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MOSSBAUER STUDY OF YTTRIUM IRON GARNET EPITAXIAL FILMS MAGNETIC MICROSTRUCTURE

V.O. KOTSYUBYNSKY, V.V. MOKLYAK, B.K. OSTAFIYCHUK

Abstract: The magnetic microstructure of the yttrium iron garnet epitaxial films surface layer were studied by conversion electronic Mossbauer spectroscopy method. The presence of two magnetically non-equvivalent positions of Fe^{3+} ions in tetrahedral sites of garnet structure and a paramagnetic phase formed by Fe^{2+} ions were fixed. Using the model of mixed magnetic and quadrupole interaction by the diagonalization of the nuclear Hamiltonian matrix the information about the spatial orientation of the cation sublattices magnetic moments was obtained and the components of electric field gradient tensor at ^{57}Fe nuclei in different crystal non-equvivalent positions were calculated.

Keywords: yttrium iron garnet epitaxial films, conversion electron Mossbauer spectroscopy, effective magnetic field, magnetic moment orientation, electric field gradient.

1. INTRODUCTION

Yttrium iron garnet $Y_3Fe_5O_{12}$ with the traditional practical application in magneto-optical devices and microwave electronics is a convenient model for the study of the ferromagnetic ordering. The crystal structure of $Y_3Fe_5O_{12}$ are assigned to space group Ia3d (O_h^{10}) and is formed by oxygen coordination polyhedra. There are cavities of three types – 24 tetrahedral and 16 octahedral are occupied by Fe^{3+} ions (*d*- and *a*-positions respectively) and 24 dodecahedral which are occupied by Y^{3+} (c-position). Magnetic ordering in Yttrium iron garnet is the result of indirect exchange interaction between Fe^{3+} from different sublattice through the oxygen ions. Magnetic moments of Fe^{3+} ions in *a*-and *d*-positions (M_a and M_d respectively) for an infinite perfect crystal are antiparallel (Neel model). For ferrite-garnet films with the substitutions of Y^{3+} ions by rare earth elements (Sm^{3+}, Lu^{3+}, Eu^{3+}) the large growth uniaxial anisotropy is appeared and the total magnetization is directed along the axis [111]. $Y_3Fe_5O_{12}$ epitaxial films due to the effect of surface demagnetization are characterized by the presence of additional planar magnetization component so the magnetization deviate from the [111] direction to the film plane. The aim of this work is the experimental setting of the spatial orientation of iron ions magnetic moments in the yttrium iron garnet epitaxial films grown on (111) plane and its relationship with parameters intracrystalline electric and magnetic fields.

2. EXPERIMENTAL DETAILS

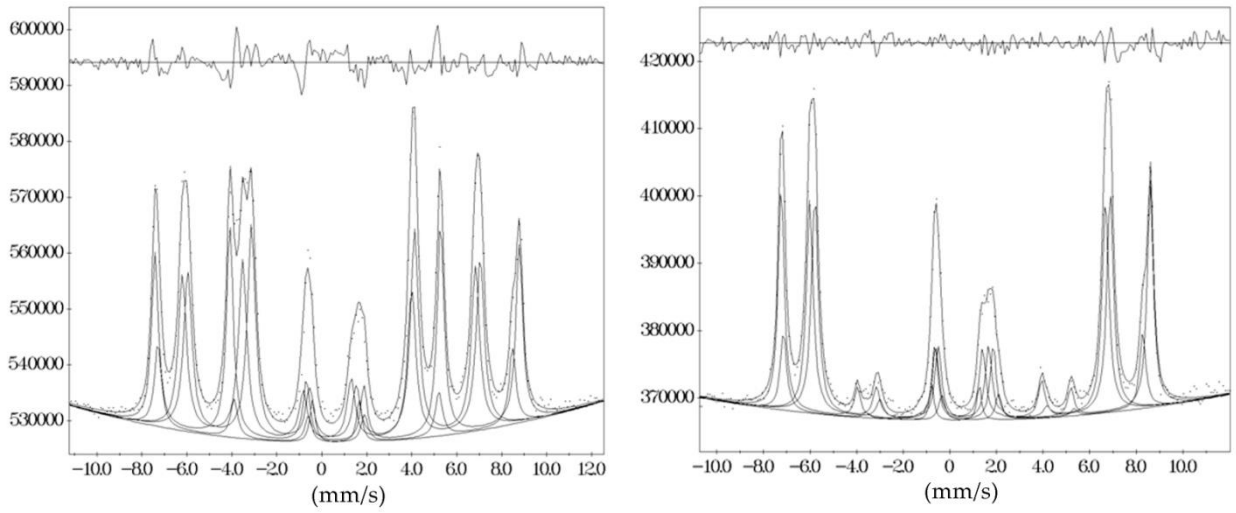
Yttrium iron garnet films were grown by liquid phase epitaxy method from Y_2O_3-Fe_2O_3-PbO-B_2O_3 melt on nonmagnetic substrate gallium gadolinium garnet $Gd_3Ga_5O_{12}$ with (111) surface plane. For Mossbauer effect probability increasing was used Fe_2O_3 enriched by isotope ^{57}Fe to 14 at.%. Films crystallographic disorientation not exceeds 1°. Films thickness was 2.85 mm. For conversion electrons registration gas proportional counter was used. The activity of Mossbauer isotope ^{57}Co was about 70mKu. Velocity zero instability and registration error were less than 0.5 channel from 256, width of the resonance lines of α-Fe was 0.30 mm/s. The external magnetic fields were formed by system of permanent magnets.

3. RESULTS AND DISCUSSION

Ferrimagnetic ordering of the $Y_3Fe_5O_{12}$ structure is associated with the magnitude of electrostatic fields directed on the nucleus of iron ions by ions of the lattice and their own electron shell. With the simultaneous existence of electric quadrupole and magnetic dipole interactions of approximately equal intensity $|e^2QU_{zz}| \approx |\mu H_{e\phi}|$ an important parameter in the formation of iron magnetically position is the angle θ between the direction of an effective magnetic field on the nucleus Fe^{57} and a direction of the electric field gradient (EFG). The crystal symmetry the EFG tensor is axially symmetric since the tetrahedral positions have symmetry axis of the 4th order and octahedral the third order. So the tensor components have to satisfy the condition (coordinate system is chosen so that the EFG tensor is diagonal): $|U_{xx}| = |U_{yy}| \le |U_{zz}|$; $\eta = (U_{xx} - U_{yy})/U_{zz} = 0$.

Symmetry axes of octahedral positions are corresponding to four possible axes <111> and can be divided into four groups of four atoms in each direction with the same value of EFG. Symmetry axes of tetrahedral positions correspond to the axes <100>. Thus, in general, the garnet structure contains 7 crystal-, and thus magnetically equivalent positions for ions Fe^{3+}, which correspond to the 7 partial components of mossbauer spectrum. In single-crystal ferrite-garnet films (FGF), grown on a substrate with a cut plane (111), there are three possible EFG directions for Fe^{3+} ions in d-sublattice with polar angle $\theta^a_{1,2,3} = 54°44'$; for 1/4 of Fe^{3+} ions in the a-sublattice $\theta^a_4 = 0°$ (EFG direction on the nuclei coincides with the direction [111]), and 3/4 ions $\theta^d_{5,6,7} = 70°32'$. As a result measured experimental values of the quadrupole splitting Δ_{exp} differs from the true quadrupole splitting Δ_{real} of nuclear spin $I = 3/2$: $\Delta_{exp} = \Delta_{real} \dfrac{3\cos^2\theta - 1}{2}$.

As already mentioned, for samples $|e^2QU_{zz}| \approx |\mu H_{e\phi}|$, ie simplified equation [1] to determine the hyperfine structure levels of the nucleus is nonapplicable; generally it is necessary to use a Hamiltonian of mixed hyperfine interaction [2]. In our work, the model of a mixed quadrupole and magnetic interaction issues by diagonalization of the matrix of the nuclear Hamiltonian . Coordinate system is chosen so that the zi axis is parallel to U_{zz}^i, β^i angles are polar and α^i are azimuthal angles between the directions of the effective magnetic field and zi axes . We used a methodical approach proposed in [3]. Diagonalizing the Hamiltonian of hyperfine interactions we established the position of the γ- sextet partial resonance lines in the form of a Lorentzian combination. The parameters that are changed in the approximation process are: the amplitude, the isomer shift δ, the magnetic field H_{ef} , the value of the axial components of the EFG U_{zz}, the β polar angle relative to the orientation of H_{ef} U_{zz} EFG (z axis of the laboratory coordinate system); the polar angle of γ-quantum beam orientation relative to U_{zz} EFG (range of changes is ±2°, calculated with respect to the values geometrically considered). Approximation results of the CEM spectra are shown in the table 1 and in Fig. 1.



(a) *(b)*

Fig. 1. Conversion electron Mossbauer spectra of the single-crystal film of $Y_3Fe_5O_{12}$, cut plane (111): a) without the external magnetic field; б) within the external magnetic field of 2.8 kOe

To simplify the problem and to find the absolute values of U_{zz} components for different nonequivalent positions the survey the external magnetic field $H_{ext} \approx 2.8$ kOe was applied perpendicularly to the sample surface. In this case the individual magnetic moments of the iron ions were oriented along the direction of the external magnetic field. As shown in Fig. 1 in the partial sextet the intensities of lines 2 and 5 are <8%. These values do not change with increasing of the H_{ext} and are defined by the divergence of γ- quantum beam and experiment geometry. Although, as shown above on the basis of crystallographic assumptions the experimental spectrum must be a superposition of three partial sextet, the nature of the obtained spectra allowed to make an acceptable conclusions about approximations only assuming the presence of two d-positions with different orientations and values of effective magnetic field H_{ef} on iron nuclei.

Crystallographic position	**β°**	**γ°**	**U_{zz}, x10^{21} V/m²**	**H, kOe**	**δ_s, mm/s**	**ω, mm/s**	**S, %**
single-crystal film of $Y_3Fe_5O_{12}$, orientation plane (111)							
a_1	2.9 ± 0.7	70.9	0.60 ± 0.02	503.0 ± 0.1	0.64	0.34	26.7
a_2	61.4 ± 1.6	0.0	0.59 ± 0.02	487.4 ± 0.4	0.63	0.34	8.9
d_1	168.2 ± 0.8	54.7	1.32 ± 0.03	409.2 ± 0.2	0.32	0.43	28.5
d_2	150.2 ± 1.6	54.7	-0.36 ± 0.04	394.4 ± 0.2	0.47	0.47	33.4
D	-	-	-	-	0.61	0.34	2.5
single-crystal film of $Y_3Fe_5O_{12}$, orientation plane (111) in the magnetic field of 2.8 kE							
a_1	46.0 ± 0.8	70.9	0.51 ± 0.10	491.5 ± 0.1	0.67	0.31	28.5
a_2	6.6 ± 5.8	0.0	0.50 ± 0.11	478.2 ± 0.4	0.53	0.31	9.5
d_1	248.7 ± 1.4	54.7	2.09 ± 0.21	400.3 ± 0.2	0.48	0.32	24.7
d_2	261.0 ± 0.8	54.7	-1.52 ± 0.08	387.3 ± 0.2	0.38	0.36	35.2
D	-	-	-	-	0.72	0.31	2.2

Tab. 1. Measurements of the partial components of the experimental mossbauer spectra

The two variant of iron atoms neighbor surrondings in d-positions is defined by stoichiometry distortion of anionic sublattice and uncontrolled entry into garnet structure of impurity atoms from solution - melt in the final stages of epitaxy. It is known [4] that ions Pb^{2+} and Pb^{4+} occupy the octahedral positions displacing the Fe^{3+} with probability of 0.4 and 0.3 respectively. Another uncontrolled impurity is the ions of Pt^{4+} which occupy only a-position. According to [5] from the surface layer of the film thickness of 65 nm more than 2/3 of the conversion electrons are obtained. Low-energy region of the amplitude spectrum (photoelectrons, conversion electrons from the depths of > 85-95 nm) is cut by hardware discriminator and thus the experimental spectrum is formed by an integrated registration of conversion electrons from the depths of < 90 nm. According to [6] the thickness of the transition layer, which is characterized by cationic heterogeneity is < 80 nm. Cationic distribution of the transition layer is largely determined by technological conditions of epitaxy-supercooling temperature of melt and substrate rotation speed. The varies of these factors cause the formation of nonequilibrium surface layer with a concentration of atomic defects ≤ 0.005 per formula unit. These concentrations did not significantly affect the crystalline order, but even slight distortion of the local environment results in changes in the direction of EFG and absolute values of its axial component with the distortions of superexchange interaction. All these factors lead to the emergence of two crystal and magnetic nonequivalent d-positions with noncollinear magnetic moments. Fig. 2. shows the diagram of the effective magnetic fields spatial orientation at the nuclei of ^{57}Fe and the electric fields gradients of individual sublattices. It is known [2] that the effective magnetic field at the core of iron ion and its magnetic moment are antiparallel to each other. Thus, our studies made it possible to establish the magnetic moments spatial orientation of the individual sublattices . We found noncollinearity of magnetic moments of magnetic and crystal nonequivalent iron positions, which is ≈5÷25°, ie there is violation of antiferromagnetic order. It has established that the imposition of an external magnetic field ≈2.8 kOe does not eliminate noncollinearity of magnetic moments.

The above mentioned defects are confirmed by the values of the d- and a-positions populations ratio (n_d/n_a). This parameter is very close to the crystallographic stoichiometric. A significant narrowing of lines in an external magnetic field confirms the presence of magnetically nonequivalent positions of iron in each of the crystallographic nonequivalent sublattices . Reducing the effective magnetic fields at the nuclei of Fe^{3+} in an external magnetic field is almost the same for all selected crystallographic positions. The change of the isomer shift value in an external magnetic field can be caused by a redistribution of the density of s-electrons in Mossbauer nuclei locations and the symmetry of dipped surroundings makes the decisive influence. The values of the axial tensor components for a EFG position are identical within experimental error due to uniformity of dipped surroundings symmetry of Mossbauer nucleus for a_1 and a_2 positions.

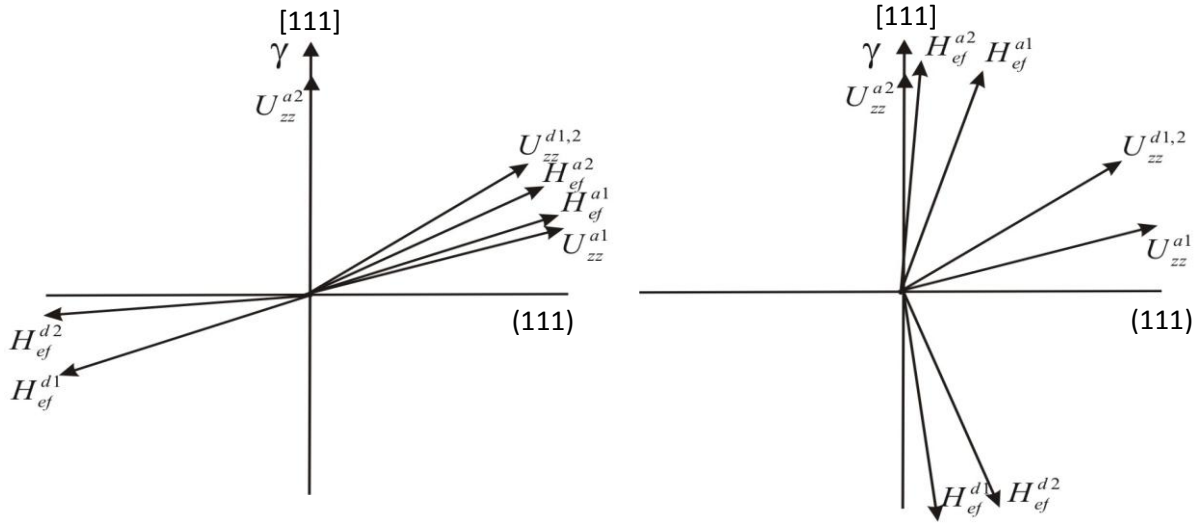


Fig. 2. Diagrams of the effective magnetic fields spatial orientation at the ^{57}Fe nuclei and the electric fields gradients of an individual sublattices

The presence of doublet components corresponding to Fe^{3+} ions in the paramagnetic state in the spectrums of all samples was revealed. The fixation of this part is beyond the error limits. Quadrupole splitting of these doublet components does not depend on the external field and is about 2.05± 0.05 mm/s which can be explained by the presence of a surface layer of iron ions whose valence is reduced from 3+ to 2+. This is result of a large concentration of point defects in the anion sublattice in the surface area and the increasing covalence of the chemical bond in the transition layer film-air. The presence of ferrous iron in the surface layer of the film is confirmed by the values of isomer shift for the paramagnetic component.

4. CONCLUSION

The magnetic microstructure of iron-yttrium garnet epitaxial films is studied. The presence of two magnetically non-equivalent positions of Fe^{3+} which occupy tetrahedral sites are established in the surface layer of the YIG film of orientation (111). The information about the spatial orientation of the magnetic moments of the individual sublattices, experimental values of the parameters of hyperfine interaction and tensor components of the electric field gradient at the nucleus are obtained. The presence of ferrous iron in the surface layer YIG due to the non-stoichiometry of anionic lattice of transition layer film – air has been revealed.

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Address: V.O.Kotsyubynsky, V.V. Moklyak, B.K. Ostafiychuk: Vasyl Stefanyk Precarpathian National University, 57, Shevchenko Str., Ivano- Frankivsk, 76025, Ukraine.

E-mail: v_kotsuybynsky@mail.ru.

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Коцюбинський В.О., Мокляк В.В., Остафійчук Б.К. Мессбауерівські дослідження магнітної мікроструктури епітаксійних плівкок залізо-ітрієвого гранату. *Журнал Прикарпатського університету імені Василя Стефаника*, **1** (1) (2014), 81–86.

Методом конверсійної електронної мессбауерівської спектроскопії проведено дослідження тонкої магнітної мікроструктури приповерхневого шару епітаксійної плівки залізо-ітрієвого гранату орієнтації (111). Встановлено наявність двох магнітонееквівалентних позицій іонів Fe^{3+} в тетраедричних вузлах структури граната та парамагнітну фазу, яка формується іонами Fe^{2+}. Застосовуючи метод діагоналізації матриці ядерного гамільтоніану змішаної магнітної дипольної та електричної квадрупольної взаємодій, отримано інформацію про просторову орієнтацію магнітних моментів окремих катіонних підграток досліджуваної структури та значення компонент тензора градієнта електричного поля на ядрах ^{57}Fe у різних кристалічнонееквівалентних позиціях.

Ключові слова: залізо-ітрієвий гранат, конверсійна електронна мессбауерівська спектроскопія, ефективне магнітне поле, тензор градієнта електричного поля.