MGR INVESTIGATIONS IN $Ga_{0,8}Fe_{0,02}S_6$ CRYSTALS

GEIS SULTANOV, MAZAHIR ALDJANOV, ELMIRA KERIMOVA

Institute of Physics, Azerbaijan Academy of Science,
Baku. Az - 1143, H. Javid st. 33

The magnetic and Mossbauer investigation of GaS:Fe crystals have been carried out. In the temperature region 80÷300 K magnetic susceptibility is found to be weakly dependent on temperature. The value of quadrupole splitting determined from the room-temperature Mossbauer spectrum is equal to ΔE_Q=2.95 ±0.03 mm/s. In GaS:Fe iron is assumed to substitute for gallium and to exist in low-spin divalent state This assumption is confirmed by a good agreement between the experimental and theoretical values of ΔE_Q obtained from the calculation of the $[GaFe^{2+}S_6]^{8-}$ impurity complex electronic structure by the Hukkel's method.

Introduction

According to crystallographic data [1] GaS has hexagonal structure with space group of $P6_3/mmC$ and lattice parameters: a=3.587Å and c=15.492Å . Because of Ga and S atoms location the crystalline structure of GaS can be presented as alternation of dense packed layers...S-Ga-Ga-S... moreover each atom of Ga us tetraedrically connected with three atoms of S and one atom of Ga, thus R(Ga-S)=2.33Å , R(Ga-Ga)=2.447Å (fig.l) and are clouse to the value of sum of and covalent radiuses *(R* cov Ga=1.23Å and *R* cov S=1.04E) that indicates to covalent character of chemical bond.
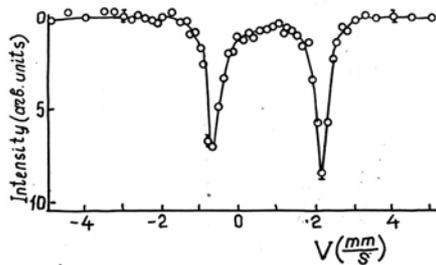
Fig.1. Mössbauer spectra of GaS:Fe at room temperature.

The fact that each Ga atom is connected with three S atoms and one Ga atom indicates to the fact that chemical bond of Ga atoms must be anisotropy. In fact, such anisotropy of chemical bond is sharply displayed in many physical properties of this crystal [2-4].

That's why the investigation of chemical bond anysotropy in GaS is in interested. Method of nuclear gammaresonance (NGR) is one of method widely used in investigation of chemical bond and its anysotropy. Such parameters of NGR as a result of quadrupole splitting and effect possibility, strongly depends on anysotropy of chemical bond. The pollycrystallic $Ga_{0.98}Fe_{0.02}S$ sample have been used during investigations.

Experimental results

Mössbauer spectrum of GaS:Fe has a from of well allowed quadrupole dublet with quadrupole splitting ΔE_Q=2.95±0.03 mm/s (fig.l). The temperature dependence in range of 80-300K of magnetic susceptibility of GaS:Fe crystal is represented on. Experimental values of $\chi(T)$ weakly depend on temperature. The interpretation of quadrupole splitting value in Mossbauer spectra of ion compositions are usually carried out within the theory of lygand field (see for example [5]). But in many cases such method is found to be too roudh. That's why numerical quantocemical methods of Mossbauer parameters calculation have been developed for the last year.

We carried out quantochemical calculation of electron structure of impure complexes by widened Hynkel method [6]. Table data have been taken from [7]. Calculation of Mossbauer parameters have been carried out on program used in [8].

Calculation and discussion of results

Quadrupole splitting for ^{57}Fe nucleuses with spin of state J=1/2 and excited one J=3/2 is determined by expression [5]

$$\Delta E = \tfrac{1}{2} e^2 gQ\left(1+\eta^{2/3}\right)^{1/2} \tag{1}$$

where $eg = V_{zz} + \left(\partial^2 V / \partial Z^2\right)_0$ -z-component of electric field gradient tenzor on nucleus, $\eta = \left(V_{xx} - V_{yy}\right)/V_{zz}$ -asymmetry parameter, *eQ*-nuclear quadrupole moment, moreover for nucleuses Q=0.21 barn [4.5].

According to [5], and η values can be determined from following formula:

$$\left(V_{zz}\right)_{val} = e\left\{\tfrac{4}{7}(1-R)_{3d} <\tfrac{1}{r^3}>_{3d}\left[N_{x^2-y^2} + N_{z^2} + N_{xy} - \tfrac{1}{2}\left(N_{xz} - N_{yz}\right)\right] + \tfrac{4}{5}(1-R)_{4p} <\tfrac{1}{r^3}>_{4p}\left[-N_{px} + \left(N_{px} - N_{py}\right)\right]\right\} \tag{3}$$

$$\left(\eta V_{zz}\right)_{val} = e\left[\tfrac{6}{7}(1-R)_{3d} <\tfrac{1}{r^3}>_{3d}\left(N_{yz} - N_{xz}\right) + \tfrac{6}{7}(1-R)_{4p} <\tfrac{1}{r^3}>_{4p}\left(N_{py} - N_{px}\right)\right] \tag{4}$$

Where "val" and "lat" indexes concern to the introduction of Fe valence electrons and lygand one. As it follow, for example, from [9, 10], valence introductions of five *3d*-and three *p*-orbitals are equal to

$$\left(V_{zz}\right)_{val} = \left(1-\gamma_\infty\right)\sum \frac{e_i\left(3z_i^2 - r_i^2\right)}{r_i^5} \tag{5}$$

$$\left(\eta V_{zz}\right)_{val} = \left(1-\gamma_\infty\right)\sum \frac{3x_i\left(x_i^2 - y_i^2\right)}{r_i^5}$$

where $(1-R)_d$ and $(1-R)_{4p}$-Shternheymer factors for $3d$ and $4p$ electrons, $<1/r^3>3d$ and $<1/r^3>4p$ –average values of reverse cubes of radiuses of $3d$- and $4p$-membrans, N_α- populations of α orbitals.

According to [10, 5], $(1-R)_{3d}$=0,68, and $<1/r^3>3d$ values depend on valent state of Fe ion; forming (calculating) 4.78 a.e. for Fe^{3+} and 4.44 a.e. for Fe^{2+}.

Introductions of $4p$ electrons to quadrupole splitting are usually not large huge and approximate correlation can be used in their estimation [11]:

$$(1-R)_{4p} <1/r^3>4p=1/3 \ (1-R)_{3d} <1/r^3>3d$$

Lattice introductions are calculated on following formulas [4]:

$$\left(V_{zz}\right)_{val} = \left(1-\gamma_\infty\right)\sum \frac{e_i\left(3z_i^2 - r_i^2\right)}{r_i^5}$$

$$\left(\eta V_{zz}\right)_{val} = \left(1-\gamma_\infty\right)\sum \frac{3x_i\left(x_i^2 - y_i^2\right)}{r_i^5}$$

Where x_i, y_i, z_i-decart coordinates of lygands in axles system, connected with metal, -metal r_i-lygand distance, e_i-lygand charges. Besides, it's usually assumed that $(1-\gamma_\infty)$=12 [5,6].

To determine unknown values in (1)-(5) we applied to widen Hynkel method.

As its known, standard numerical method of quantum chemistry allows to calculate electron structure final system only. That's why to obtain a sensible results we need right part of crystal, the calculation will be made for.

From GaS crystalline structure, examined above, one can see that minimum cluster, reproducing (showing) crystallochemical peculiarities of whole lattice have to be chosen like eight atoms Ga_2S_6 grouping which is represented on fig.2.
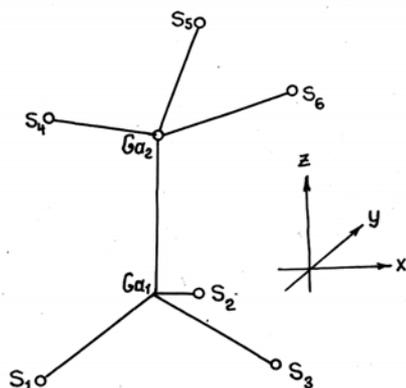
Fig.2 . Structure of Ga_2S_6 cluster.

Decart coordinates of atoms calculated from known crystallographic data are given in table 1.

Table 1.
Decart coordinates of atoms of $[Ga_2S_6]^8$ cluster.

Atom	x, Å	y, Å	z, Å
Ga_1	0	0	0
Ga_2	0	0	2.448
S_1	0	-2.071	-1.075
S_2	-1.793	1.035	-1.075
S_3	1.793	1.035	-1.075
S_4	0	-2.071	3.523
S_5	-1.793	1.035	3.523
S_6	1.793	1.035	3.523

Right cluster charge, obtained in neutral crystal can be determined by following method. As one atom lygand S atom has oxidation degree equal to -2. Then, due GaS to crystal electro neutrality, atom should be given oxidation degree equal to +2. Thus, we deal with $[Ga_2S_6]^{1-}$ cluster. It is important to stress that oxidation degree equal to +2 doesn't contradict to well known fact that Ga is three valent, quite the opposite, it's proved by GaS structure peculiarities. In fact, oxidation degree equal to +2 means that only 2 valent of atom are saturated as a result of interaction with S atom. In this case the saturation of third valent is possible because of Ga-Ga covalent bond formation only, which is vally taken place.

In connection with this fact we made a calculation of $[GaFe^{2+}Se]^{8-}$ and $[GaFe^{3+}S_6]^{7-}$ clusters containing Fe atoms in 2 more stable oxidations degrees by means of widen Hynkel method. In connection with the magnetic measurements results, Fe atoms are considered to be low-spin. Clusters structure replies are shown on fig.2 with substitution Ga_2 to Fe.

The composition and energies of some bordering MO of $[GaFe^2S_6]^{2-}$ cluster are given. $[GaFe^{3+}Se_6]^{7-}$ cluster is different for the reason it has not one electron. It follow that upper of both clusters maintain considerable introduction Fe of atom AO. That's why their Mossbauer parameters must be too different, which principally gives a possibility to determine valent state of Fe atoms in GaS:Fe. Besides one can see that comparatively large splitting and high degree of electron decolization is typical for B3MO and low vacant MO. It proved that the conclusion about low spin state of *Fe* atoms is correct. Finally, unlike the $[Ga_2S_6]$ clusters, $[GaFeSe_6]$ clusters do not maintain metal. Metal bond: the lowest orbital, in which AO of S, P_z and dZ^2 types are represented completely is $\varphi_{30}\Delta E_Q$ orbital.

Calculated popularization of Fe atoms AO and charges of all cluster's atoms are given in table 2.

Table 2
Calculated popularization of *Fe* atoms AO and charges of all cluster's atoms.

Clusters	Charges of atoms			Populations								
	$e(S)$	e(Ga)	e(Fe)	$4S$	$4P_y$	$4P_z$	$4P_x$	d_{xy}	d_{yz}	d^2_{xy}	d_{xz}	$d_{x^2-y^2}$
$[GaFe^{2+}S_6]^{8+}$	-1.52 -1.38	1.28	-0.64	0.40	0.14	0.04	0.14	1.42	1.65	1.75	1.65	1.42
$[GaFe^{3+}Se_6]^{7-}$	-1.52 -1.24	1.28	0.02	0.40	0.08	0.04	0.08	1.26	1.55	1.75	1.55	

Upper number corresponds to GaS_3 group; under number-to Fe_2S_3 group.

As it is expected, S atoms carry negative charges, moreover charges in GaS groups are larger that in FeS_3, groups. It indicates to large electropositiveness of Ga in comparison with Fe, which also has a reflection in correlation of Ga and Fe charges. Orbitals population of *Fe* atoms changes enough (visibly) in the process to transition from $[GaFe^{2+}Se]^{1-}$ clusters to $[GaFe^{3+}Se_6]^{1-}$ one that should be displayed in theoretical values of quadrupole splitting. ΔE_Q values calculated on (1.!)-(!.5) formulas for both type of cluster in the processes of consistent increasing of mentioned introduction are given it table 3. One can see that anysotropy of electron density splitting on Fe atom gives only a half of full value of ΔE_Q.

Table 3

Theoretical values of $\Delta E_Q(mm/s)$ for $[GaFe^{2+}S_6]^{8-}$ and $[GaFe^{3+}Se_6]^{7-}$ clusters.

Clusters	Group				
	Fe	Ga-Fe	S_3Ga-Fe	S_3Ga-FeS$_3$	S_3Ga-eS*$_3$
$[GaFe^{2+}S_6]^{8-}$	2.2	2.71	2.45	2.9	2.82
$[GaFe^{3+}Se_6]^{7-}$	3.18	3.79	3.56	4.01	3.9

In the beginning this results is seemed to be a little unexpected, but it becomes quite clear, if large positive charge o atoms and large value of field gradient created by single charge are taken into consideration.

Three *S* atoms complete formally the coordination sphere of Fe atoms to tetrahedr. How-ever ΔE_Q does not decrease, but increases, that is interpreted by differences of Ga and S charges mark. Introduction of S atoms in is not large in general. It allow to considering obtained estimation of to be reliable enough, even when S atoms is located in clusters border, hence error in estimation of their charge can be large.

As GaS atoms are the nearest to *S* atoms in *GaS* crystal, then negative charge in atoms is probably overestimated.

Considering ΔE_Q values given in last three columns one can see that the model of $[GaFe^{3+}Se_6]^{7-}$ cluster is not satisfactory independently of *e(S)* estimation, as theoretical values of E_Q are different from experimental ΔE_Q=2.66 mm/s by 2. Quite opposite, $[GaFe^{2+}S_6]^{8-}$ cluster is corresponds to experiment very well. That's why we can confidentially make a conclusion that impure center in crystals GaS:Fe has structure of $[GaFe^{2+}S_6]^{8-}$.

[1] *Kuhn. Chey A.* Acta Cryst. (1976), B.32. 983.

[2] *K.K.Mamedov, M.A.Aldjanov, I.Q.Kerimov, M.I. Mextiyev.* FTT, 1977, 20, №1, 41.

[3] *G.D.Guseinov, A.L.Rasulov, E.M.Kerimova, M.Z.Ismailov.* Phys. Letters, 1966, 22, 562.

[4] *M.A. Aldjanov, M.D. Najafzade, Z.Y. Seidov.* FTT, 1999, 41, №01, 24.

[5] Chemical application of Mössbauer spectroscopy. M. "Mir", 1970, 502.

[6] *S.P. İonov, B.N. Qaribov.* J.Phys. Chem, 1980, 54, №11, 2721.

[7] *S.Alvares.* Table of Iterated Ionization Potetials for Extended Huckel Calculations, Itaca University, 1984.

[8] *V.I. Khlestkov, B.N. Burkin, R.E. Qeribov.* 1985, №2, 146.

[9] *M.Weissbluth, J.E. Maling,* I.Chem. Phys., 1976, 47, №10, 4166.

[10] *M.Weissbluth,* Coopevativity and electronic properties, Berlin, Springer, 1974, 212.

[11] *A.Tranvein.* Mössbauer spectroscopy on heme protein, Struct. and Bond, 1974, №20, 101.

Q.D. Sultanov, M.A. Alcanov, E.M. Kərimova

Ga$_{0.8}$Fe$_{0.02}$S$_6$ KRİSTALINDA MESSBAUER SPEKTRİNİN TƏDQİQİ

GaS:^{57}Fe kristalında aparılan maqnit və Messbauer tədqiqatları 80÷300 K temperatur oblastında maqnit qavrayıcılığının temperaturdan zəif asılılığını müəyyənləşdirdi.

Otaq temperaturunda Messbauer spektrindən təyin olunmuş kvadrupol parçalanmanın qiyməti *E*=2,95mm/san. *E*-nin təcrübi qiyməti ilə GaFe^{2+}S$_6$ aşqar kompleksinin elektron quruluşunun MK-hesablanması əsasında alınmış nəzəri qiyməti arasındakı uyğunluqla təsdiqlənir.

Г.Д. Султанов, М.А. Алджанов, Э.М. Керимова

ИССЛЕДОВАНИЕ МЕССБАУЭРОВСКИХ СПЕКТРОВ КРИСТАЛЛОВ Ga$_{0,8}$Fe$_{0,02}$S$_6$

Проведены магнитные и мессбауэровские исследования кристаллов GaS:Fe. Установлена слабая температурная зависимость магнитной восприимчивости в области температур 80÷300К. Величина квадрупольного расщепления, определенная из мессбауэровского спектра при комнатной температуре, равна *E*=2,95мм/сек. Сделанное предположение дает хорошее согласие между экспериментальным и теоретическим значением величины *E*, полученным на основе результатов МК- расчета электронного строения примесного комплекса GaFe^{2+}S$_6$.