MÖSSBAUER INVESTIGATION OF STATIC-DISORDER CRYSTALLINE MEDIA II.CRYSTAL-CHEMISTRY ASPECTS OF TETRAGONAL AND TRIGONAL GERMANATES (GEHLENITE AND GALLATE STRUCTURES)

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Abstract: The second part of the static-disordered crystalline media by ^{57}Fe Mössbauer investigation technique, contains a detailed discussion of some crystal chemistry aspects of the new syhtetic ferrigehlenits and ferri and/or trivalent lanthanides gallats. On this line, the effect of the type and size of the lanthanide ions in these structures on the unit cell parameters, on the chemical bond energy and on the presence of the superexchanges interactions are pointed out and discussed.

1. CRYSTAL CHEMISTRY ASPECTS OF THE ^{57}FE MÖSSBAUER INVESTIGATED GEHLENITES AND GALLATES

1.1 INTRODUCTION

Generally from ternary system CaO_2 - Ga_2O_3 - GeO_2, one can synthesized crystals

- **$Ca_2Ga_2GeO_7$**, with melilite structure, with the tetragonal symmetry $P\bar{4}2_1m$; the izostructural natural crystal is the gehlenite one **$Ca_2Al_2SiO_7$** [3], which crystallizes with the unit cell parameters $a = (7,890\pm0,002)$ Å, $c = (5.204\pm0,002)$ Å);
- **$Ca_3Ga_2Ge_3O_{12}$** with grenat structure (unit cell parameter $a = 12,250$ Å),
- **$Ca_3Ga_2Ge_4O_{14}$** (so well-known **Ca**-gallate) having the trigonal symmetry *P 321*, which crystallizes in cu $a = (8,069\pm0,002)$ Å, $c = (4,962\pm0,001)$ Å; no izostructural natural compound one found.

1.2 MELILITE STRUCTURE

Ferrigehlenites 1, 2, 3 are the members of the family characterizing by a melilite type crystalline structure and containing high extremely iron quantities. The representative member of this structure type is gehlenite **$Ca_2Al_2SiO_7$.** The space group of this crystalline structure is $P\bar{4}2_1m$, with Z=2 units of formulas per unit cell.

The melilite structure of tetragonal Ca-gallo-germanate (**$Ca_2Ga_2GeO_7$**) is formed by sequential layers of large oxygen polyhedrons **A** (4c), named Thompson cubes, which are occupied by Ca^{2+} , and two type of tetrahedrons linked into five-member rings. The larger tetrahedron **T1** (2a) is less distorted and has $\bar{4}$ symmetry. That is occupied by Ga^{3+} ions. The smaller tetrahedron **T2** (4e) is more distorted and has mm2 symmetry. Ga^{3+} and Ge^{4+} randomly occupy **T2** in 1:1 ratio.

A **$Ca_2Ga_2GeO_7$** izostructural natural compound is **$Ca_2Al_2SiO_7$**. Al^{3+} and Si^{4+} randomly occupy **T2**-tetrahedrons, in the same proportion as in tetragonal Ca-gallo-germanate.

a) **Paramagnetic region**

The all spectra of the ferrigehlenites show two distinct quadrupolar vicinities of ^{57}Fe Mössbauer isotope in the paramagnetic region.

The small values of the central shift parameter and the absence of a notable temperature of the quadrupole splitting values imply high spin ferric state of iron ions, which are located in tetrahedrons, as trivalent gallium or aluminum in **$Ca_2Ga_2GeO_7$** or its izostructural natural compound **$Ca_2Al_2SiO_7$**.

The isomer shift values, which are obtaining by the extraction of second order Doppler shift, shows the covalency of the Fe^{3+}- O^{2-} chemical bond. Comparing δ values of our investigated melilites with the **Ca-Si** sample one obtains the following relations $\delta(Ba-Ge) > \delta(Sr-Ge)$ and $\delta(Sr-Si) > \delta(Ca-Si)$ for iron in both tetrahedrons. This means that the covalency is stronger as the size of Thompson cube ion decreases. The fact can be explained by the decreasing of the unit cell volume and of the iron-oxygen distances.

The highest value of Δ_Q is attributed to the ferric ions in the more distorted tetrahedron **T2** and the smallest one is attributed to Fe^{3+} in the biggest and less distorted tetrahedron **T1**.

Table 1.

Polyhedral distortion of tetrahedrons $\sigma_{T1, T2}$ and statistical occupation of **T2** by the ferric and gallium ions (in the approximation of the full occupation of Fe^{3+}:**T1**)

Sample R_{A2+} [Å] R_{Z4+} [Å]	T [K]	σ				Statistical occupation ratio in T2 by Fe^{3+}:Ge^{4+}	
		Temperature dependence		Average values		Temperature dependence	Average values
		T1	T2	T1	T2		
Ba-Ge **1.42** **0.53**	300	3.805	5.290	3.820	5.534	Fe^{3+}:Ge^{4+}=.41:.59	Fe^{3+}:Ge^{4+}=.43:.57
	77	3.697	5.508			Fe^{3+}:Ge^{4+}=.39:.61	
	20	3.894	5.366			Fe^{3+}:Ge^{4+}=.50:.50	
	17	3.975	5.637			Fe^{3+}:Ge^{4+}=.44:.56	
	13	3.729	5.867			Fe^{3+}:Ge^{4+}=.43:.57	
Sr-Ge **1.26** **0.53**	300	2.749	6.64	2.795	6.537	Fe^{3+}:Ge^{4+}=.41:.59	Fe^{3+}:Ge^{4+}=.47:.53
	77	2.792	6.358			Fe^{3+}:Ge^{4+}=.52:.48	
	20	2.749	7.007			Fe^{3+}:Ge^{4+}=.56:.44	
	19	2.792	6.703			Fe^{3+}:Ge^{4+}=.33:.67	
	18	2.93	6.211			Fe^{3+}:Ge^{4+}=.43:.57	
	17	2.760	6.304			Fe^{3+}:Ge^{4+}=.56:.44	
Sr-Si **1.26** **0.53**	300	2.816	6.045	2.852	6.360	Fe^{3+}:Si^{4+}=.38:62	Fe^{3+}:Ge^{4+}=.44:.56
	30	2.924	7.072			Fe^{3+}:Si^{4+}=.38:62	
	24	2.816	5.989			Fe^{3+}:Si^{4+}=.56:.44	
*****Ca-Si** **1.12** **0.53**	300	2.400	6.800	2.400	6.900	Fe^{3+}:Si^{4+}=..50:.50	Fe^{3+}:Si^{4+}=..50:.50
Errors	±.5	±0.560	±0.560		±0.323	±0.03	±0.03

*From [9]

Generally, the quadrupole splitting of high spin ferric ion is given by the polyhedral distortion of the next anions, in our case of the **T1** and **T2** oxygen tetrahedrons. In [9], an analytical dependence has found between the quadrupole splitting and the geometrical (angular) distortion parameter σ_T of tetrahedrons in melilite structures [10].

$$\sigma_T^2 = \frac{1}{5}\sum_{k=1}^{6}\left(\theta_k - 109.47^o\right)^2; \theta_k = \angle(O^{2-}Fe^{3+}O^{2-}); \quad (2)$$
$$\Delta_Q^{Melilite} = 0.042 + 0.371\sigma_T - 0.016\sigma_T^2; 0 < \sigma_T < 8$$

The tetrahedral distortion parameter have been deduced (see table 1) from relation (2) and taking into account the experimental values, which have extracted from the spectra (see table 4a [15]).

One remarks:

- the range of the σ_{T1} and σ_{T2} values deduced for our investigated samples, which in agreement with the values observed in [9] for **Ca-Si** ferrigallium gehlenite;
- a dependence of these parameters of the radius of Thompson cube cations and no one of the tetrahedron cations, in the limits of errors. The data evidence opposite distortion evolution of tetrahedrons with respect to radius of locating cation in Thopmson cube site; the polynomial fit of experimental σ_T data gives and predicts the empirical dependence and evolution of tetrahedrons with the A ionic sort in Thompson cubes (see formula 3);

$$\sigma_{fitT1}(R_{A^{2+}}) = 17.42(3.58) - 25.38(5.09)R_{A^{2+}} + 10.68(1.80)R_{A^{2+}}^2$$
$$\sigma_{fitT2}(R_{A^{2+}}) = 12.79(1.05) - 4.59(0.75)R_{A^{2+}} \quad (3)$$

the very slowly dependencies of the geometrical parameter (of course between different limits) relative to the temperature correspond to the temperature dependencies of quadrupole splitting for high spin of ferric ion;
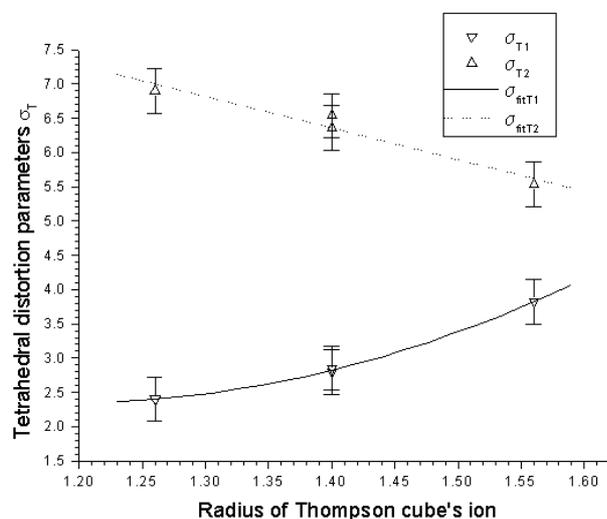
Figure 1. - The experimental σ_T (R_A) dependencies in Mössbauer investigated melilite structures and their polynomial fit.

The relative occupancies of the tetrahedral positions are denoting the preference of ferric ions for the biggest tetrahedrons. In the limits of the errors, those are fully occupied, the rest of Fe^{3+} enter in the distorted tetrahedrons, in competition with the Ge^{4+}. Supposing the full occupation of **T1** by ferric ions, the new normalization of the relative area from table 4a [15] shows the **T2**-occupancies of the two ionic sorts. One can observe that the ferric ions do not occupay the half of the **T2**-sites and in this approximation one can give the crystallo-chemical formula for the ferrigehlenite $<A^{2+}>_2[Fe^{3+}]^{T1}Fe_{x/2}^{3+}$, $Z_{1-x/2}]_2^{T2} O_7$, where A=Ba, Sr; Z=Ge, Si and $x \in [0.\div1.]$. Moreover, x - values are slightly different for our samples due to the size of A^{2+} ions, see figure 2. Also one remarks the low values of the Sr-Si sample.

The extracted data from melilite spectra suggest that occupancies of ferrigehlenite Ba-Ge, Sr-Ge and Ca-Si are linearly dependence, regressing vs. the size of Thompson cube's cation and probably no notable variation of the Z^{4+} size. However the value obtain for Sr-Si are not in agreement with this suggested conclusion.   XRD   on   this   sample   established   the   presence   of   cation-vacancies $Sr_2[Fe_{.99}\square_{.01}]^{T1}[Fe_{.43}Si_{.555}\square_{.015}]_2^{T2} O_7$. In the errors limits the data extracted from Mössbauer spectra of Sr-Si are in agreement with the XRD data, so we concluded that the linearly regressing dependence vs. R_A^{2+} , which has observed for the other samples, is valuable.
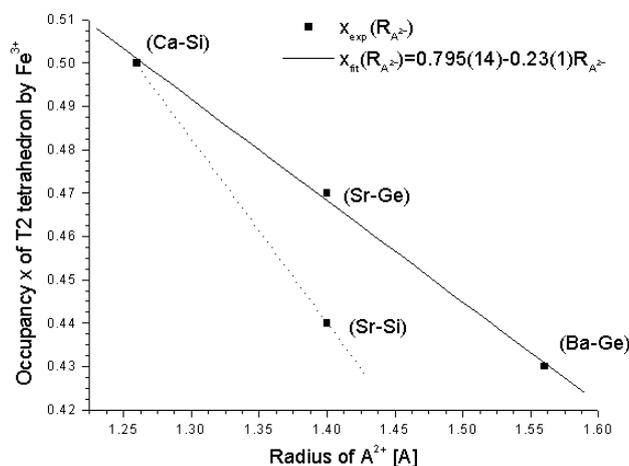

Figure 2. - The Fe^{3+}:**T2** occupancy vs. R_{A2+}

The line widths of the doublets' resonances, which have determined from spectra are different for the Mössbauer signals of the two tetrahedrons. Generally, one remarks that the resonances are two times more as attempted one, $\Gamma_{exp} \gtrsim 2(\Gamma = 2\Gamma_{nat})$. Moreover, the resonances corresponding to $^{57}Fe:T1$ are broader as those corresponding to $^{57}Fe:T2$ and they have the tendency to increase as the temperature decrease, far away to para-ferromagnetic phase transition critical point. These means than the Mössbauer technique detects the many and very slightly different crystalline fields at ^{57}Fe sites. As temperature decreasing they are tendency to increase their intensities and in the spectra to produce an increasing of the line widths. The different crystalline fields appeared due to the randomly occupation of the **T2** tetrahedrons by Fe^{3+} and Ge^{4+}/Si^{4+} ions. Because the surrounding of the **T1**-tetrahedron is formed by 4 **T2**-tetrahedrons, which are occupied by competition between Fe^{3+} and Ge^{4+}/Si^{4+} and **T2** surrounding is formed by 2 **T1**- and only one **T2**-tetrahedrons the line width of resonances the **T1** doublet is larger as of the **T2** one.

b) **Magnetic ordering region**

At LHeT all new ferrigehlenites with extremely high content of iron show magnetic ordering. In each case the very rather and complex spectra have fitted with two sextets $P_1(H)$ and $P_2(H)$, having very large line widths resonances and distinct values of the hyperfine magnetic fields H_{hf}, quadrupole $\Delta' = \Delta_Q(3cos^2\theta - 1)/4$ (for asymmetry parameter $\eta = 0$.) and center shift. According to these data, two magnetic sublattices are seemed to be present in melilite samples.

The difference $\delta_C(300K) - \delta_C(4.2K) \approx \delta_{SODS}$ so, the isomer shift of melilite has approximately no temperature dependence. That is clearly evidenced for (Ba-Ge) sample.

The small intensities of hyperfine magnetic fields are quiet unusually for the high spin Fe^{3+} state (5·11.T). The most probable sources are:

• the increseasing of the covalency Fe - O by the decreasing of unit cell volumes when the R_{A2+} decrease; that explains the higher values of H_{hf} in the case of (Sr-Z) compounds;
• the important role, which is played by the angle Fe-O-Fe in the superexchange mechanism; indeed this angle in the melilite structure is very different of 180° [11];
• the presence of non-magnetic ions in the structure, as Ge^{4+} or Si^{4+}.

The low values of Δ' suggest that magnetic fields are not along the main axis V_{ZZ} of electric field gradient and the opposite signs of quadrupole shifts imply the relative opposite alignment of the two magnetic fields. That means an antiferromagnetic phase of ferrigehlnites.

The values of critical temperatures T_N is a measure of superexchange integrals' energy

The very broader line widths observed in magnetic ordering region can explain only by the presence of a lot of different crystalline magnetic fields at Mössbauer isotope sites. The author suggests that fact is generate by the randomly distributions of Fe^{3+} in smaller tetrahedrons. The different values of line widths for the two magnetic sextets suggest that $P_1(H)$ and $P_2(H)$ are corresponding to more and respectively less different hyperfine magnetic fields seemed by Fe^{3+} in the bigger and smaller tetrahedrons.

Finally must remark the area ratio between the two sextets, which in the error limits is about 3:1.

1.3. TRIGONAL GALLO-GERMANATE STRUCTURES

The trigonal gallo-germanates, which investigated by Mössbauer spectroscopy are containing ferric and some rear earth trivalent ions, $Ln_yA_{3-y}Fe_{2+y}Ge_{4-y}O_{14}$ (Ln=La, Nd; A=Sr, Ba). They have the symmetry characterizing by the spatial groups *P321* (Sr-samples) and *P3* (Ba-samples) [12]. The typical member of this family is calcium-gallate, **Ca₃Ga₂Ge₄O₁₄.**

The trigonal gallo-germanate structure consists of successive tetrahedron layers perpendicular to the *c*-axis ($z/c \approx 0$.), alternating with interlayers ($z/c \approx 0.5$) of large oxygen polyhedrons **A** (so named Thompson cubes, 3e-position, symmetry 2) and octahedrons **Oh** (1a-position, symmetry 32). In this structure similarly to tetragonal gallo-germanate structure, there are two types of the tetrahedrons **T1** and **T2**. **T1-**tetrahedrons are locating at the two-fold axis, position 3f, surrounding the octahedron, according to triple axis law. **T2** -tetrahedrons are on the triple axis at 2d-position. All geometrical argues suggest that T2 These compounds belong to static-disordered crystalline media is due to the random distribution of more than a single sort of ion over similar lattice sites, without any reconstruction of the polyhedrons. So, in the typical member of the family the static disorder is due to the random occupation of Ga^{3+} and Ge^{4+} ions 2:1, in **T1**-tetrahedrons.

a) **Paramagnetic region**

All investigated sample exibit a superposition of least three quadrupole doublets, from room temperature down to about 16K, showing practically the same shape. That means, ^{57}Fe seems the three distinct

neighborhoods. The second order Doppler shift δ_{SODS} has estimated to be about of -5.10^{-4} mm/s/K. The values of parameters δ and Δ_Q and their temperature dependencies show certainly the high spin of ferric ion in the octahedral and tetrahedral sites of the trigonal gallo-germanate structure. The strong distorted tetrahedrons are characteristic for the tetragonal and trigonal gallo-germanates. Δ_Q values of two doublets are very closed to the corresponding values for the similar doublets of investigated melilites, so these doublets have assigned to Fe^{3+}:**T1** and the third doublet, characterizing by the smaller quadrupole splitting to Fe^{3+}:**Oh.** The Mössbauer investigation of trigonal gallo-germanate evidences two kinds of **T1**-tetrahedrons. One of them **T1**, has the similar δ and Δ_Q values as those of **T1**, the other **T1'** has these parameters close to **T2** in the melilite structure. So, two kind of **T1**-tetrahedrons are considered, corresponding to the different origin. Some of them are similar to **T1** tetrahedrons of tetragonal gallo-germanate and other of them are proceeding from **T2**. That is because, one of **T2** tetrahedron of melilite structure**,** breaks the five-member ring, turns and takes position on the two-fold rotation axis, due to the formation of the **Oh**-octahedrons. The corresponding designation is **T1** and respectively **T1'** (see figure 3 [17])**.**
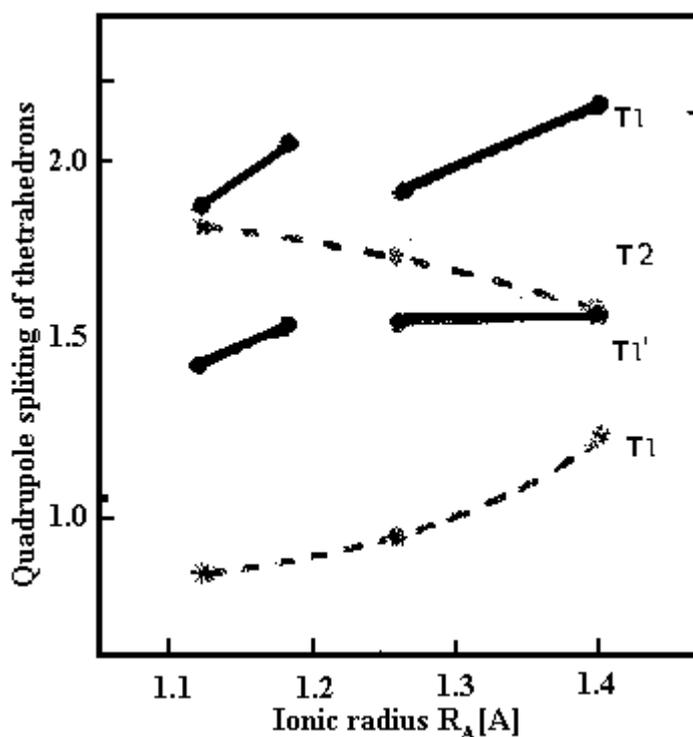

Figure 3. - Quadrupole splits of the two tehrahedrons in the tetragonal (star) and trigonal (triangle) iron germanates

That result, which has extracted from Mössbauer spectra, is other experimental fact, which confirms the crystalline and geometrical argues and XRD data, about of the existence and provenience of two sorts of **T1**-tetrahedrons in this crystalline media.

Following the same line of the crystalline and geometrical argues, we suggest that **Oh**-octahedron is formed from one of tetragonal gallo-germanate **T1-**tetrahedron. Both the octahedrons and the tetrahedrons evidence a distorted oxygen polyhedrons around the tetra- or three valence cations.

Relative areas of the quadrupole doublets, which have determined from the trigonal gallo-germanate spectra are not respect the ratio **Oh:T1:T1'**=1:2:1. That suggest a randomly occupation not only of **T1'** and but **Oh** and **T1** too. The main consequence of above-mentioned suggestion is the increasing of the lattice site number, which could be randomly occupied by different sorts of ions (in our case by Fe^{3+} and Ge^{4+}/Si^{4+}), without reconstruction of the polyhedrons, depending with the concentration of different ions. so, the static disorder in such crystalline media is given by occupation of the **Oh -**octahedrons and **T1** and **T1'** tetrahedrons by different sorts of ions. Taking into account the relation

$$x + y = 2 + z$$
$$x : y = (a_{T1} + a_{T2}) : a_{Oh} \qquad (4a)$$
$$x = x_{T1} + x_{T1'}; \; y = x_{Oh}; \; z = x_A$$

where x, y, z designates the molar content of the trivalent ions (Fe^{3+}/Ga^{3+}) in T1, T1', Oh and of Ln^{3+} in Thompson cube sites, one can determine their values

Table 2.
The Molar fractions of the trivalent ions in trigonal gallo-germanate structures

Trigonal germante sample	X	Ln	M	z	y	x=2-y+z	x_{T1}
Ba	Ba	-	Fe	0.	0.72	1.28	0.62
Sr	Sr	-	Fe	0.	0.72	1.28	0.70
Sr(La)	Sr	La	Fe	1.	0.84	2.16	1.33
Sr(Nd)	Sr	Nd	Fe	1.	0.99	2.01	1.15
Sr-gallate [14]	Sr	-	Ga	0.	0.40	0.53	-
Ca-gallate [14]	Ca	-	Ga	0.	1.00	1.00	-
Ca(Nd)-gallate [14]	Ca	Nd	Ga	1.	y	x=2-y+z	-

and the crystallo-chemical formula of the investigated samples.

$$\left\langle X_{1-z/3}^{2+}, Ln_{z/3}^{3+} \right\rangle_3^A \left\{ M_y^{3+}, Ge_{1-y}^{4+} \right\}^{Oh} \left[M_{2/3+z/3-y/3}^{3+}, Ge_{1/3-z/3+y/3}^{4+} \right]_3^{T1} \left[Ge^{4+} \right]_2^{T2} O_{14} \quad (4b)$$

The obtained molar fractions of our investigated samples confirm the supposition of the random **Oh**-site occupations by three- and four-valence ion [14]. One remarks the slightly preference of Fe^{3+} for the **Oh**-sites. The random distribution of three- and four-valence ions between **T1** and **T1'** tetrahedrons could be determined from the ratio of relative areas of corresponding doublets for each of the Mössbauer investigated sample. For a simple qualitative discussion of data we shall take into account one tetrahedral quadrupole doublet with the weighted values of the parameters $\delta(T)$, $\Delta_Q(T)$, $\Gamma(T)$ and occupancy x, in stead of the two **T1**- and **T2**-tetrahedral doublets.

Analyzing the data of table 5a [15], one observes a dependence of spectral parameters (δ, Δ_Q, Γ, x and y) with respect of size of cation in Thompson cube site for all ^{57}Fe occupied positions. That one can explain by the changes of the unit cell volume V, inter-ionic distances and mainly on the weighted electronegativity χ_w and the ionic character of $A^{2+}(Ln^{3+})$-O^{2-} chemical bond energy $F(A)$, which are induced by the changes weighted radius R_w of cation in Thompson cube site. The following relations define the above-mentioned quantities:

$$R_w = \frac{1}{3}\left[zR_{Ln} + (1-z)R_A \right];$$

$$\chi_w = \frac{1}{3}\left[z\chi_{Ln} + (1-z)\chi_A \right] \quad (5)$$

$$F(A) \propto (\chi_w - \chi_O)^2$$

Generally higher value of F(A) means a higher electronegativity difference and a stronger ionic character of the chemical bond. The values of the R_w, χ_w and $F(A)$ are given in the table 3.

Table 3.
Estimated values of R_w, χ_w and $F(A)$ for some trigonal gallo-germantes

Compound	R_w [Å]	χ_w	F(A)
$Ca_3Ga_2Ge_4O_{14}$	1.120	1.000	5.954
$Sr_2NdFe_3Ge_3O_{14}$	1.207	1.013	5.890
$Sr_2PrFe_3Ge_3O_{14}$	1.213	1.010	5.905
$Sr_2LaFe_3Ge_3O_{14}$	1.227	1.000	5.954
$Sr_3Ga_2Ge_4O_{14}$	1.250	0.950	6.200
$Ba_2LaFe_3Ge_3O_{14}$	1.340	0.960	6.150
$Ba_3Fe_2Ge_4O_{14}$	1.420.	0.890	6.502

In figures 4a and 4b are plotted the dependencies of $F(A)$, V vs. R_w and spectral parameters vs. $F(A)$.
First of all one observes the linear fit dependence of the unit cell volume and of the

cation-oxygen chemical bond energy in Thompson cube, with respect the weighted radius of
its ion (see layers 1 and 2 of figure 4a). Moreover, one can remark two different dependencies (see layer 2 of
figure 4a) of *F(A)* for samples with and without the rear earth ions in these sites.

That is in agreement with the results reported in [8], where a stronger crystal field was observed in the
alkaline earth germantes at Cr^{3+} in comparison with the crystal field found for the same ion in the rear earth
gallates. The polynomial fits of the center shift and quadrupole split parameters exhibit the following parabolic
dependencies of them to cation-oxygen chemical bond energy (see layers 3 and 4 of figure 4a).
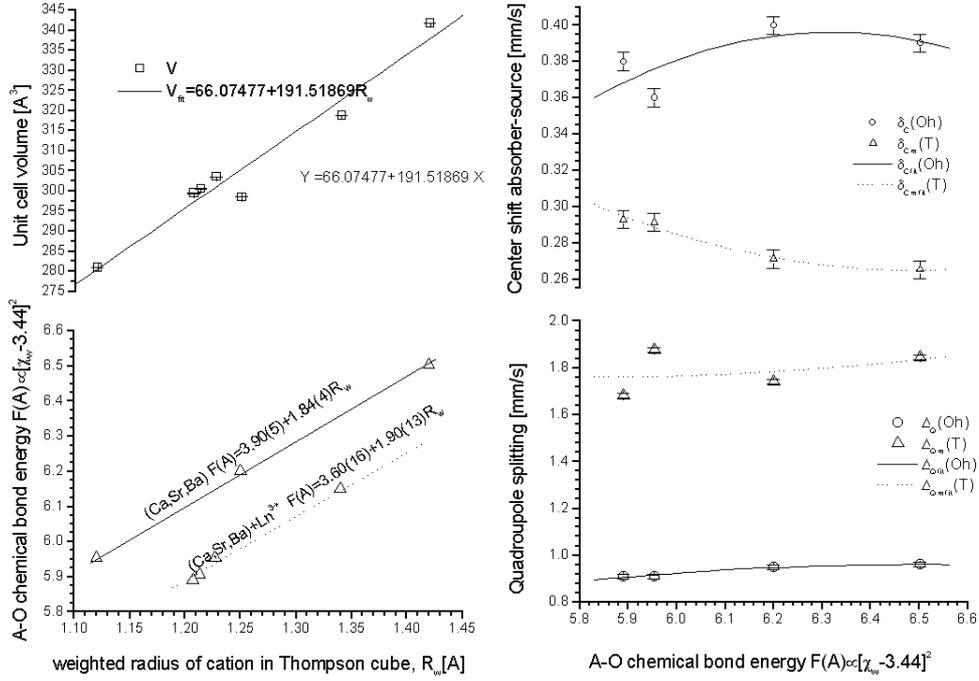
Figure 4a. - The plots of dependencies of *F(A)*, *V* vs. R_w and parameters δ_C and Δ_Q vs. *F(A)*.

$$\delta_C(Oh) = -5.56198 + 1.88513F(A) - 0.14911F^2(A)$$

$$\Delta_{Qfit}(Oh) = -5.47443 + 1.98268F(A) - 0.15272F^2(A)$$

$$\delta_{Cm}(T) = 3.75383 - 1.07515F(A) + 0.08283F^2(A)$$
(6a)

$$\Delta_{Qmfit}(T) = 7.40934 - 1.93734F(A) + 0.16613F^2(A)$$

The empirical functions show opposite tendencies of the two parameters, corresponding opposite
distortion of the octahedron and tetrahedrons, which are statistically occupied by
tetra- and three-valence ions.

The similar and notable dependence of the cation-oxygen chemical bond energy in Thompson cube
exhibits by **Oh** and **T** occupancies and the corresponding resonance line widths (see layers and 2 of figure 4b).
That means a direct effect of the ionic character of the cation-oxygen in Thompson cube on the occupancies
and the crystal field broadening at Oh and T sites, in these crystalline media. The found empirical relation are:

$$\Gamma(Oh) = 19.6431 - 6.09236\ F(A) + 0.48065\ F^2(A)$$

$$y = 58.90508 - 18.40165F(A) + 1.45393F^2(A)$$

$$\Gamma_m(T) = 18.00804 - 5.63362F(A) + 0.45387\ F^2(A)$$
(6b)

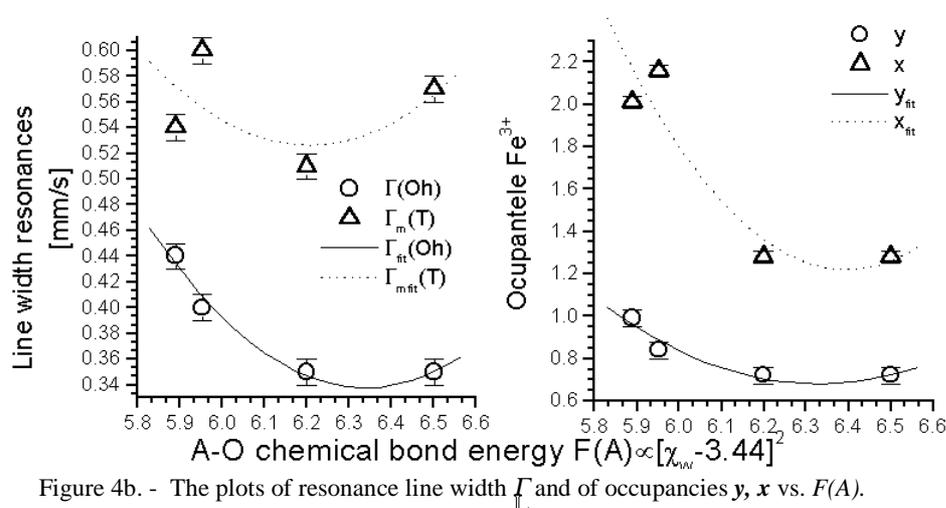$$x = 152.93264 - 47.44585F(A) + 3.70948\ F^2(A)$$

Figure 4b. - The plots of resonance line width Γ_L and of occupancies *y, x* vs. *F(A)*.

b) **Magnetic ordering region**

The Mössbauer investigation of trigonal germanates (some ferrigallates with alkali and rear earth) show the magnetic ordering at very low temperature, under 16K, and only for samples containing the trivalent rear earth in Thompson cubes (see figure 5). That can be explain by the increasing of the high spin ferric ions in the compounds, which is induced by the presence of trivalent lantanide in Thompson cube. The increasing of magnetic ions in trigonal germanates permits the superexchange interaction by oxygen as intermediate ion, Fe^{3+}- O^{2-} - Fe^{3+} and magnetic chain can be formed. The size of Ln^{3+} determines the size of the unit cell and the degree of the oxygen polyhedrons surrounding the ferric ions and finally the length of Fe^{3+}- O^{2-} bond and the angle $\angle(Fe^{3+}-O^{2-}- Fe^{3+})$ and the strength of superexchange interactions. That explain the higher values of hyperfine magnetic fields in Sr-Nd relative to the magnetic fields of Sr-La and the poor resolution of last one spectrum at LHeT. In trigonal structures, the observed hyperfine magnetic fields have not the attempted values (≈55T), because the length of Fe^{3+}- O^{2-} bond are long and the $(Fe^{3+}-O^{2-}- Fe^{3+})$ angles are much different from 180^0, depending of the distortion degree of oxygen polyhedrons surrounding Fe^{3+} . The magnetic trigonal germanate are antiferromagnetically like the ferrigehleties.

The obtained 4.2K quadrupole shifts Δ' are much smaller than those found in the paramagnetic state for both octahedral and tetrahedral Fe^{3+} species (Tab.5a). It denotes that the corresponding magnetic hyperfine fields are not directed along the z main axis of the EFG tensor (V_{ij}), i.e. the θ angle in the relation $\Delta' = \Delta_Q (3cos^2 \theta-1)/4$ is different from zero. Moreover, the very small ε values (practically $\Delta' ≈0$) found for Sr(Nd) sample, especially for the tetrahedral sites (Tab.1), show that \the respective magnetic fields point a θ=54.73⁰ direction.

The spectra in the magnetic ordering region evidence two or three sextets (magnetic sublattices), corresponding to the three magnetic chains. The relative area and the center shift suggest to assign them to chains manly formed by the ferric ions in octahedral and respectively tetrahedral sites. All magnetic sublattices are characterizing by very large line widths of resonances.
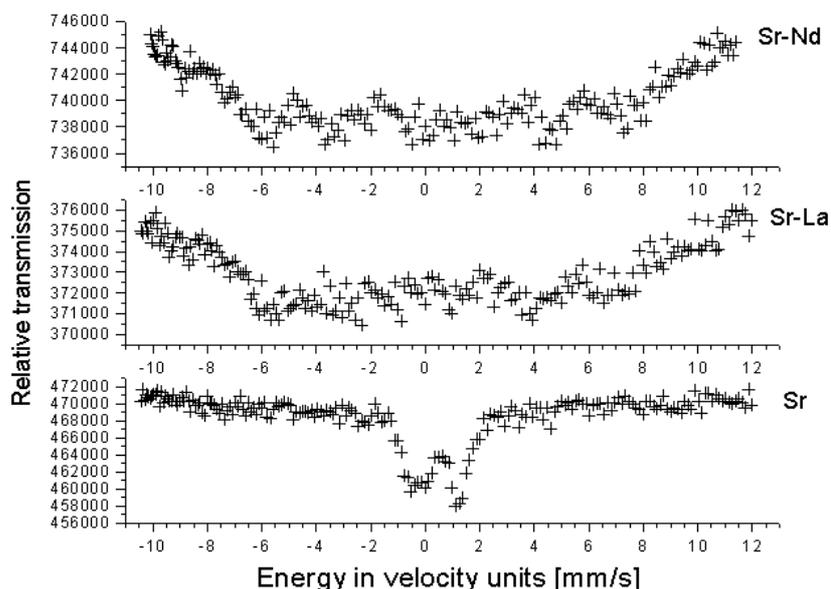
Figure 5. - The LHeT spectra of iron Sr and Sr-Ln germanates.

The very large line widths found for all 4.2K hyperfine sextets and particularly for the octahedral ones suggest that in fact there is a dispersion of magnetic fields seemed by the Mössbauer isotope at each occupied positions and particularly at Oh sites. As in the case of the ferrigehlenites, the Mössbauer spectra show the presence of the static disorder in the crystalline media of trigonal germanates.

2. CONCLUSIONS

The ^{57}Fe Mössbauer of the new ferrigehlenites and iron-rear earth gallates shows:

1. different proportion of the oxides in the ternary system CaO_2 - Ga_2O_3 - GeO_2, can synthesis tetragonale crystals $Ca_2Ga_2GeO_7$, (melilite structure), cubic crystals $Ca_3Ga_2Ge_3O_{12}$ (with grenat structure), and trigonal crystals $Ca_3Ga_2Ge_4O_{14}$;
2. adding the trioxide of iron and/or lanthanide to synthesized crystals and processing carefully, one can obtain the same structures with Fe^{3+} and Ln^{3+} as constituents ad without polyhedron changes, depeding of their concentration.;
3. the effect of the ferric ion presence is notable at low temperature by the establishment of the superexchange interactions and in consequence of the antiferromagnetic phases; that means these crystalline media can be host for magnetic interactions and a new class of magnetic materials can be obtain;
4. the effect of the type of lantanide locating the Thompson cube site on the unit cell parameters, occupancies of small oxygen polyhedrons by the trivalent ions and on the electric and magnetic crystal field dispersion at octahedral and tetrahedral sites; a new class of crystal, using as host of the laser ions and the perspective of tunable laser are possible;
5. the effect of the iron and lanthanide trivalent ions is the static-disorder at different sites of the tetragonal and trigonal germanates.

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