

MÖSSBAUER INVESTIGATION OF STATIC-DISORDER CRYSTALLINE MEDIA I. ^{57}Fe NGR SPECTRA ON TETRAGONAL AND TRIGONAL GALLO-GERMANATE

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Abstract: By changing the chemical composition across the crystalline medium, the static disorder crystals can be obtained. The class of static-disorder crystalline media proved a interesting scientific properties as well as practical importance. So, a special attention was paid in the last ten years, due to their application in the field of tunable laser or of attractive piezoelectric properties. On the other hand the Mössbauer spectroscopy is one of the powerful non-destructive spectroscopic technique, which can detect any local changes of electrical, magnetic and geometric properties, by its narrow resonance line-width of Mössbauer isotope. The aim of this article is to present recent experimental results of the ^{57}Fe Mössbauer investigation on some static-disordered crystalline media of practical interest, like of melilite and trigonal gallo-germanate crystalline structure type.

1. INTRODUCTION

1.1 WHAT ARE THE STATIC-DISORDER CRYSTALLINE MEDIA?

An ideal crystal is an endless, three-dimensional, periodic built up by atoms, ions or molecules. Due to the periodicity, every constituent is regularly repeated in the three-dimensional space, *i.e.* every asymmetry of that has exactly the same one orientation and conformation as its neighbor to the left, the right, the top, the bottom, the front, and to the back. But, an *ideal crystal* does not exist, in the nature we find only *real crystal*. In any *real crystal*, there are several lattice defects and/or impurities and frequently some constituents (atoms, ions, parts of molecules, or in some extreme cases whole molecules) are found in crystalline sites and/or crystallographic independent orientation, others than in the *ideal crystal*. Generally, the disorder is associates with a random distribution or the spatial orientations of the constituents on crystalline sites.

In principle one can distinguish two types of structural disorder, the positional disorder and the substitutional one.

The positional disorder is a **type** of the "normal case" of disorder: One atom occupies more than a single site. This can happen in a single unit cell (dynamical disorder, a real motion in the solid state) or distributed among different unit cells (static disorder, sort of a look alike motion). In the positional disorder, one can distinguish two extreme cases. The case of the discrete positional disorder, in which the molecule can possess two (or seldom more) well defined energetically similar positions. This can be recognized relatively easy as split atomic sites and in consequence of that two or more contributions in the spectra of different techniques will be evidenced. The case of the continuous positional disorder, in which the any rotational angle of the molecules or part of them is more or less energetically similar, it is hard to describe and to recognize this situation by the most techniques. Usually the most of them reduces the problem to analyze and refine the spectra for two or three sites per atom.

The second type of disorder is the substitutional one, which describes a situation where the same site in two unit cells is occupied by different types of atoms. This type of disorder is especially known from minerals and salt like crystals. So for example, in some zeolites Al- and Si-atoms share the same sites. A special case of substitutional disorder that is relatively common is partial occupation of atom sites.

The substitution of one constitutive ion A of the crystal by another B can induce statistical structural elements (variety of A - polyhedrons). The substitutional disorder produces a grate number of the centers, connecting by electron-excitation-energy migration. Such collective of centers is named as quasi-centers.

In the structural disordered crystalline media of second type, appear a variety non-stoichiometric phases and the variety of A-polyhedrons consists in the dependence of their geometry (distances and number of neighbors) by the number of B ions. **A such structural disordered crystalline media is called structural-dynamic disordered crystalline media**, because the degree of the structural disorder depends of the number of the substituted ions. In the second case the statistical occupation of a given lattice site, no reconstruction of the A-polyhedrons, depending with the concentration of B ions, appears. That means the ab-initio A-polyhedrons are connected with the statistical

occupation of different ions (heterovalency cations, too). **A such crystalline media is called structural-static disordered crystalline media** In the presented oral lecture the static-disordered crystalline media are considered to be in the above-mentioned definition.

1.2 WHY ARE INVESTIGATED THE STATIC-DISORDER CRYSTALLINE MEDIA?

Recently, special attention was paid to the class of disordered crystalline media for their interesting properties of the scientific as well as practical importance as:

1. Host matrices for tunable laser activator;
2. Piezoelectric crystals with attractive electromechanical coupling factor;
3. Materials having special magnetic properties depending of the doping ions;

The past decade has seen extraordinary advances in the development of crystalline solid-state lasers due to the concurrent developments of high-power semi-conductor diode lasers and new high quality laser gain materials. The potential applications of the solid-state lasers induced new a fundamental research for the wide range of physical phenomena, which are observed in such materials. A particular problem is **broadening of optical transitions in laser gain media**. The spectral width of absorption and, more importantly, fluorescence bands is a key parameter in determining potential applications of laser gain media. There is a current desire to find materials with very broad fluorescence bands that might be employed in tunable and ultra-short-pulse lasers. Inhomogeneous broadening occurs due to distributions in the physical characteristics of impurity sites. The most applicability of the mentioned fundamental research is **the transition-metal ions for tunable solid-state lasers**, as: Ti^{3+} : YAP¹, Cr^{3+} -doped in mixed fluorides, Cr^{3+} -doped in garnets². More recently, demonstration of laser oscillation and subsequent commercialization of the Cr^{3+} : YAG laser system operating in the near infrared region (1.3 - 1.5 μm) has further increased interest in extending the tuning range of solid state lasers. On the other hand rare-earth (Ln^{3+}) doped disordered materials are often considered suitable systems for practical devices such as all solid-state lasers. This is because structural disorder leads to differing crystal-field potentials at spatially differing Ln^{3+} ion sites. As a consequence, there arises an inhomogeneous broadening of the spectral-line-profiles, which can lead to enhanced efficiencies for laser diode pumping and limited tunability over the emission bandwidth of the Ln^{3+} transitions. It is also possible that energy matches for energy transfer and up-conversion processes can be improved, thereby increasing the efficiencies of such processes. On the other hand, the inhomogeneous broadening may also adversely affect the laser efficiency as the broader the emission band. The lower efficiency is determined by the value of the stimulated emission cross-section. Thus, the threshold for laser action could be expected to be higher. So, there is particular interest in extending and in planning to study processes such as inhomogeneous broadening and to growth the disordered crystal media as solid-state lasers.

The short-term frequency stability of most commercial and defense RF electronics is determined by the quartz crystal resonator used in system oscillators. Typical quartz crystal oscillators operate at below 100 MHz and their output signal is multiplied to obtain the frequency of interest. The oscillator output signal spectrum is composed of two distinct regions : a flicker-of-frequency (30 dB/decade) near-carrier noise region and a constant level white phase noise (floor) level improves with resonator signal handling (drive level) capability. When the oscillator signal is frequency multiplied to microwave the phase noise increases with the multiplication ratio. From a low-phase noise stand point, an improved resonator (compared to quartz) needs to exhibit a higher relative Q and operate at a higher frequency with a higher relative drive level. Quartz crystals have been chemically thinned to oscillate in the 100 MHz –1 GHz range but this process is expensive and yields fragile crystals.

New ferrigehlenites with extremely high iron content suggested the possibility to predict and to moderate the magnetic properties of melilites structures, containing germanium and silica. Moreover they are interesting as precursors of the trigonal gallo-germanate in the synthesis process. **Trigonale gallo-germanates** are considered the possible host matrices for tunable laser activator (Cr^{3+} , Nd^{3+}), due to their acentric lattice positions and the corresponding large polyhedrons. The representative member of this family is calcium gallium germanate CGGO, $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$. **Langasite (LGS)** is a new **non-ferroelectric, piezoelectric material** [1 –5]. It has temperature-stable crystal orientations, similar to quartz, but with five times higher acoustic Q and three times higher piezoelectric coupling coefficients. This offers the possibility of fabrication of **voltage-controlled oscillators, resonators, and wide bandwidth filters with low-phase noise, high temperature stability, and larger tuning range**. In addition, langasite, LGS and its derived crystals such as langatite, $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ (LGTO) and langanite,

¹ YAP=YAlO₃

² YAG=Y₃Al₅O₁₂

$\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$, (LGNO) having a gallate structure similar to CGGO. So, that kind of materials has attractive laser, electromechanical, and acoustic properties [1 – 8].

1.3 THE CAPABILITY OF NGR TECHNIQUE TO INVESTIGATE THE STATIC-DISORDERED CRYSTALLINE MEDIA.

The NGR (or well-known Mössbauer) spectroscopy is a non-destructive **nuclear** method of investigation, so that is a useful method as a quantitative, qualitative and analytical tool to evidence and to measure:

- various phases simultaneously present,
- the controlled doping of materials with the Mössbauer constitutive or substituted ions (host of Mössbauer nuclei),
- different processes induced by the changes of external parameters , pressure and/or temperature, etc.

From a Mössbauer spectrum one can be extracted and analyzed spectral parameters:

1. parameters of spectrum intensity as the full area A_{exp} , and partial areas A_i of the absorption resonance line or of the different detected sublattices; those are depending of:
 - number of the emitted and absorbed recoil-free γ -photons relative to the total number of γ events in source f_S and respectively in absorber f_A ,
 - the number of the Mössbauer isotopes feeling a specific neighborhood in source n_S and in absorber n_A ,
 - the full half line-width Γ , which is a sum of the source and absorber line-widths $\Gamma = \Gamma_S + \Gamma_A$; no taking into account the thick effects area of a line resonance of spectrum is given by $A_{\infty} \propto \Gamma_S f_S f_A n_S n_A$; without an absolute area measurement the relative areas are used, $a_i = A_i / A_{exp}$, $A_{exp} = \sum_i A_i$, or

$$a_{exp}(T) = A_{exp}(T) / A_{exp}(T_o); \text{ where } T_o \text{ are the critical temperature;}$$

- one must remark that a other used intensity parameter is the effect of effect ξ_o , defined ratio between the registered intensity at resonance position $N(v_o)$ and the background of spectrum $N(\infty)$ transmitted, $\xi_o = N(v_o) / N(\infty) \propto f_S f_A n_S n_A$; the connection between the area and effect is clearly $A_o \propto \Gamma \xi_o$;
- 2. hyperfine parameters as:
 - the central shift δ_C , which is a sum of two terms; the first one, the isomer shift δ is corresponding to the interaction of the nuclear distribution with the electron density at nucleus $\propto \psi(0)^2$ in source and absorber, the second term, the second Doppler shift δ_{SDS} is given by the temperature evolution of the absorber relative to the source or vice versus ;
 - quadrupole splitting Δ_Q , which is a measure of the interaction between the quadrupole moment Q_I with electric field gradient EFG,
 - the nuclear Zeeman splitting Δ_H , corresponding to the interaction of nuclear magnetic dipole moment with the magnetic field at nucleus.

Generally, the parameter of the line-width permits to detect any change of the crystal field at Mössbauer isotope, by its variation $\Delta\Gamma$ with the ambient - conditions.

The broadening of the full half line-width, $\Delta\Gamma > \Gamma_{nat} / 2$, is given by: change in the mean life time of the excited nuclear state, diffusion and Brownian motion of atoms and molecules, relaxation effects, spin-flip processes, super-paramagnetism, fluctuations near the critical temperature (electric, magnetic or structural phase transitions) and finally by changes of hyperfine electric and/or magnetic fields.

The small variations of hyperfine fields correspond to the slightly static crystal fields on the Mössbauer isotopes. Generally, the dispersion of the static crystalline fields can be arise from distinct neighborhoods, from the local polyhedral distortion, or different relative population occupation of the surrounding sites of Mössbauer nuclides, due to the substitution disorder (in the first, second third,.. surrounding shells). That implies the dispersion of the crystalline fields on the Mössbauer nuclide can be very easy recognize, due to the narrow line-width of its line resonance, $\Delta_{CF} \geq \Gamma_{nat} (^{57}\text{Fe}) \cong 4.67 \cdot 10^{-9} \text{ eV}$. So due to this advantage, the Mössbauer spectroscopy will be proved as a very efficient technique to detect qualitatively and quantitatively the physics and chemistry aspects of disordered crystalline media.

The substitution disorder can be recognized by a broadening of the full line-width resonance, corresponding to the variety of polyhedral neighborhoods. In the case of static-structural disorder, the variety of the polyhedral neighborhoods is given by the random occupation of the polyhedral corners by the different ionic sorts, accepted by

the crystalline structure. In this case, the broadening of the half line-width increases to the decreasing of the temperature.

Taking into account the scientific interest and the exciting possible application of such materials, the advantages and the possibilities of NGR technique, the author of this article propose to present obtained results of ^{57}Fe -NGR investigation on some static-disordered crystalline media like melilites and trigonal gallo-germanates.

2. EXPERIMENTAL ASPECTS

2.1 GENERALLY

The polycrystalline sample of ferrigehlenite (with extremely high Fe^{3+} content), like $A_2\text{Fe}_2\text{ZO}_7$ (A=Ba, Sr; Z=Ge, Si) and iron germanate, like $A_3\text{Fe}_2\text{Z}_4\text{O}_{14}$ and respectively $\text{LnA}_2\text{Fe}_3\text{Ge}_3\text{O}_{14}$ (A=Ba, Sr; Ln=La, Nd;) were prepared by solid phase synthesis and analyzed by x-ray diffraction (XRD) [11-13]. The obtained unit cell parameters are listed in table 1.

Table 1.
The unit cell parameters of XRD investigated samples

Type of structure	Compound	a [Å]	b^* [Å]	c [Å]	α°	β°	γ°
Melilite (Tetragonal gallo-germanate)	$\text{Ba}_2\text{Fe}_2\text{GeO}_7$	8.330	8.330	5.590	90	90	90
	$\text{Sr}_2\text{Fe}_2\text{GeO}_7$	8.130	8.130	5.350			
	$\text{Sr}_2\text{Fe}_2\text{SiO}_7$	8.050	8.050	5.230			
	$\text{Ca}_2\text{Al}_2\text{GeO}_7$	7.890	7.890	5.204			
	$\text{Ca}_2\text{Ga}_2\text{SiO}_7$	7.896	7.896	5.207			
Trigonal gallo-germanate	$\text{Ba}_3\text{Fe}_2\text{Ge}_4\text{O}_{14}$	8.854	14.813	5.211	~30	90	90
	$\text{Sr}_3\text{Fe}_2\text{Ge}_4\text{O}_{14}$	8.270	14.324	5.040			
	$\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$	8.076	13.988	4.974			
Errors		± 0.003	± 0.003	± 0.003	± 7	-	-

*In the case of trigonal gall-germanate $b=2ac\cos\alpha$

The listed samples of table 1 have been investigated by ^{57}Fe -NGR spectroscopy, using a conventional constant acceleration transmission spectrometer and $^{57}\text{Co}(\text{Cr})$ or $^{57}\text{Co}(\text{Rh})$ sources at room temperatures. The spectra were carried out on a large temperature range 300K÷4.2K. Low temperature measurements were carried out with a continuous flow Oxford Instruments cryostat. The accuracy of the temperature control was better than $\pm 0.5\text{K}$.

The spectra were fitted for sum of doublet and/or sextet models with Lorentzian line shape of the resonances, using the χ^2 criteria (by a least-squares fitting program in the assumption of Lorentzian line shape). Each of models have considered as a sum of two and six resonance line, having the same line-widths and ratio of intensities 1:1 and respectively 3:2:1.

The main spectral parameters of the doublet and sextet models, which one can extract from NGR spectra, are center shift δ_C , quadrupole splitting Δ_Q and magnetic one Δ_H , half line-width Γ , effect ε and relative area a of model. The above-mentioned parameters are defined for each of these models as one shows in table 2.

The errors of extracted spectral parameters have determined in the following approximation:

- the long distance between the nearest resonances: $|v_2 - v_1| \gg \Gamma$

$$\sigma_{v_o} = \frac{2\sqrt{2}}{\sqrt{\pi N(\infty)} \frac{\Gamma_o}{\Delta n}}; \sigma_{\varepsilon_o} = \frac{\Gamma_o \sqrt{2}}{\varepsilon_o \sqrt{\pi N(\infty)} \frac{\Gamma_o}{\Delta n}}; \sigma_{\Gamma_o} = \frac{4\Gamma_o}{\varepsilon_o \sqrt{\pi N(\infty)} \frac{\Gamma_o}{\Delta n}}; \sigma_{N(\infty)} = \sqrt{N(\infty)} \quad (1a)$$

- the appropriate resonances $|v_2 - v_1| \leq \Gamma$

$$\sigma_{v_k} \approx \sqrt{|\Delta v|^2} = \frac{\Gamma_l}{\Gamma_k} \cdot \frac{1}{\left[1 + 4\left(\frac{v_k - v_1}{\Gamma_1}\right)^2\right]^2} \sqrt{\frac{\varepsilon_l}{\varepsilon_k} \cdot |v_k - v_1|} \quad (1b)$$

The other errors of spectral parameters of the doublet and sextet models have been determinate using the usual formula of the error propagation.

$$\sigma_{\Delta} = \begin{cases} \sqrt{\sigma_{v_1}^2 + \sigma_{v_2}^2} \\ or \\ \sqrt{\sigma_{v_1}^2 + \sigma_{v_2}^2 + \sigma_{v_5}^2 + \sigma_{v_6}^2} \\ 2 \end{cases}; \sigma_{\delta} = 2\sigma_{\Delta}; \sigma_A = \begin{cases} A_o \sqrt{\left(\frac{\sigma_{\varepsilon_o}}{\varepsilon_o}\right)^2 + \left(\frac{\sigma_{\Gamma_o}}{\Gamma_o}\right)^2}; A_o \sqrt{\sum_{k=1}^2 \left(\frac{\sigma_{A_k}}{A_k}\right)^2} \\ A \sqrt{\sum_{k=1}^6 \left(\frac{\sigma_{A_k}}{A_k}\right)^2} \end{cases} \quad (1c)$$

Table 2.

The computer fitting functions and the extracted spectral parameters for each of models

Model	Computer fitting function	Formulas of spectral parameter
Singlet	$N(\infty) \left[1 - \frac{\varepsilon_o \cdot \frac{\Gamma_o}{2}}{(v - v_o)^2 + \left(\frac{\Gamma_o}{2}\right)^2} \right]$	$\delta_C = v_o; \varepsilon_o = \frac{N(\infty) - N(v_o)}{N(\infty)}; A_o \propto \varepsilon_o \Gamma_o$ $\Gamma_o = v_{+\frac{1}{2}} - v_{-\frac{1}{2}}; I(v_{\pm\frac{1}{2}}) = I(v_o)/2$
Doublet	$N(\infty) \left[1 - \sum_{k=1}^2 \frac{\varepsilon_k \cdot \frac{\Gamma_k}{2}}{(v - v_k)^2 + \left(\frac{\Gamma_k}{2}\right)^2} \right]$	$\delta_C = \frac{v_2 + v_1}{2}; \Delta_Q = v_2 - v_1$ $\varepsilon = \frac{\varepsilon_1 + \varepsilon_2}{2}; \Gamma = \frac{\Gamma_1 + \Gamma_2}{2}; A_Q = \sum_{k=1}^2 A_k$
Sextet	$N(\infty) \left[1 - \sum_{k=1}^6 \frac{\varepsilon_k \cdot \frac{\Gamma_k}{2}}{(v - v_k)^2 + \left(\frac{\Gamma_k}{2}\right)^2} \right]$	$\delta_C = \frac{v_2 + v_1 + v_5 + v_6}{4}; \Delta_H = v_6 - v_1$ $\frac{\Delta_Q(3\cos^2\theta - 1)}{4} = \frac{v_2 - v_1 + v_6 - v_5}{2}$ $\varepsilon = \frac{\varepsilon_1 + \varepsilon_6}{2}; \Gamma = \frac{\Gamma_1 + \Gamma_2 + \Gamma_5 + \Gamma_6}{2}; A_H = \sum_{k=1}^6 A_k$

2.2 EXPERIMENTAL ASPECTS

In the figures 1 and 2 are shown the spectra of the high iron content of ferrighlenites and some trigonal gallo-germanates with Ln and Fe. The table 3 gives a list of ^{57}Fe -NGR investigated samples.

The tables 4a, 4b and 5a, 5b give the determined values of spectral parameters for RT and low temperatures spectra.

Table 3.

List of of ^{57}Fe -NGR investigated samples.

No.	Structure	Sample	Formula
1	Melilite	Ba-Ge	$\text{Ba}_2\text{Fe}_2\text{GeO}_7$
2		Sr-Ge	$\text{Sr}_2\text{Fe}_2\text{GeO}_7$

3		Sr-Si	Sr ₂ Fe ₂ SiO ₇
4	Trigonal gallo-germante	Ba	Ba ₃ Fe ₂ Ge ₄ O ₁₄
5		Sr	Sr ₃ Fe ₂ Ge ₄ O ₁₄
6		Sr(La)	Sr ₂ LaFe ₃ Ge ₄ O ₁₄
7		Sr(Nd)	Sr ₂ NdFe ₃ Ge ₄ O ₁₄

RT Mössbauer spectra of ferrigehlenites have fitted by a superposition of two doublet species, showing very closed intensities. In each of the investigated sample the sublattice, with a smaller center shift and larger quadrupole splitting, evidences a larger half line-width of resonances.

Table 4a.

Spectral parameters of Mössbauer investigated ferrigehlenites in paramagnetic region

Sample	T [K]	δ^* [mm/s]		Δ_Q [mm/s]		Γ [mm/s]		<i>a</i>	
		T1	T2	T1	T2	T1	T2	T2	T1
Ba-Ge	300	.20	.17	1.22	1.56	.30	.31	.55	.45
	77	.28	.27	1.19	1.60	.32	.33	.56	.44
	20	.34	.31	1.24	1.57	.39	.37	.50	.50
	17	.32	.29	1.26	1.62	.30	.30	.53	.47
	13	.30	.29	1.20	1.67	.37	.37	.54	.46
Sr-Ge	300	.18	.14	.94	1.72	.33	.30	.55	.45
	77	.27	.23	.93	1.77	.37	.34	.49	.51
	20	.24	.21	.92	1.81	.45	.41	.52	.48
	19	.25	.21	.96	1.81	.47	.44	.57	.43
	18	.25	.23	.89	1.75	.60	.64	.54	.46
	17	.21	.23	.96	1.74	.38	.35	.47	.53
Sr-Si	300	.21	.15	.96	1.70	.39	.30	.59	.41
	30	.29	.23	.99	1.87	.56	.43	.57	.43
	24	.32	.35	.96	1.69	.56	.53	.47	.53
Errors		±0.01		±0.02		±0.02		±0.05	

* The center shift is referred to metallic iron;

Table 4b.

LHeT parameters of Mössbauer investigated ferrigehlenites

Sample	Magnetic species	δ^* [mm/s]	Δ_Q^{**} [mm/s]	Γ [mm/s]	H[T]	<i>a</i>	V [Å ³]	T _N [K]
Ba-Ge	P ₁ (H)	0.44	+0.11	2.89	32.6	0.75	388	12
	P ₂ (H)	0.72	-0.21	1.53	34.4	0.25		
Sr-Ge	P ₁ (H)	0.23	+0.23	2.61	34.6	0.79	354	16
	P ₂ (H)	0.51	-0.28	1.58	37.0	0.21		
Sr-Si	P ₁ (H)	0.18	+0.32	2.92	33.6	0.69	339	21
	P ₂ (H)	0.37	-0.12	2.04	36.6	0.28		
Errors		±0.02	±0.02	±0.02	±5.0	±0.05	±1.0	±0.5

* The center shift is referred to metallic iron; ** $\Delta_Q' = \Delta_Q(3\cos^2\theta - 1)/4$

LHeT spectra have been fitted by two sextets, characterizing by very large half line-widths, which are centered to 34T and respectively to 36T and different values of the other parameters. The sublattice of the smaller hyperfine magnetic field is more intense for each of samples.

Figure 1. - RT and LHeT Mössbauer spectra of investigated high iron content melilites. The magnetic phase transition of Sr-Ge is shown.

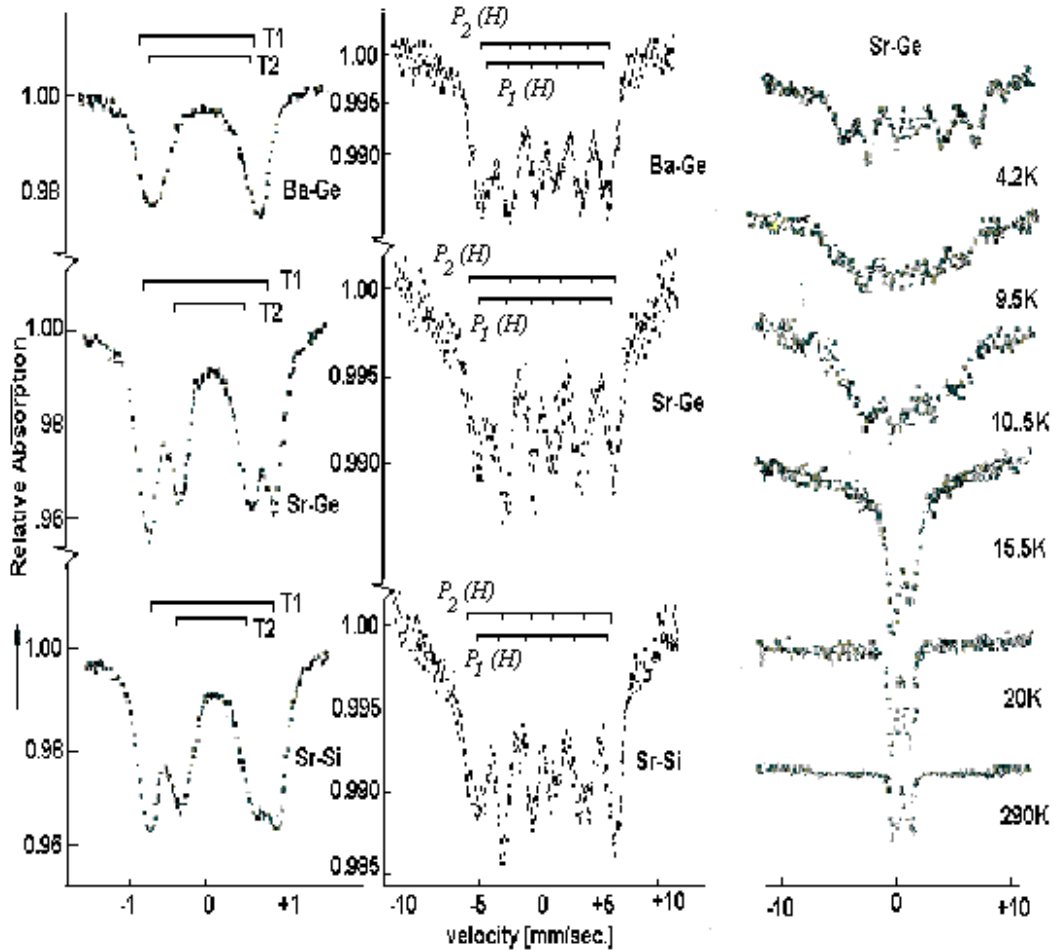


Table 5a.

Parameters of investigated trigonal gallo-germanate in paramagnetic region

Sample	T[K]	δ_c' [mm/s]			Δ_o [mm/s]			I [mm/s]			a		
		Oh	T1	T1'	Oh	T1	T1'	Oh	T1	T1'	Oh	T1	T1'
Ba	300	.39	.26	.27	.96	2.15	1.56	.35	.37	.40	.37	.31	.32
	77.0	.38	.28	.28	.98	2.04	1.57	.45	.39	.41	.45	.26	.29
	4.2	.24	.16	.20	.96	2.07	1.51	.50	.50	.45	.38	.35	.27
Sr(La)	300.0	.36	.29	.28	.91	2.04	1.54	.40	.38	.42	.28	.43	.29
	77.0	.43	.26	.27	.87	1.96	1.53	.55	.45	.50	.38	.25	.37
	45.0	.30	.28	.19	.99	2.02	1.58	.56	.45	.46	.35	.28	.37
Sr(Nd)	300.0	.38	.31	.27	.91	1.87	1.43	.44	.37	.35	.33	.38	.29
	77.0	.25	.16	.15	.92	2.00	1.56	.45	.42	.40	.32	.33	.35
	30.0	.37	.30	.29	.85	2.04	1.52	.46	.42	.40	.34	.35	.31
Errors	± 5	$\pm .006$			$\pm .01$			$\pm .01$			$\pm .04$		

* The center shift is referred to metallic iron.

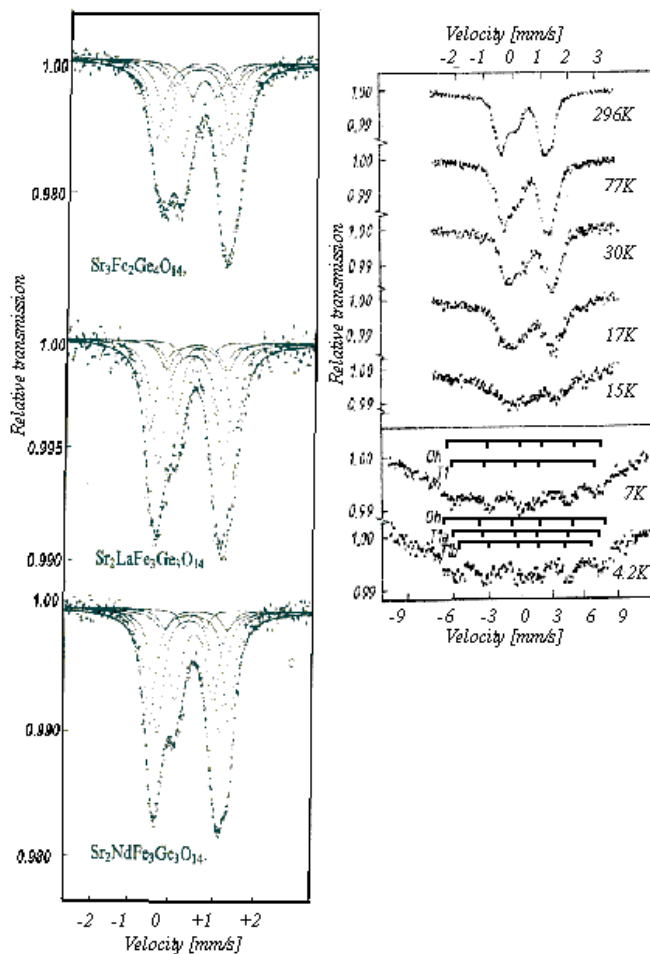
Mössbauer spectra of investigated trigonal gallo-germanate exhibit a superposition of two or more doublet models in the paramagnetic region (from RT down to about 16K), showing the same shape of second order Doppler shift of $-5. \times 10^{-4}$ mm/s/K.

Table 5b.
Low temperature parameters of some trigonal gallo-germanate spectra

Sample	T [K]	Species	H [T]	δ^* [mm/s]	Δ^{**} [mm/s]	Γ [mm/s]	a
Sr(La)	4.2	Oh	46.8	.35	.45	.68	.22
		T	41.2	.24	.28	.71	.44
		T'	35.5	.20	.32	.72	.34
Sr(Nd)	7.0	Oh	44.1	.47	-.09	1.00	.34
		T	40.8	.30	-.03	1.00	.66
Sr(Nd)	4.2	Oh	46.3	.35	.14	.99	.36
		T	42.0	.31	.07	.70	.45
		T'	38.5	.29	.01	.70	.18
Errors	$\pm .5$		$\pm .5$	$\pm .01$	$\pm .02$	$\pm .02$	$\pm .05$

* The center shift is referred to metallic iron; ** $\Delta' = \Delta_0(3\cos^2\theta - 1)/4$

Figure 2. - RT Mössbauer spectra of investigated trigonal gallo-germanates and the changes of the shape line of



Sr(Nd) during the magnetic phase transition.

SUMMARY

The ^{57}Fe Mössbauer investigation of the new ferrigehehenites and iron-rare earth gallates shows:

1. two or three distinct quadrupole doublets of ^{57}Fe Mössbauer isotope in the paramagnetic region;
2. the small values of the central shift parameter and the absence of a notable temperature dependence of the quadrupole splitting values, which imply high spin ferric state of iron ions, locating in polyhedrons with 4- or 6-coordination number;
3. adding the trioxide of iron and/or lanthanide to synthesized, one can obtain the same structures with Fe^{3+} and Ln^{3+} as constituents;
4. the large line widths of resonances, pointing out the presence of several crystal fields very slightly different non-depending of Fe^{3+} and Ln^{3+} concentration;
5. the nuclear gamma resonance technique is capable to evidence the static-disorder in crystalline media containing the Mössbauer isotopes.

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