrinsic properties are possible by means of nuclear spectroscopic techniques.

An example is a recent Mössbauer study of $Ba_3Co_2Fe_{24}O_{41}$ (Co_2-Z) compounds [36]. This ferrite shows a peculiar temperature dependence of the magnetic anisotropy : at low temperature it has a cone of easy magnetization, undergoes a transition to planar order at $T = 230$ K, and a second transition from planar to axial configuration at $T = 515$ K occurs. In figure 15 the temperature dependence of the angle θ between the c-axis and the magnetic moment direction deduced from Mössbauer spectra is shown. This data was obtained by measuring in the Mössbauer spectra for single crystal specimens the area submitted by the peaks relative to the transitions $\Delta m = 0. \pm 1$. In fact as already well known, the intensities of the lines in the Mössbauer spectra have a well defined dependence from the angle between the γ-rays direction and the direction of the hyperfine magnetic field at the ^{57}Fe nuclei. Therefore a detectable relative variation of the line intensities occurs in correspondence to spin reorientation transitions. The quadrupole splitting ΔE_q below the Curie temperature is a further parameter that is sensitive to the direction of the H_{hf}. A detailed analysis of the temperature dependence of ΔE_q has been made for the most intensive sextet displayed by the Mössbauer spectra and an abrupt jump at the transition temperature $T = 230$ K was found. Moreover the comparison of the experimental temperature dependence of the anisotropy constants K_1 and K_2 with the ones deduced from the sublattice magnetizations allowed for a better understanding of the role played by Co in determining the behaviour of the magnetic anisotropy in Co_2Z.

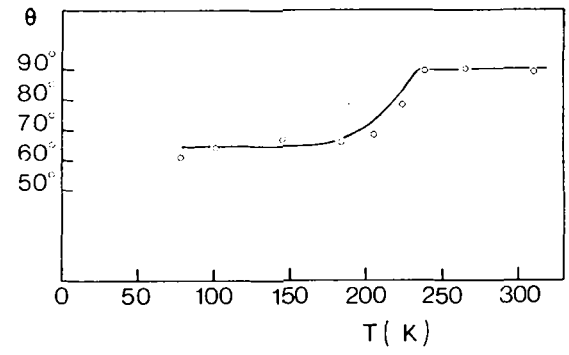

FIG. 13. — Temperature dependence of the angle θ between the C axis and the magnetic moment direction. Open circles refer to values deduced from Mössbauer spectra. The full line refers to the magnetic measurements. (ALBANESE, G., *et al.*, *J. Phys. C : Solid State Phys.* **9** (1976) 1313).

Neutron diffraction investigations have been performed in $Ba_{3-x}Sr_xZn_2Fe_{24}O_{41}$ [37, 38] in order to study modifications of the magnetic structure by replacing Ba with Sr, a problem analogous to that of $(BaSr)Zn_2$-Y compound mentioned in section 3. The spectra give evidence of the formation of a magnetic block structure. However for a detailed description of the involved spin configuration some difficulties seem to arise. In fact in the Z-structure the situation is more complex as compared with Y and M structures since the four layer blocks with spinel structure are separated alternatively by a single layer and by two adjacent layers containing Ba ions. This fact together with the large variety of cationic lattice sites gives rise to a variety of ways for subdividing the unit cell into magnetic blocks and the choice among the possible block configurations is therefore not always univocal. In order to clarify the possible spin structures, further data on the intrinsic properties and basic interactions of Z-ferrites are necessary. A suitable approach could be to first determine the sublattice magnetization and the spin order in a Z-type ferrite with a well defined cation distribution and subsequently to pass on to selective substitutions of iron by non magnetic ions.

6. **Conclusions.** — The application of nuclear spectroscopic methods yielded a considerable amount of

significant data on the intrinsic properties and the basic interactions of the hexagonal ferrites. It has been possible to clarify the influence of the cationic distribution and the sublattice magnetization on the saturation magnetization, the magnetic anisotropy and the spin order.

In particular, detailed information on the intrinsic properties of the substituted ferrites has been obtained.

Peculiar magnetic orders as angled block and block helical spin configurations have been evidenced; the appearance of such magnetic structures seems to be characteristic of hexagonal ferrites as a consequence of the complexity of their unit cell and of the net of superexchange interactions among the numerous magnetic sublattices.

The data collected up to now represent a first step towards the sistematic description of the magnetic properties of the hexagonal ferrites in terms of basic interactions. They may prove important in order to get a better adaptability of these materials to specific technical applications.

References

[1] Went, J. J., Ratheneau, G. W., Gorter, E. W. and Van Dosterhout, G. W., *Philips Rechn. Rev.* **13** (1951/52) 194.

[2] Smit, J. and Wijn, H. P. J., *Ferrites* Philips Technical Library, Eindhoven.

[3] Gorter, E. W., *Proc. IEEE* **104B** (1957) 255.

[4] Wieringen, J. S. and Rensen, J. G., *Z. Angew. Phys.* **21** (1966) 69.

[5] Van Wieringen, J. S., *Philips Tech. Rev.* **28** (1967) 33.

[6] Albanese, G., Carbucicchio, M. and Deriu, A., *Phys. Stat. Sol. (a)* **23** (1974) 351.

[7] Streever, R. L., *Phys. Lett.* **27A** (1958) 563.

[8] Streever, R. L., *Phys. Rev.* **186** (1969) 285.

[9] Asti, G. and Rinaldi, S., to be published on the *Proceedings of Joint MMM-Intermag Conference, Pittsburg* 1976.

[10] Albanese, G., Asti, G. and Batti, P., *Nuovo Cimento* **54B** (1968) 339.

[11] Albanese, G., Asti, G. and Batti, P., *Nuovo Cimento* **58B** (1968) 467.

[12] Albanese, G., Asti, G. and Batti, P., *Nuovo Cimento* **58B** (1968) 480.

[13] Rensen, J. G., Schulkes, J. A. and Van Wieringen, J. S., *J. Physique Colloq.* **32** (1971) C1-924.

[14] Belov, V. F., Khimich, J. A., Shipko, M. N., Zheludev, I. S., Korneev, E. V. and Ovanesyan, N. S., *Sov. Phys.-JETP* **37** (1973) 1089.

[15] Albanese, G., Carbucicchio, M. and Deriu, A., *Nuovo Cimento* **15B** (1973) 147.

[16] Kreber, E. and Gonser, U., *Appl. Phys.* **1** (1973) 339.

[17] Bertaut, E. F., Deschamps, A., Pauthenet, R. and Pickart, S., *J. Physique* **20** (1959) 404.

[18] Namtalishvili, M. I., Aleshko-Ozhevskii, O. P. and Yamzin, I. I., *Sov. Phys. Solid State* **13** (1972) 2137.

[19] Aleshko-Ozhevsckii, O. P. and Yamzin, I. I., *Sov. Phys. JETP* **29** (1969) 655.

[20] Koroleva, L. I. and Mitina, L. P., *Soc. Phys. Solid State* **13** (1971) 526.

[21] Koroleva, L. I. and Mitina, L. P., *Phys. Stat. Sol. (a)* **5** (1971) K 55.

[22] Albanese, G., Carbucicchio, M. Deriu, A., Asti, G. and Rinaldi, S., *Appl. Phys.* **7** (1975) 227.

[23] Moriya, T., *Phys. Rev.* **120** (1960) 91.

[24] Enz, U. J., *Appl. Phys.* **32** (1961) 22S.

[25] Sizov, V. A., Sizov, R. A. and Yamzin, I. I., *Sov. Phys. JETP* **26** (1968) 736.

[26] Streever, R. L., Aucoin, T. R. and Caplan, P. J., *J. Phys. Chem. Solids* **32** (1971) 519.

[27] Albanese, G., Asti, G., Lamborizio, C., *J. Appl. Phys.* **39** (1968) 1198.

[28] Petrov, M. P. and Kunevich, A. V., *Sov. Phys. Solid State* **13** (1972) 278.

[29] Albanese, G., Asti, G. and Carbucicchio, M., *Lett. Nuovo Cimento* **14** (1975) 207.

[30] Albanese, G., Asti, G. and Carbucicchio, M., *Appl. Phys.* **11** (1976) 81.

[31] Albanese, G. and Asti, G., *IEEE Trans.* **6** (1970) 158.

[32] Petrov, M. P. and Kunevich, A. V., *Sov. Phys. JETP* **36** (1973) 1184.

[33] Sizov, R. A. and Zaitzev, K. N., *Sov. Phys. JETP* **39** (1974) 176.

[34] Sizov, R. A. and Yamzin, I. I., *Sov. Phys. Dokl.* **11** (1966) 379.

[35] Yamrin, I. I., Sizov, R. A., Zheludev, I. S., Perekalina, J. M. and Zalesskii, A. V., *Sov. Phys. JETP* **23** (1966) 395.

[36] Albanese, G., Deriu, A. and Rinaldi, S., *J. Phys. C* **9** (1976) 1313.

[37] Sizov, V. A. and Yamzsin, I. I., *Sov. Phys. JETP* **28** (1969) 619.

[38] Namtalishvili, M., Aleshko-Ozhevskii, O. P. and Yamzin, I. I., *Sov. Phys. JETP* **35** (1972) 370.