INVESTIGATION OF SOME HEXAGONAL FERRITES WITH AN M STRUCTURE BY EMPLOYING THE MOSSBAUER EFFECT

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Some hexagonal ferrites with an M structure are investigated by using the Mossbauer effect. It is shown that four magnetic sublattices are observed in $BaFe_{12}O_{19}$ and $SrCo_{0.42}Fe_{11,16}O_{19}$ ferrites at room temperature. The presence of additional lines indicates the existence of impurity layers. It is found that in the given ferrites spin-orbit interaction makes a large contribution to the magnetic anisotropy. The decrease of the magnetic field strength at the Fe^{57} nuclei which occurs when Co and Ti are introduced into an Sr ferrite indicates that the 3d-electrons are redistributed among the Co, Ti and Fe ions.

1. INTRODUCTION

HEXAGONAL ferrites have large magnetic anisotropy. It is assumed that the dipole-dipole interaction does not play an important role in the M structure. The main contribution to the energy of the magnetic crystallographic anisotropy is apparently made by the spin-orbit interaction. It is due to the quenching of the orbital motion, which in turn is due to deivation of the symmetry of the local environment of the iron ions from cubic. This deviation leads to a quadrupole splitting in the Mossbauer spectra. Thus, the Mossbauer-effect method makes it possible to investigate the influence of spin-orbit interaction on the magnetic anisotropy of iron ions.

The purpose of the present study was to investigate hexagonal ferrites with M structure by the Mossbauer-effect method.

2. EXPERIMENTAL PROCEDURE AND SAMPLES

The Mossbauer effect in hexagonal ferrites was investigated with a setup of an electrodynamic type, the block diagram of which is shown in Fig. 1. The relative motion of the source (with velocity v(t)) was produced by a special vibrator (1). We used uniformly-accelerated motion. The γ quanta passing through the absorber (3) were registered with a detector (4) comprising an NaI(Tl) crystal with an FÉU-13 photomultiplier. The signal from the detector was fed to a discriminator (5) and then to a multichannel pulse analyzer of the AI-256 type (6). The time interval during which counting in each channel took place was constant. Therefore, in the absence of resonant absorption of the γ quanta, the number of pulses in each channel was independent of the channel number.

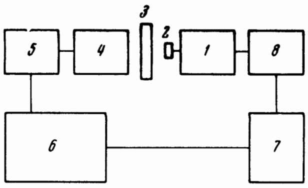

FIG. 1. Block diagram of experimental setup.

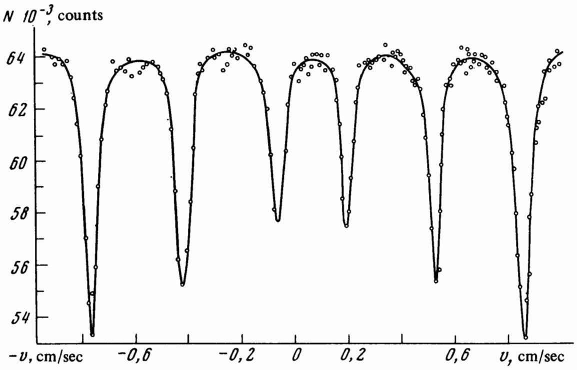

FIG. 2. Mossbauer spectrum of Fe_2O_3.

The spectrum was scanned once during each period of motion. By way of an example, Fig. 2 shows the well known spectrum of iron oxide Fe_2O_3. To calibrate the channel in velocity units, we compared the positions of the extreme peaks of the spectrum of iron oxide with the data of[1], which were obtained with precision apparatus at a constant speed.

The vibrator power-supply block consisted of two dc amplifiers (8) with negative feedback and a generator of the NGPK-3M type (7). This generator was also used to supply starting pulses to trigger the multichannel analyzer, thus ensuring a firm connection between the speed of motion and the channel number. The vibrator was a system of two magnets, in the gaps of which there were suspended, on annular springs, coils interconnected by a rigid rod. The source (2) was fastened to this rod. The source employed was Co^{57} in a matrix of stainless steel with activity 8.6 mCi. The diameter of the active spot was 5 mm. The half-width of the component of the experimental absorption line in nitroprusside and the magnitude of the effect were respectively 0.38 mm/sec and 16% (at an absorber thickness equivalent to 20 mg/cm² of natural iron).

The Mossbauer spectrum were measured on crystals, grown from the melt, of hexagonal ferrites with M structure ($BaFe_{12}O_{19}$; $SrCo_{0.42}Ti_{0.42}Fe_{11}$; ${}_{16}O_{19}$; $SrFe_{12}O_{19}$). A similar structure is possessed by mag-

Table I

Number of sub-lattice	Oxygen surrounding of Fe^{3+} ions		
	Tetra-hedron	Trigonal bipyramid	Octa-hedron
I			6↑
II	2↓		
III			2↓
IV		1↑	
V			1↑

netoplumbite. The hexagonal unit cell of such a structure consists of nine layers of oxygen ions. Each layer in the unit cell contains four large ions. In four succeeding layers, the large ions are the oxygen ions, but each fifth layer has besides the three oxygen ions also one strontium (or barium) ion. In this structure, the trivalent iron ions occupy sites of three different types. Besides the tetrahedral and octahedral positions, there is here also a five-fold surrounding, constituting a trigonal bipyramid. Such sites are contained in layers with barium (strontium) ions. There are twelve iron ions in each formula unit of the barium ferrite. They are distributed as follows: two ions occupy tetrahedral positions, one ion is located in the trigonal bipyramid. The remaining ions occupy octahedral sites. It is possible to separate three types of octahedral voids in the M structure[2].

The investigated compounds contain five sublattices (see Table I)[1]. One should expect complicated Mossbauer spectra in this case.

3. RESULT AND DISCUSSION

Figure 3 shows the spectrum of the hexagonal ferrite $BaFe_{12}O_{19}$. We see that the Mossbauer spectrum is a complicated structure, due to the superposition of Zeeman six-line splitting pictures I, II, III, IV from the iron nuclei, located in different crystallographic positions (sublattices I, II, III, IV).

Sixteen spectral components are resolved relatively distinctly. Line 1 is slightly broadened and has a lower intensity than the single line 2, which has a high intensity. Attention is called to the broadened lines 7 and 9, which have identical intensities, and also to line 16, which has a gentle outward slope, making it possible to assume a superposition of not less than two lines. Comparing the intensities of the components with the distribution of the iron ions over the sublattices (with account taken also of the line broadening), we can resolve the spectrum of polycrystalline $BaFe_{12}O_{19}$ into four six-line spectra with a chemical shift characteristic of the ions Fe^{3+}. However, the spectrum contains additional lines, which are not characteristic of the single-crystal $BaFe_{12}O_{19}$[3]. They form one more six-line spectrum with a chemical shift $\sim$2 mm/sec, a quadrupole splitting $\Delta = 0.29$ mm/sec, and a magnetic local field $H_l = 440$ kOe. This spectrum is possibly due to the presence in the sample of layers having a different structure.

In the Mossbauer spectrum of $SrFe_{12}O_{19}$ (Fig. 4),

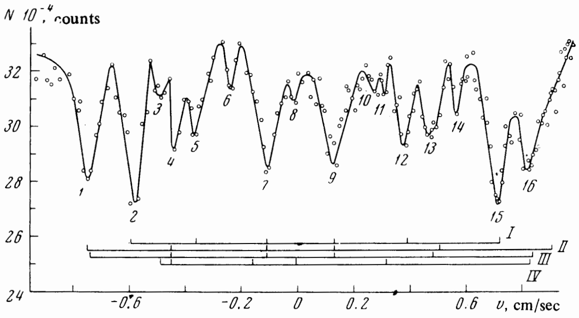

FIG. 3. Mossbauer spectrum of $BaFe_{12}O_{19}$.

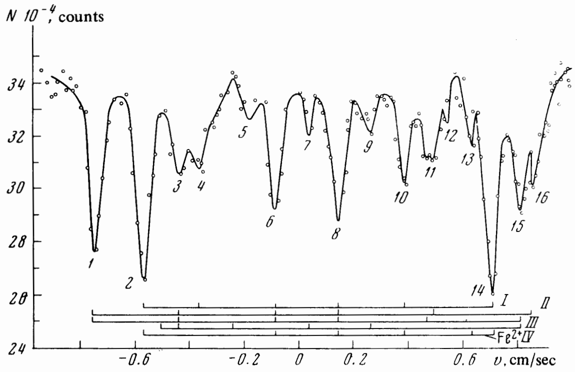

FIG. 4. Mossbauer spectrum of $SrFe_{12}O_{19}$.

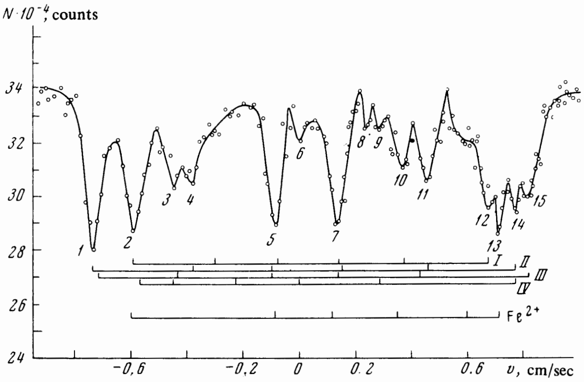

FIG. 5. Mossbauer spectrum of $SrCo_{0.42}Ti_{0.42}Fe_{11.16}O_{19}$.

there are likewise 16 distinctly resolved components. A distinction feature of this spectrum is the splitting of the outermost right-hand line into two components (lines 15 and 16, Fig. 4). The spectrum of $SrFe_{12}O_{19}$ can also be resolved into four six-line spectra I, II, III, IV with a chemical shift δ characteristic of the trivalent iron, and one spectrum corresponding to the layers of another structure with Fe^{2+} ions ($H_l = 397$ kOe, $\Delta = 1.41$ mm/sec, $\delta = 1.74$ mm/sec). Antiferromagnetic ordering giving rise to losses to the rotational hysteresis, which was observed by Shchurova et al.[4], can apparently occur on the boundaries of these impurity atoms.

The magnetic properties of the investigated samples were studied in[4]. The overall view of the spectrum remained the same when the Fe^{3+} in the strontium ferrites were replaced by Co^{2+} and Ti^{4+} ions (Fig. 5).

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[1] In Table I we indicate the number of iron ions and the direction of magnetic moment in the sublattices.

There are 15 distinctly resolved components. Analysis shows that the line-intensity ratios, the line widths, and the distances between lines all change. Line 2 becomes less intense, whereas line 1 has maximum intensity. Line 15 of the Sr ferrite (Fig. 4) is split in this spectrum into two components. Additional low intensity lines 9 and 12 also appear.

It is possible to separate here four six-line spectra with a chemical shift corresponding to Fe^{3+}, and one spectrum with a chemical shift close to Fe^{2+} (δ = 1.52 mm/sec, Δ = 0.95 mm/sec, and H_l = 385 kOe).

An analysis of the presented spectra, in terms of the line intensity, the line width, and the distribution of the Fe ions in the sublattices, shows that it is possible to separate in the investigated ferrites the four magnetic sublattices listed in Table I. The fifth sublattice of the Fe^{3+} ions did not appear in our experiments. Apparently, just as in[3], the spectrum due to the fifth sublattice coincides in the investigated samples with the spectrum due to the iron ions in the third sublattice.

Table II gives the Mossbauer parameters of the spectra of the investigated samples.

Table II

n	δ, mm/sec	Δ, mm/sec	H_l, kOe
	$BaFe_{12}O_{19}$		
I	0.40	0,27	419
II	0.54	0,25	510
III	0.43	0,23	500
IV	0.505	1.12	405
	$SrFe_{12}O_{19}$		
I	0.53	0.33	418
II	0.42	0.18	503
III	0.24	0.05	488
IV	0.40	1,27	403
	$SrCo_{0,42}Ti_{0,42}Fe_{11,16}O_{19}$		
I	0.393	0.06	392
II	0,272	0.145	490
III	0.23	0,09	466
IV	0.107	0.88	418

Here n – number of sublattice.

It is seen from the table that all the sublattices have a noticeable quadrupole splitting. In the barium and strontium ferrites, the largest value of Δ was observed for Fe^{3+} nuclei located in the first and fourth sublattices. The local surrounding of the Fe^{3+} ions, located in the second and third sublattices of $SrFe_{12}O_{19}$, deviate insignificantly from cubic symmetry (Δ = 0.18 and 0.05 mm/sec). Substitution of strontium ions for the barium ions lowers the quadrupole splitting of the third sublattice. However, the magnetic anisotropy constant, together with large quadrupole splitting of the first and for sublattices, changes little (k_1 equals 3.3×10^6 erg/cm^3 for $BaFe_{12}O_{19}$ and 3.6×10^6 erg/cm^3 for $SrFe_{12}O_{19}$).

When some of the Fe^{3+} ions are replaced by Co and Ti ions in the strontium ferrite, the deviation of the local symmetry of the surroundings for the Fe^{3+} ions in the first, second, and fourth sublattices, decreases. Simultaneously, the magnetic anisotropy decreases strongly ($k_1 = 1.8 \times 10^5$ erg/cm^3).

Thus, the magnetic crystallographic anisotropy of $SrCo_{0.42}Ti_{0.42}Fe_{11.16}O_{19}$ is due mainly to the iron ions in the first, second, and fourth sublattices. In the barium and strontium ferrites, all the sublattices (especially the first and fourth) make a noticeable contribution to the magnetic anisotropy. The correlation between the anisotropy constant k_1 and the magnitude of the quadrupole splitting makes it possible to assume that in the investigated compounds the spin-orbit interaction exerts a strong influence on the magnetic anisotropy.

When strontium replaces barium, the magnetic fields at the iron nuclei (in table II) in the second and fourth sublattices remains practically unchanged. In the barium and strontium ferrites, the magnetic fields at the nuclei located in the first and third sublattices are also the same. However, in $SrCo_{0.42}Ti_{0.42}Fe_{11.16}O_{19}$ the local magnetic fields at the Fe^{57} nuclei in the first and third sublattices are much weaker than H_l in barium and strontium ferrites.

The deviation of the symmetry of the local surrounding of the Fe ions from cubic, and the covalence of the chemical bond, make positive contributions to the negative magnetic field due to the exchange polarization of the ion core of the iron. The resulting field then decreases. The quadrupole splitting for the first and third sublattices in $SrCo_{0.42}Ti_{0.42}Fe_{11.16}O_{19}$ is smaller than the quadrupole splitting for the corresponding sublattices in the barium and strontium ferrites. The decrease of H_l when the iron ions are partly replaced by Co and Ti ions cannot be attributed to the deviation of the symmetry of the surrounding from cubic (the symmetry, to the contrary, increases). It is seen from Table II that the chemical shift for the iron nuclei situated in the first and third sublattices changes little when the barium is replaced by strontium and the iron ions are replaced by Co and Ti ions. Consequently, the positive contribution to the magnetic field at the nuclei (localized in the first and third sublattices), due to the covalence of the chemical bond, also changes little. When the Fe^{3+} are partly replaced by Co^{2+} and Ti^{4+} ions, the value of δ for the second and fourth sublattices decreases to almost one-half. The magnetic field at the Fe^{57} nuclei in these sublattices remain practically unchanged.

Thus, the weakening of the magnetic fields at the nuclei by introduction of Co and Ti in Sr ferrite cannot be attributed to the covalence of the chemical bond and to deviation of the symmetry of the surrounding of the Fe^{3+} ions from cubic. The weakening of the magnetic fields at Fe^{57} nuclei in the first and third sublattices may be due to a redistribution of the magnetic 3d-electrons among the Co, Ti, and Fe ions as a result of indirect exchange interaction.

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