## Azerbaijan Journal of Physics


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Azerbaijan National Academy of Sciences
Department of Physical, Mathematical and Technical Sciences

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ANAS, G.M.Abdullayev Institute of Physics
Tel.: (99412) 439-51-63, 439-32-23
Fax: (99412) 447-04-56
E-mail: jophphysics@gmail.com
Internet: www.physics.gov.az

It is authorized for printing:

Published at "SəRQ-QəRB"
17 Ashug Alessger str., Baku
Typographer: Aziz Gulaliyev
Sent for printing on: $\qquad$ 201
Printing approved on: $\qquad$ 201
Physical binding: $\qquad$ 201_ Number of copies: 200

# MATHEMATICA IN INTEGRATION OF SL(3,C) SELF-DUALITY EQUATIONS 

M.A. MUKHTAROV<br>Institute of Mathematics and Mechanics<br>370602, Baku, F.Agaev str. 9, Azerbaijan

New solutions of the Yang-Mill's self-duality equation are constructed by means of discrete symmetry transformations and MATHEMATICA software for the algebra $\operatorname{SL}(3, C)$. The obtained solutions are expressed in terms of determinants of special type matrixes.

Keywords: self-duality, symmetry, semisimple algebra.
PACS: 02.30.Jr.

1. Over the last few years self-dual Yang-Mills equation has attracted a fair amount or attention. It has been shown $[1-8]$ that a large number of one, two and ( $1+2$ )dimensional integrable models such as Korteweg-de Vries, N-waves, Ernst, Kadomtsev-Petviashvili, Toda lattice, nonlinear Schrodinger equations and many others can be obtained from the four-dimensional self-dual Yang-Mills equation by symmetry reduction and by imposing the constraints on Yang-Mills potentials.

The universality of the self-dual Yang-Mills (SDYM) model as an integrable system has been confirmed in the paper [9] where the general scheme of the reduction of the Belavin-Zakharov Lax pair for selfduality [10] has been represented over an arbitrary subgroup from the conformal group of transformations of $R_{4}$ space. As the result of this reduction one has the Lax pair representation for the corresponding differential equations of a lower dimension.

The problem of constructing of the instanton solutions in the explicit form for semisimple Lie algebra, rank of which is greater than two, remains also important for the present time.

The effective group-theoretical methods have been developed by the author together with Prof. A.N. Leznov of construction of the exact solutions of the Yang-Mill's self-duality equations.

The algebraic perturbation method, known in the scientific literature as Leznov-Mukhtarov method, the Riemann problem method and a method of discrete transformations have allowed to obtain for the first time new classes of exact decisions of self-duality equations of for an arbitrary semisimple algebras [11-17].

2 . In section we present the discrete symmetry transformation method of solution the self-duality equation.

Self-dual equations are the systems of equations for the parameters of a group element $G$ considering as the functions of four independent arguments $z, \bar{z}, y, \bar{y}$.

$$
\begin{equation*}
\left(G_{\bar{z}} G^{-1}\right)_{z}+\left(G_{\bar{y}} G^{-1}\right)_{y}=0 \tag{2.1}
\end{equation*}
$$

where $G_{t}=\partial_{t} G$.
The system of equations (2.1) can be partially solved

$$
G_{\bar{z}} G^{-1}=+f_{y}, G_{\bar{y}} G^{-1}=-f_{z}
$$

where the element $f$ takes values in the algebra of corresponding group.

System of equations on $f$ has the following form

$$
\begin{equation*}
f_{z \bar{z}}+f_{y \bar{y}}+\left[f_{z}, f_{y}\right]=0 \tag{2.2}
\end{equation*}
$$

Following [12], for the case of a semisimple Lie algebra and for an element $f$ being a solution of (2.2), the following statement takes place:

There exists such an element $S$ taking values in a gauge group that

$$
\begin{align*}
& S^{-1} \frac{\partial S}{\partial y}=\frac{1}{\tilde{f}_{-}}\left[\frac{\partial \tilde{f}}{\partial y}, X_{M}\right]-\frac{\partial}{\partial \bar{z}} \frac{1}{\tilde{f}_{-}} X_{M}  \tag{2.3}\\
& S^{-1} \frac{\partial S}{\partial z}=\frac{1}{\tilde{f}_{-}}\left[\frac{\partial \tilde{f}}{\partial z}, X_{M}\right]+\frac{\partial}{\partial \bar{y}} \frac{1}{\tilde{f}_{-}} X_{M}
\end{align*}
$$

Here $X_{N}$ is the element of the algebra corresponding to its maximal root divided by its norm, i.e.,

$$
\left[X_{M}^{+}, X^{-}\right]=H,\left[H, X^{ \pm}\right]= \pm 2 X^{ \pm}
$$

- $\tilde{I}_{-}$- is the coefficient function in the decomposition of $\tilde{f}$ of the element corresponding to the minimal root of the algebra, $\tilde{f}=\sigma f \sigma^{-1}$ and where $\sigma$ is an automorfism of the algebra, changing the positive and negative roots.

In the case of algebra $\operatorname{SL}(3, C)$ we'll consider the case of three dimensional representation of algebra and the following form of $\sigma=\left(\begin{array}{ccc}0 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0\end{array}\right)$.

The discrete symmetry transformation, producing new solutions from the known ones, is as follows:

$$
\begin{equation*}
\frac{\partial F}{\partial y}=S \frac{\partial \tilde{f}}{\partial y} S^{-1}+\frac{\partial S}{\partial \bar{z}} S^{-1} \quad, \frac{\partial F}{\partial z}=S \frac{\partial \tilde{f}}{\partial z} S^{-1}-\frac{\partial S}{\partial \bar{y}} S^{-1} \tag{2.4}
\end{equation*}
$$

3. Let's represent the explicit formulae for transformation of the self-duality equations in the case of $\mathrm{SL}(3, \mathrm{C})$ algebra

$$
\begin{equation*}
f=\alpha_{1} X_{1}^{+}+\alpha_{2} X_{2}^{+}+\alpha_{1,2} X_{1,2}^{+}+\tau_{1} h_{1}+\tau_{2} h_{2}+a_{1} X_{1}^{-}+a_{2} X_{2}^{-}+a_{1,2} X_{1,2}^{-} \tag{3.1}
\end{equation*}
$$

In connection with the general scheme, first of all, it is necessary to find the solution of the equations (2.4) for the SL(3,C) valued function $S$ for given $f$, solution of self-duality equation (2.2).

From (2.3) it is clear that $S$ is upper triangular matrix and can be represented in the following form:

$$
\begin{equation*}
S=\exp \beta_{1} X_{1}^{+} \exp \beta_{1,2} X_{1,2}^{+} \exp \beta_{2} X_{2}^{+} \exp \beta_{0} H \tag{3.2}
\end{equation*}
$$

where $H=h_{1}+h_{2}$.
After substitution of the last representation of $S$ into (2.4), we have at every step of the recurrent procedure the following relations

$$
\begin{align*}
\beta_{0} & =\ln \alpha_{1,2}, \beta_{1}=\alpha_{2}, \beta_{2}=\alpha_{1} \\
\left(\beta_{1,2}\right)_{y} & =\left(\alpha_{1,2}\right)_{\bar{z}}-\left(\delta_{1}+\delta_{2}\right)_{y} \alpha_{1,2}-\left(\alpha_{1}\right)_{y} \alpha_{2}  \tag{3.3}\\
\left(\beta_{1,2}\right)_{z} & =-\left(\alpha_{1,2}\right)_{\bar{y}}-\left(\delta_{1}+\delta_{2}\right)_{z} \alpha_{1,2}-\left(\alpha_{1}\right)_{z} \alpha_{2}
\end{align*}
$$

As the initial solution we'll take the explicit solution $f$ belonging to the algebra of upper triangular matrixes:

$$
\begin{equation*}
f=\alpha_{1} X_{1}^{+}+\alpha_{2} X_{2}^{+}+\alpha_{1,2} X_{1,2}^{+}+\tau_{1} h_{1}+\tau_{2} h_{2} \tag{3.4}
\end{equation*}
$$

The component form of self-duality equations for this case is following

$$
\begin{gather*}
\square \tau_{i}=0, \square \alpha_{i}=\left\{\delta_{i}, \alpha_{i}\right\}_{y, z}, \quad i=1,2, \\
\square \alpha_{1,2}=\left\{\delta_{1}+\delta_{2}, \alpha_{1,2}\right\}_{y, z}, \tag{3.5}
\end{gather*}
$$

where $\square=\frac{\partial^{2}}{\partial z \partial \bar{z}}+\frac{\partial^{2}}{\partial y \partial \bar{y}} ; \delta_{1}=2 \tau_{1}-\tau_{2}, \delta_{2}=2 \tau_{2}-\tau_{1}$ and figure brackets of two functions $g_{1}$ and $g_{2}$ denotes : $\left\{g_{1}, g_{2}\right\}_{y, z}=\frac{\partial g_{1}}{\partial y} \frac{\partial g_{2}}{\partial z}-\frac{\partial g_{2}}{\partial y} \frac{\partial g_{1}}{\partial z}$.

The general solution of system (3.5) takes the form

$$
\begin{gather*}
\tau_{i}=\oint_{c} \tau_{i}(\lambda) d \lambda, \alpha_{i}=\oint_{c} \alpha_{i}(\lambda) \exp \left(-\bar{\delta}_{i}(\lambda)\right) d \lambda, \\
\bar{\delta}_{i}(\lambda)=\oint_{c} \frac{\left.d \lambda^{\prime} \delta_{i}\left(\lambda^{\prime}\right)\right) d \lambda^{\prime}}{\lambda-\lambda^{\prime}}, i=1,2, \\
\alpha_{1,2}=\oint_{c} \alpha_{1,2}(\lambda) \exp \left(-\bar{\delta}_{1}(\lambda)-\bar{\delta}_{2}(\lambda)\right) d \lambda+\oint_{c} \alpha_{1}(\lambda) \exp \left(-\delta_{1}(\lambda)\right) d \lambda \oint_{c} \frac{d \lambda^{\prime} \alpha_{2}\left(\lambda^{\prime}\right) \exp \left(-\delta_{2}\left(\lambda^{\prime}\right)\right)}{\lambda-\lambda^{\prime}} \tag{3.6}
\end{gather*}
$$

Here the circle integration goes over the complex parameter $\lambda$ and all integrated functions are arbitrary functions of three independent variables $(y+\lambda \bar{z}, z-\lambda \bar{y}, \lambda)$.

By the direct check one can be convinced that (3.6) are the solutions of equations (3.5).
Let's represent two types of Backlund transformation by means of which one can construct new types of solutions of equations (3.5) from the known solution (3.6). For solutions of first two equations of (3.5) this two Backlund transformations are the same:

$$
\begin{align*}
\left(\alpha_{i}^{k}\right)_{\bar{z}}-\left(\delta_{i}\right)_{y} \alpha_{i}^{k} & =\left(\alpha_{i}^{k+1}\right)_{y} \\
-\left(\alpha_{i}^{k}\right)_{\bar{y}}-\left(\delta_{i}\right)_{z} \alpha_{i}^{k} & =\left(\alpha_{i}^{k+1}\right)_{z}, i=1,2 \tag{3.7}
\end{align*}
$$

For solutions of the third equation of the system (3.5) they are different:

$$
\left(\alpha_{1,2}^{0, k}\right)_{\bar{z}}-\left(\delta_{1}+\delta_{2}\right)_{y} \alpha_{1,2}^{0, k}-\left(\alpha_{1}^{k}\right)_{y} \alpha_{2}^{k}=\left(\alpha_{1,2}^{0, k+1}\right)_{y}
$$

$$
\begin{equation*}
-\left(\alpha_{1,2}^{0, k}\right)_{\bar{y}}-\left(\delta_{1}+\delta_{2}\right)_{z} \alpha_{1,2}^{0, k}-\left(\alpha_{1}^{k}\right)_{z} \alpha_{2}^{k}=\left(\alpha_{1,2}^{0, k+1}\right)_{z} \tag{3.8}
\end{equation*}
$$

and

$$
\begin{align*}
\left(\alpha_{1,2}^{k, 0}\right)_{\bar{z}}-\left(\delta_{1}+\delta_{2}\right)_{y} \alpha_{1,2}^{k, 0}+\alpha_{1}^{k}\left(\alpha_{2}^{k}\right)_{y} & =\left(\alpha_{1,2}^{k+1,0}\right)_{y} \\
-\left(\alpha_{1,2}^{k, 0}\right)_{\bar{y}}-\left(\delta_{1}+\delta_{2}\right)_{z} \alpha_{1,2}^{k, 0}+\alpha_{1}^{k}\left(\alpha_{2}^{k}\right)_{z} & =\left(\alpha_{1,2}^{k+1,0}\right)_{z} \tag{3.9}
\end{align*}
$$

Note that starting, zero step of upper transformations procedure coincides with initial solutions (3.6).
Let's return to the solution of the equation (3.3) at the first step of the recurrent procedure.
Comparing (3.3) and (3.9) we came to the conclusion that $\beta_{1,2}=\alpha_{1,2}^{0,1}$.
Finally, knowing all components of matrix $S$ and using (3.9) we can express the solution

$$
F=F_{1}^{+} X_{1}^{+}+F_{2}^{+} X_{2}^{+}+F_{1,2}^{+} X_{1,2}^{+}+F_{1}^{0} h_{1}+F_{2}^{0} h_{2}+F_{1}^{-} X_{1}^{-}+F_{2}^{-} X_{2}^{-}+F_{1,2}^{-} X_{1,2}^{-}
$$

of self-duality equations at the first step of the recurrent procedure in terms of chains (3.7)-(3.9):

$$
\begin{aligned}
F_{1}^{0} & =\tau_{1}+\frac{\alpha_{1,2}^{1,0}}{\alpha_{1,2}^{0,0}}, F_{2}^{0}=\tau_{2}+\frac{\alpha_{1,2}^{0,1}}{\alpha_{1,2}^{0,0}} \\
F_{1,2}^{-} & =\frac{1}{\alpha_{1,2}^{0,0}}, F_{1}^{-}=\frac{\alpha_{2}^{0}}{\alpha_{1,2}^{0,0}}, F_{2}^{-}=-\frac{\alpha_{1}^{0}}{\alpha_{1,2}^{0,0}} \\
F_{1}^{+} & =-\frac{1}{\alpha_{1,2}^{0,0}}\left|\begin{array}{cc}
\alpha_{1}^{0} & \alpha_{1}^{1} \\
\alpha_{1,2}^{0,0} & \alpha_{1,2}^{1,0}
\end{array}\right|, F_{2}^{+}=-\frac{1}{\alpha_{1,2}^{0,0}}\left|\begin{array}{cc}
\alpha_{2}^{0} & \alpha_{2}^{1} \\
\alpha_{1,2}^{0,0} & \alpha_{1,2}^{0,1}
\end{array}\right| \\
F_{1,2}^{+} & =\frac{1}{\alpha_{1,2}^{0,0}}\left|\begin{array}{ll}
\alpha_{1,2}^{0,0} & \alpha_{1,2}^{0,1} \\
\alpha_{1,2}^{1,0} & \alpha_{1,2}^{1,1}
\end{array}\right|
\end{aligned}
$$

Using the self-duality equations of the for the group-valued element

$$
G_{\bar{z}} G^{-1}=+f_{y}, G_{\bar{y}} G^{-1}=-f_{z}
$$

the relations can be rewritten as

$$
\theta_{i}\left(S_{n} \sigma g_{n}\right)_{x_{i}}\left(S_{n} \sigma g_{n}\right)^{-1}=\left(f_{n+1}\right)_{x_{i}}
$$

So we see that the group valued elements $g_{n+1}$ and $g_{n}$ are connected by the relation

$$
\begin{equation*}
g_{n+1}=S_{n} \sigma g_{n} \tag{3.10}
\end{equation*}
$$

Let's represent the explicit formulae of the recurrent procedure of obtaining the group-valued element solutions. At every step, as it shown in [5], $S$ is upper triangular matrix and can be represented in the following form:

$$
\begin{equation*}
S_{n}=\exp \left(\beta_{1}\right)_{n} X_{1}^{+} \exp \left(\beta_{1,2}\right)_{n} X_{1,2}^{+} \exp \left(\beta_{2}\right)_{n} X_{2}^{+} \exp \left(\beta_{0}\right)_{n} H \tag{3.11}
\end{equation*}
$$

where $H=h_{1}+h_{2}$ and for $g_{n}$ we use the following parameterization:

$$
\begin{align*}
g_{n} & =\exp \left(\eta_{1}^{+}\right)_{n} X_{1}^{+} \exp \left(\eta_{1,2}^{+}\right)_{n} X_{1,2}^{+} \exp \left(\eta_{2}^{+}\right)_{n} X_{2}^{+} \exp \left(\left(t_{1}\right)_{n} h_{1}+\left(t_{2}\right)_{n} h_{2}\right) \times \\
& \times \exp \left(\eta_{2}^{-}\right)_{n} X_{2}^{-} \exp \left(\eta_{1,2}^{-}\right)_{n} X_{1,2}^{-} \exp \left(\eta_{1}^{-}\right)_{n} X_{1}^{-} \tag{3.12}
\end{align*}
$$

with

$$
g_{0}=\exp \left(\eta_{1}^{+}\right)_{0} X_{1}^{+} \exp \left(\eta_{1,2}^{+}\right)_{0} X_{1,2}^{+} \exp \left(\eta_{2}^{+}\right)_{0} X_{2}^{+} \exp \left(\left(t_{1}\right)_{0} h_{1}+\left(t_{2}\right)_{0} h_{2}\right)
$$

as an initial solution.
Hereafter, $X_{1}^{ \pm}, X_{2}^{ \pm}, X_{1,2}^{ \pm}, h_{1}, h_{2}$ are the generators of $\operatorname{SL}(3, C)$ algebra.
Following the general scheme from [5] we have at
(0)-step:

$$
\left(t_{i}\right)_{0}=\tau_{i}^{-1} \equiv v_{i},\left(\eta_{i}^{+}\right)_{0}=\alpha_{i}^{-1}, i=1,2,\left(\eta_{1,2}^{+}\right)_{0}=\alpha_{1,2}^{-1,0}
$$

The further calculation we deliver to Mathematica program:

$$
\begin{aligned}
& \mathrm{X}_{1}^{+}=\left(\begin{array}{lll}
0 & 1 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{array}\right) ; \quad \mathrm{X}_{2}^{+}=\left(\begin{array}{ccc}
0 & 0 & 0 \\
0 & 0 & 1 \\
0 & 0 & 0
\end{array}\right) ; \quad \mathrm{X}_{1,2}^{+}=\left(\begin{array}{ccc}
0 & 0 & 1 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{array}\right) ; \\
& \mathrm{X}_{1}=\left(\begin{array}{ccc}
0 & 0 & 0 \\
1 & 0 & 0 \\
0 & 0 & 0
\end{array}\right) ; \quad \mathrm{X}_{2}^{-}=\left(\begin{array}{ccc}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 1 & 0
\end{array}\right) ; \quad \mathrm{X}_{1,2}=\left(\begin{array}{lll}
0 & 0 & 0 \\
0 & 0 & 0 \\
1 & 0 & 0
\end{array}\right) ; \\
& \mathbf{h}_{1}=\left(\begin{array}{ccc}
1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 0
\end{array}\right) ; \quad \mathbf{h}_{\mathbf{2}}=\left(\begin{array}{ccc}
0 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{array}\right) ; \mathbf{w}=\left(\begin{array}{ccc}
0 & 0 & 1 \\
0 & 1 & 0 \\
-1 & 0 & 0
\end{array}\right) ; \\
& \mathrm{G}_{0}=\operatorname{MatrixExp}\left[\mathrm{n}_{1} \mathrm{X}_{1}^{+}\right] \text {MatrixExp}\left[\mathrm{n}_{1,2} \mathrm{X}_{\mathbf{1}, 2}^{+}\right] \text {MatrixExp }\left[\mathrm{n}_{2} \mathrm{X}_{2}^{+}\right] \text {MatrixExp[ }\left[\mathrm{r}_{1} \mathrm{~h}_{1}\right] . \\
& \mathbf{S}_{1}=\text { MatrixExp }\left[\mathrm{b}_{1} \mathrm{X}_{1}^{+}\right] \text {MatrixExp }\left[\mathrm{b}_{1,2} \mathrm{X}_{1,2}^{+}\right] \text {MatrixExp }\left[\mathrm{b}_{2} \mathrm{X}_{2}^{+}\right] \text {MatrixExp }\left[\mathrm{b}_{0}\left(\mathbf{h}_{\mathbf{1}}+\mathrm{h}_{2}\right)\right] \text {; } \\
& \mathrm{G}_{1}=\mathrm{S}_{1} \cdot \mathrm{w}^{2} \mathrm{G}_{0} ; \\
& \text { MatrixForm[ } \left.\mathrm{G}_{1}\right]
\end{aligned}
$$

$\mathrm{G}_{1} / .\left(\mathrm{b}_{1} \mathrm{~b}_{2}+\mathrm{b}_{1,2}\right) \rightarrow \mathrm{a}_{1,2}[1,0] / \mathrm{n}_{1} \mathrm{n}_{2}+\mathrm{n}_{1,2} \rightarrow \mathrm{a}_{1,2}[0,-1] / \mathrm{b}_{0} \rightarrow \log \left[\mathrm{a}_{1,2}[0,0]\right] /$.

$$
\begin{aligned}
\mathrm{b}_{1} & \rightarrow \mathrm{a}_{1}[0] \\
/ \cdot \mathrm{b}_{2} & \rightarrow \mathrm{a}_{2}[0] / . \mathrm{n}_{1} \rightarrow \mathrm{a}_{1}[-1] / \mathrm{n}_{2} \rightarrow \mathrm{a}_{2}[-1]
\end{aligned}
$$

$$
\begin{aligned}
& \left\{\left\{-\Phi^{-\log \left[a_{1,2}[0,0]\right]+r_{1}} a_{1,2}[1,0], ⿷^{-r_{1}+r_{2}} a_{1}[0]-e^{-\log \left[a_{1,2}[0,0]\right]-r_{1}+r_{2}} a_{1}[-1] a_{1,2}[1,0],\right.\right. \\
& \left.e^{\log \left[a_{1,2}[0,0]\right]-r_{2}}+e^{-r_{2}} a_{1}[0] a_{2}[-1]-e^{-\log \left[a_{1,2}[0,0]\right]-r_{2}} a_{1,2}[0,-1] a_{1,2}[1,0]\right\}, \\
& \left\{-e^{-\log \left[a_{1,2}[0,0]\right]+r_{1} a_{2}[0], e^{-r_{1}+r_{2}}{ }_{-\infty}-\log \left[a_{1,2}[0,0]\right]-r_{1}+r_{2} a_{1}[-1] a_{2}[0], ~}\right. \\
& e^{-r_{2}} a_{2}[-1]-e^{-\log \left[a_{1,2}[0,0]\right]-r_{2}} a_{2}[0] a_{1,2}\left[^{[0,-1]\}}\right. \text {, } \\
& \left\{-a^{\left.\left.-\log \left[a_{1,2}[0,0]\right]+r_{1},-e^{-\log \left[a_{1,2}[0,0]\right]-r_{1}+r_{2}} a_{1}[-1],-\Phi^{-\log \left[a_{1,2}[0,0]\right]-r_{2}} a_{1,2}[0,-1]\right\}\right\}}\right.
\end{aligned}
$$

$\mathrm{G}_{1}=$ FullSimplify[\%]

$$
\mathrm{G}_{1}=\text { FullSimplify }\left[\% / \mathrm{a}_{1}[0] \mathrm{a}_{2}[-1] \rightarrow \mathrm{a}_{1,2}[1,-1]-\mathrm{a}_{1,2}[0,0]\right.
$$

$$
f \cdot a_{1}[-1] a_{2}[0] \rightarrow a_{1,2}[0,0]-a_{1,2}[-1,1]
$$

$$
\begin{aligned}
& \left\{\left\{-\frac{e^{r} a_{1,2}[1,0]}{a_{1,2}[0,0]}, \frac{e^{-r_{1}+r_{2}\left(a_{1}[0] a_{1,2}[0,0]-a_{1}[-1] a_{1,2}[1,0]\right)}}{a_{1,2}[0,0]},\right.\right. \\
& \left.\frac{e^{-r_{2}\left(a_{1,2}[0,0] a_{1,2}[1,-1]-a_{1,2}[0,-1] a_{1,2}[1,0]\right)}}{a_{1,2}[0,0]}\right\}, \\
& \left\{-\frac{e^{r} 1 a_{2}[0]}{a_{1,2}[0,0]}, \frac{-e^{-r} 1+r_{2} a_{1,2}[-1,1]}{a_{1,2}[0,0]}, \frac{-r^{-r}\left(-a_{2}[0] a_{1,2}[0,-1]+a_{2}[-1] a_{1,2}[0,0]\right)}{a_{1,2}[0,0]}\right\}, \\
& \left.\left\{-\frac{e^{r} 1}{a_{1,2}[0,0]},-\frac{e^{-r_{1}+r_{2}} a_{1}[-1]}{a_{1,2}[0,0]},-\frac{e^{-r_{2}} a_{1,2}[0,-1]}{a_{1,2}[0,0]}\right\}\right\}
\end{aligned}
$$

$\mathrm{T}_{2}[1]=\mathrm{G}_{1}[[3,3]] ;$
$\mathrm{T}_{1}[\mathrm{l}]=\mathrm{Mnors}\left[\mathrm{G}_{1}\right][[3,3]] ;$
$\alpha_{2}[1]=\mathrm{G}_{1}[[2,3]] / \mathrm{T}_{2}[1] ;$
$\beta_{2}[1]=\mathrm{G}_{1}[3,2] 1 / \mathrm{T}_{2}[1] ;$
$\beta_{1}[1]=$ Mnors $\left[\mathrm{G}_{1}\right]\left[[3,2] 1 / \mathrm{T}_{1}[1] ;\right.$
$\alpha_{1}[1]=\operatorname{Mnors}\left[\mathrm{G}_{1}\right][[2,3]] / \mathrm{T}_{1}[1] ;$
${ }^{\alpha}{ }_{1,2}[1]=-\operatorname{Mnors}\left[\mathrm{G}_{1}[[1], 3]\right] / \mathrm{T}_{1}[1] ;$
$\beta_{1,2}[1]=-$ Mnors $\left[\mathrm{G}_{1}\right][3,1] / / \mathrm{T}_{1}[1]$;
FullSimplifyT $\left.\mathrm{T}_{2}[1]\right]$
$-\frac{e^{-r} 2 a_{1,2}[0,-1]}{a_{1,2}[0,0]}$

$$
\begin{aligned}
& \left\{\left\{-\frac{e^{r_{1}} a_{1,2}[1,0]}{a_{1,2}[0,0]}, \frac{e^{-r_{1}+r_{2}}\left(a_{1}[0] a_{1,2}[0,0]-a_{1}[-1] a_{1,2}[1,0]\right)}{a_{1,2}[0,0]},\right.\right. \\
& \left.\frac{e^{-r_{2}}\left(a_{1}[0] a_{2}[-1] a_{1,2}[0,0]+a_{1,2}[0,0]^{2}-a_{1,2}[0,-1] a_{1,2}[1,0]\right)}{a_{1,2}[0,0]}\right\},\left\{-\frac{e^{r} 1 a_{2}[0]}{a_{1,2}[0,0]},\right. \\
& \left.\frac{e^{-r_{1}+r_{2}}\left(-a_{1}[-1] a_{2}[0]+a_{1,2}[0,0]\right)}{a_{1,2} 2^{[0,0]}}, \frac{e^{-r_{2}\left(-a_{2}[0] a_{1,2}[0,-1]+a_{2}[-1] a_{1,2}[0,0]\right)}}{a_{1,2}[0,0]}\right\}, \\
& \left.\left\{-\frac{e^{r_{1}}}{a_{1,2}[0,0]},-\frac{e^{-r_{1}+r_{2}} a_{1}[-1]}{a_{1,2}[0,0]},-\frac{e^{-r_{2}} a_{1,2}[0,-1]}{a_{1,2}[0,0]}\right\}\right\}
\end{aligned}
$$

FullSimplify[ $\left.\mathrm{T}_{1}[1]\right]$

$$
\begin{aligned}
& \frac{e^{-r} 1\left(-\left(a_{1}[-1] a_{2}[0]+a_{1,2}[-1,1]\right) a_{1,2}[0,-1]+a_{1}[-1] a_{2}[-1] a_{1,2}[0,0]\right)}{a_{1,2}[0,0]^{2}} \\
& \mathrm{~T}_{1}[1]=\text { FullSimplify }\left[\% / a_{1}[-1] a_{2}[0] \rightarrow a_{1,2}[0,0]-a_{1,2}[-1,1]\right. \\
& \left.\quad / \cdot a_{1}[-1] a_{2}[-1] \rightarrow a_{1,2}[0,-1]-a_{1,2}[-1,0]\right] \\
& -\frac{e^{-r} 1 a_{1,2}[-1,0]}{a_{1,2}[0,0]}
\end{aligned}
$$

FullSimplify[ $\left.\beta_{1}[1]\right]$

$$
\begin{aligned}
& \frac{e^{2 r 1-r_{2}} a_{2}[-1] a_{1,2}[0,0]}{-\left(a_{1}[-1] a_{2}[0]+a_{1,2}[-1,1]\right) a_{1,2}[0,-1]+a_{1}[-1] a_{2}[-1] a_{1,2}[0,0]} \\
& \beta_{1}[1]=\text { FullSimplify }\left[\% / a_{1}[-1] a_{2}[0] \rightarrow a_{1,2}[0,0]-a_{1,2}[-1,1]\right. \\
& \left.\quad / \cdot a_{1}[-1] a_{2}[-1] \rightarrow a_{1,2}[0,-1]-a_{1,2}[-1,0]\right] \\
& -\frac{e^{2 r_{1}-r_{2}} a_{2}[-1]}{a_{1,2}[-1,0]}
\end{aligned}
$$

FullSimplify $\left[\beta_{1,2}[1]\right]$

$$
\begin{aligned}
& \frac{e^{r_{1}+r_{2}}\left(a_{1}[-1] a_{2}[0]+a_{1,2}[-1,1]\right)}{\left(a_{1}[-1] a_{2}[0]+a_{1,2}[-1,1]\right) a_{1,2}[0,-1]-a_{1}[-1] a_{2}[-1] a_{1,2}[0,0]} \\
& \beta_{1,2}[1]=\text { FullSSmplify }\left[\% / . a_{1}[-1] a_{2}[0] \rightarrow a_{1,2}[0,0]-a_{1,2}[-1,1]\right. \\
& \left.\quad f \cdot a_{1}[-1] a_{2}[-1] \rightarrow a_{1,2}[0,-1]-a_{1,2}[-1,0]\right] \\
& \frac{e_{2}^{r_{1}+r_{2}}}{a_{1,2}[-1,0]}
\end{aligned}
$$

$\mid$ FullSimplify[ $\left.\beta_{2}[1]\right]$

$$
\frac{e^{-\mathrm{r}_{1}+2 \mathrm{r}_{2}^{-} \mathrm{a}_{1}[-1]}}{\mathrm{a}_{1,2}[0,-1]}
$$

FullSimplify $\left[\alpha{ }^{\alpha}{ }^{[1]}\right]$

$$
\begin{aligned}
& \frac{a_{1,2}[0,0]\left(-a_{1}[0] a_{1,2}[0,-1]+a_{1}[-1] a_{1,2}[1,-1]\right)}{-\left(a_{1}[-1] a_{2}[0]+a_{1,2}[-1,1]\right) a_{1,2}[0,-1]+a_{1}[-1] a_{2}[-1] a_{1,2}[0,0]} \\
& \alpha_{1}[1]=\text { FullSimplify }\left[\% / a_{1}[-1] a_{2}[0] \rightarrow a_{1,2}[0,0]-a_{1,2}[-1,1]\right. \\
& \left.\quad / a_{1}[-1] a_{2}[-1] \rightarrow a_{1,2}[0,-1]-a_{1,2}[-1,0]\right] \\
& \frac{a_{1}[0] a_{1,2}[0,-1]-a_{1}[-1] a_{1,2}[1,-1]}{a_{1,2}[-1,0]}
\end{aligned}
$$

FullSimplify[ $\left.\alpha_{2}[1]\right]$

$$
a_{2}[0]-\frac{a_{2}[-1] a_{1,2}[0,0]}{a_{1,2}[0,-1]}
$$

FullSimplify $\left[{ }^{\alpha} 1,2[1]\right]$

$$
\frac{a_{1,2}[0,0]\left(a_{1}[0]\left(a_{2}[0] a_{1,2}[0,-1]-a_{2}[-1] a_{1,2}[0,0]\right)+a_{1,2}[-1,1] a_{1,2}[1,-1]\right)}{-\left(a_{1}[-1] a_{2}[0]+a_{1,2}[-1,1]\right) a_{1,2}[0,-1]+a_{1}[-1] a_{2}[-1] a_{1,2}[0,0]}+a_{1,2}[1,0]
$$

$$
\alpha_{1,2}[1]=\text { FullSimplify }\left[\% / a_{1}[-1] a_{2}[0] \rightarrow a_{1,2}[0,0]-a_{1,2}[-1,1]\right.
$$

$$
\left.f \cdot a_{1}[-1] a_{2}[-1] \rightarrow a_{1,2}[0,-1]-a_{1,2}[-1,0]\right]
$$

$\frac{a_{1}[0]\left(-a_{2}[0] a_{1,2}[0,-1]+a_{2}[-1] a_{1,2}[0,0]\right)-a_{1,2}[-1,1] a_{1,2}[1,-1]}{a_{1,2}[-1,0]}+a_{1,2}[1,0]$

## Expand[\%]

$$
\begin{aligned}
& -\frac{a_{1}[0] a_{2}[0] a_{1,2}[0,-1]}{a_{1,2}[-1,0]}+\frac{a_{1}[0] a_{2}[-1] a_{1,2}[0,0]}{a_{1,2}[-1,0]}-\frac{a_{1,2}[-1,1] a_{1,2}[1,-1]}{a_{1,2}[-1,0]}+a_{1,2}[1,0] \\
& \alpha_{1,2}[1]=\text { FullSimplify }\left[\% / a_{1,2}[1,0] \rightarrow a_{1}[0] a_{2}[0]+a_{1,2}[0,1] /\right. \\
& \left.\quad a_{1,2}[1,-1] \rightarrow a_{1}[0] a_{2}[-1]+a_{1,2}[0,0] / . a_{1,2}[0,-1] \rightarrow a_{1}[-1] a_{2}[-1]+a_{1,2}[-1,0]\right] \\
& \frac{1}{a_{1,2}[-1,0]}\left(-a_{1}[0] a_{2}[-1]\left(a_{1}[-1] a_{2}[0]+a_{1,2}[-1,1]\right)+\right. \\
& \left.\quad\left(a_{1}[0] a_{2}[-1]-a_{1,2}[-1,1]\right) a_{1,2}[0,0]+a_{1,2}[-1,0] a_{1,2}[0,1]\right) \\
& \alpha_{1,2}[1]=\text { FullSimplify }\left[\% / a_{1}[-1] a_{2}[0] \rightarrow a_{1,2}[0,0]-a_{1,2}[-1,1]\right] \\
& -\frac{a_{1,2}[-1,1] a_{1,2}[0,0]}{a_{1,2}[-1,0]}+a_{1,2}[0,1]
\end{aligned}
$$

The second step.

$$
\begin{aligned}
\mathrm{B}_{1}=\frac{-\mathrm{a}_{1}[0] \mathrm{a}_{1,2}[1,0]+\mathrm{a}_{1}[1] \mathrm{a}_{1,2}[0,0]}{\mathrm{a}_{1,2}[0,0]} ; \mathrm{B}_{2}=\frac{-\mathrm{a}_{2}[0] \mathrm{a}_{1,2}[0,1]+\mathrm{a}_{2}[1] \mathrm{a}_{1,2}[0,0]}{\mathrm{a}_{1,2}[0,0]} ; \\
\mathrm{B}_{0}=\log \left[\frac{-{ }^{-}{ }_{1,2}[1,1] \mathrm{a}_{1,2}[0,0]+\mathrm{a}_{1,2}[1,0] \mathrm{a}_{1,2}[0,1]}{\mathrm{a}_{1,2}[0,0]}\right] ;
\end{aligned}
$$

$$
\mathrm{B}_{1,2}=\frac{1}{\left(\mathrm{a}_{1,2}[0,0]\right)^{\wedge} 2} \mathrm{a}_{1,2}[0,0]\left(\mathrm{a}_{1,2}[1,2] \mathrm{a}_{1,2}[0,0]-\mathrm{a}_{1,2}[1,1] \mathrm{a}_{1,2}[0,1]\right) \mathrm{a}_{1,2}[0,1]
$$

$$
\left(a_{1,2}[1,1] a_{1,2}[0,0]-a 1,2[1,0] a_{1,2}[0,1]\right) ;
$$

$\mathrm{S}_{2}=$ MatrixExp $\left[\mathrm{B}_{1} \mathrm{X}_{1}^{+}\right]$MatrixExp $\left[\mathrm{B}_{1,2} \mathrm{X}_{1,2}^{+}\right]$MhtrixExp $\left[\mathrm{B}_{2} \mathrm{X}_{2}^{+}\right]$MatrixExp $\left[\mathrm{B}_{0}\left(\mathrm{~h}_{1}+\mathrm{h}_{2}\right)\right]$; $\mathrm{G}_{2}=\mathrm{S}_{2} \cdot \mathrm{w}^{2} \mathrm{G}_{1} ; \mathrm{T}_{2}[2]=\mathrm{G}_{2}[[3,3]] ; \mathrm{T}_{1}[2]=$ Mnors $\left[\mathrm{G}_{2}\right][[3,3]] ;$
$\left.\alpha_{2}[2]=\mathrm{G}_{2}[2,3]\right] / \mathrm{T}_{2}[2] ; \beta_{2}[2]=\mathrm{G}_{2}[[3,2]] / \mathrm{T}_{2}[2] ; \beta_{1}[2]=\operatorname{Mnors}\left[\mathrm{G}_{2}\right][[3,2]] / \mathrm{T}_{1}[2] ;$
${ }^{\alpha}{ }_{1}[2]=$ Mnors $\left[\mathrm{G}_{2}\right][[2,3]] / \mathrm{T}_{1}[2] ; \alpha_{1,2}[2]=-$ Mnors $\left[\mathrm{G}_{2}\left[[[1,3]] / \mathrm{T}_{1}[2] ;\right.\right.$
$\beta_{1,2}[2]=-$ Mnors [G 2$][[3,1]] / \mathrm{T}_{1}[2]$ FullSimplify $\left.\mathrm{T}_{2}[2]\right]$

$$
\frac{a^{-r} 2\left(a_{1,2}[0,0] a_{1,2}[1,-1]-a_{1,2}[0,-1] a_{1,2}[1,0]\right)}{-a_{1,2}[0,1] a_{1,2}[1,0]+a_{1,2}[0,0] a_{1,2}[1,1]}
$$

FullSimplify[T $\left.{ }^{[2]}\right]$

$$
\begin{aligned}
& \left(a ^ { - r } \left(a_{1,2}[0,0]\left(a_{1}[0]\left(a_{2}[0] a_{1,2}[0,-1]-a_{2}[-1] a_{1,2}[0,0]\right)+a_{1,2}[-1,1] a_{1,2}[1,-1]\right)-\right.\right. \\
& \left.\left.\quad\left(\left(a_{1}[-1] a_{2}[0]+a_{1,2}[-1,1]\right) a_{1,2}[0,-1]-a_{1}[-1] a_{2}[-1] a_{1,2}[0,0]\right) a_{1,2}[1,0]\right)\right) / \\
& \left(a_{1,2}[0,0]\left(-a_{1,2}[0,1] a_{1,2}[1,0]+a_{1,2}[0,0] a_{1,2}[1,1]\right)\right)
\end{aligned}
$$

$\mathrm{T}_{1}[1]=$ FullSimplify $\left[\% 44 / \mathrm{a}_{1,2}[1,-1] \rightarrow \mathrm{a}_{1,2}[0,0]+\mathrm{a}_{1}[0] \mathrm{a}_{2}[-1]\right.$
$\left.f \cdot \mathrm{a}_{1,2}[0,-1] \rightarrow \mathrm{a}_{1,2}[-1,0]+\mathrm{a}_{1}[-1] \mathrm{a}_{2}[-1] / \mathrm{a}_{1}[-1] \mathrm{a}_{2}[0] \rightarrow \mathrm{a}_{1,2}[0,0]-\mathrm{a}_{1,2}[-1,1]\right]$
$\left(a^{-r} 1\left(a_{1}[-1] a_{1}[0] a_{2}[-1] a_{2}[0]+a_{1}[0]\left(a_{2}[0] a_{1,2}[-1,0]+a_{2}[-1]\left(a_{1,2}[-1,1]-a_{1,2}[0,0]\right)\right)+\right.\right.$ $\left.a_{1,2}[-1,1] a_{1,2}[0,0]-a_{1,2}[-1,0] a_{1,2}[1,0]\right) /\left(-a_{1,2}[0,1] a_{1,2}[1,0]+a_{1,2}[0,0] a_{1,2}[1,1]\right)$
chl $=\left(a_{1}[-1] a_{1}[0] a_{2}[-1] a_{2}[0]+a_{1}[0]\left(a_{2}[0] a_{1,2}[-1,0]+a_{2}[-1]\left(a_{1,2}[-1,1]-a_{1,2}[0,0]\right)\right)+\right.$ $\left.\mathrm{a}_{1,2}[-1,1] \mathrm{a}_{1,2}[0,0]-\mathrm{a}_{1,2}[-1,0] \mathrm{a}_{1,2}[1,0]\right) ;$
FullSimplify[chl $\left./ a_{1,2}[1,0] \rightarrow a_{1,2}[0,1]+a_{1}[0] a_{2}[0] / a_{1}[-1] a_{2}[0] \rightarrow a_{1,2}[0,0]-a_{1,2}[-1,1]\right]$ $a_{1,2}[-1,1] a_{1,2}[0,0]-a_{1,2}[-1,0] a_{1,2}[0,1]$

$$
\begin{aligned}
& \mathrm{T}_{2}[2]= \\
& \mathscr{e}^{-\mathrm{r}} 1\left(\mathrm{a}_{1,2}[-1,1] \mathrm{a}_{1,2}[0,0]-\mathrm{a}_{1,2}[-1,0] \mathrm{a}_{1,2}[0,1]\right) / \\
& \quad\left(-\mathrm{a}_{1,2}[0,1] \mathrm{a}_{1,2}[1,0]+\mathrm{a}_{1,2}[0,0] \mathrm{a}_{1,2}[1,1]\right) \\
& \frac{e^{-r} 1\left(a_{1,2}[-1,1] a_{1,2}[0,0]-a_{1,2}[-1,0] a_{1,2}[0,1]\right)}{-a_{1,2}[0,1] a_{1,2}[1,0]+a_{1,2}[0,0] a_{1,2}[1,1]}
\end{aligned}
$$

FullSimplify $\left[\beta_{1}[2]\right]$

$$
\begin{aligned}
& \left.e^{2 r} r_{1}-r_{2} a_{1,2}[0,0]\left(a_{2}[0] a_{1,2}[1,-1]-a_{2}[-1] a_{1,2}[1,0]\right)\right) / \\
& \left(a_{1,2}[0,0]\left(a_{1}[0]\left(-a_{2}[0] a_{1,2}[0,-1]+a_{2}[-1] a_{1,2}[0,0]\right)-a_{1,2}[-1,1] a_{1,2}[1,-1]\right)+\right. \\
& \left.\quad\left(\left(a_{1}[-1] a_{2}[0]+a_{1,2}[-1,1]\right) a_{1,2}[0,-1]-a_{1}[-1] a_{2}[-1] a_{1,2}[0,0]\right) a_{1,2}[1,0]\right) \\
& \mathrm{Znl}=\left(a_{1,2}[0,0]\left(a_{1}[0]\left(-a_{2}[0] a_{1,2}[0,-1]+a_{2}[-1] a_{1,2}[0,0]\right)-a_{1,2}[-1,1] a_{1,2}[1,-1]\right)+\right. \\
& \left.\quad\left(\left(a_{1}[-1] a_{2}[0]+a_{1,2}[-1,1]\right) a_{1,2}[0,-1]-a_{1}[-1] a_{2}[-1] a_{1,2}[0,0]\right) a_{1,2}[1,0]\right) ;
\end{aligned}
$$

FullSimplify|

$$
\begin{aligned}
& \mathrm{Znl} / \mathrm{a}_{1,2}[1,-1] \rightarrow a_{1,2}[0,0]+a_{1}[0] a_{2}[-1] \\
& \quad \quad / a_{1,2}[0,-1] \rightarrow a_{1,2}[-1,0]+a_{1}[-1] a_{2}[-1] / a_{1}[-1] a_{2}[0] \rightarrow a_{1,2}[0,0]-a_{1,2}[-1,1] / \\
& \left.a_{1,2}[1,0] \rightarrow a_{1,2}[0,1]+a_{1}[0] a_{2}[0]\right] \\
& a_{1,2}[0,0]\left(-a_{1}[0] a_{2}[-1]\left(a_{1}[-1] a_{2}[0]+a_{1,2}[-1,1]\right)+\right. \\
& \left.\quad\left(a_{1}[0] a_{2}[-1]-a_{1,2}[-1,1]\right) a_{1,2}[0,0]+a_{1,2}[-1,0] a_{1,2}[0,1]\right)
\end{aligned}
$$

FullSimplify[ $\%$ /. $\left.a_{1}[-1] a_{2}[0] \rightarrow a_{1,2}[0,0]-a_{1,2}[-1,1]\right]$
$a_{1,2}[0,0]\left(-a_{1,2}[-1,1] a_{1,2}[0,0]+a_{1,2}[-1,0] a_{1,2}[0,1]\right)$

$$
\begin{aligned}
\beta_{1}[2]= & \mathscr{e}^{2} \mathrm{r}_{1}-\mathrm{r}_{2}\left(\mathrm{a}_{2}[0] \mathrm{a}_{1,2}[1,-1]-\mathrm{a}_{2}[-1] \mathrm{a}_{1,2}[1,0]\right) / \\
& \left(-\mathrm{a}_{1,2}[-1,1] \mathrm{a}_{1,2}[0,0]+\mathrm{a}_{1,2}[-1,0] \mathrm{a}_{1,2}[0,1]\right) ;
\end{aligned}
$$

FullSimplif $y$ [ $\left.\beta_{2}[2]\right]$
$\frac{a^{-r} 1^{+2 r} r_{2}\left(a_{1}[0] a_{1,2}[0,0]-a_{1}[-1] a_{1,2}[1,0]\right)}{a_{1,2}[0,0] a_{1,2}[1,-1]-a_{1,2}[0,-1] a_{1,2}[1,0]}$
FullSimplify $\left[\beta_{1,2}[2]\right]$

$$
\begin{aligned}
& \left(e^{r} 1^{+r} 2\left(a_{1}[0] a_{2}[0] a_{1,2}[0,0]-\left(a_{1}[-1] a_{2}[0]+a_{1,2}[-1,1]\right) a_{1,2}[1,0]\right)\right) / \\
& \left(a_{1,2}[0,0]\left(a_{1}[0]\left(a_{2}[0] a_{1,2}[0,-1]-a_{2}[-1] a_{1,2}[0,0]\right)+a_{1,2}[-1,1] a_{1,2}[1,-1]\right)-\right. \\
& \left.\left(\left(a_{1}[-1] a_{2}[0]+a_{1,2}[-1,1]\right) a_{1,2}[0,-1]-a_{1}[-1] a_{2}[-1] a_{1,2}[0,0]\right) a_{1,2}[1,0]\right) \\
& \text { FullSimplify }\left[\% / \mathrm{a}_{1,2}[1,-1] \rightarrow \mathrm{a}_{1,2}[0,0]+\mathrm{a}_{1}[0] \mathrm{a}_{2}[-1]\right. \\
& f \cdot \mathrm{a}_{1,2}[0,-1] \rightarrow \mathrm{a}_{1,2}[-1,0]+\mathrm{a}_{1}[-1] \mathrm{a}_{2}[-1] / \cdot \mathrm{a}_{1,2}[1,0] \rightarrow \mathrm{a}_{1,2}[0,1]+\mathrm{a}_{1}[0] \mathrm{a}_{2}[0] \\
& \left.f . \mathrm{a}_{1}[-1] \mathrm{a}_{2}[0] \rightarrow \mathrm{a}_{1,2}[0,0]-\mathrm{a}_{1,2}[-1,1]\right] \\
& \begin{array}{r}
\left(a^{r} 1^{+r} 2 a_{1,2}[0,1]\right) /\left(-a_{1}[0] a_{2}[-1]\left(a_{1}[-1] a_{2}[0]+a_{1,2}[-1,1]\right)+\right. \\
\left.\left(a_{1}[0] a_{2}[-1]-a_{1,2}[-1,1]\right) a_{1,2}[0,0]+a_{1,2}[-1,0] a_{1,2}[0,1]\right)
\end{array} \\
& \text { FullSimplif }\left[\% / \mathrm{a}_{1}[-1] \mathrm{a}_{2}[0] \rightarrow \mathrm{a}_{1,2}[0,0]-\mathrm{a}_{1,2}[-1,1]\right] \\
& e^{\mathrm{r}^{1+\mathrm{r}}} \mathrm{a}_{1,2}[0,1] \\
& -a_{1,2}[-1,1] a_{1,2}[0,0]+a_{1,2}[-1,0] a_{1,2}[0,1] \\
& \beta_{1,2}[2]=\frac{e^{r_{1}+r_{2}} a_{1,2}[0,1]}{-a_{1,2}[-1,1] a_{1,2}[0,0]+a_{1,2}[-1,0] a_{1,2}[0,1]} \\
& e^{r_{1}+\mathrm{r}_{2}} \mathrm{a}_{1,2}[0,1] \\
& -a_{1,2}[-1,1] a_{1,2}[0,0]+a_{1,2}[-1,0] a_{1,2}[0,1] \mid
\end{aligned}
$$

At that point we stop the procedure, but it is obvious that it can easily be continued for any step and the resulting formulas correspond to those from [15].

As it is seen from formulas for algebras of the rank higher than two, the number of corresponding Backlund transformations of the initial problem solutions will be equal to the rank of the algebra. Thus, it is necessary only to overcome the routine calculations using Mathematica 4-0 software.
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# HIGH SENSITIVE $p-\mathrm{Cd}_{\mathrm{x}} \mathrm{Hg}_{1-\mathrm{x}} \mathrm{Te}$ ( $\mathrm{x}=\mathbf{0 . 2 3 - 0 . 3 ) ~ B A S E D}$ PHOTOCONDUCTOR WITH SURFACE CONVERSION LAYER 

N.J. ISMAYILOV, E.K. HUSEYNOV, A.A. ALIYEV, I.S. HASANOV, Sh.M. GULIYEV, Sh.O. EMINOV<br>Institute of Physics, National Academy of Sciences of Azerbaijan,<br>H. Javid Avenue, 33, AZ-1143, Baku, Azerbaijan<br>ismailovnamik@yahoo.com


#### Abstract

The experimental results of study for photoelectric property of $\mathrm{p}-\mathrm{Cd}_{x} \mathrm{Hg}_{1-x} \mathrm{Te}(x=0.24-0.3)$ photoconductors with conversion surface layer created by plasma treatment are presented. It is shown, that the potential barrier between p - and n -layers is reason of the sensitivity and response time $\tau_{\mathrm{s}}$ enhancement of this photoconductors at $\mathrm{T}=80 \mathrm{~K}$. The sensitivity and response time $\tau_{\mathrm{s}}$ enhance inverse proportional to background illumination level. The sensitivity $R_{v i}\left(\lambda_{m}\right)=4 \cdot 10^{5} \mathrm{~V} / \mathrm{W}$ and $\tau_{s}=(0.8-1) 10^{-5} \mathrm{~s}$ are obtained for sensitive area $1 \times 1 \mathrm{~mm}^{2}$ for a $60{ }^{0}$ field of view and $T=80 K$.


Keywords: infrared detector, photoconductivity, responsivity, response time.
PACS: 73.50.Pz, 73.50.Gr, 73.61.Ga, 73.40.Gv

## 1. INTRODUCTION

The limit performance of photoconductor mostly determined by the lifetime of excess carriers, the value of which, in turn, depends on the mechanisms of their recombination in bulk and on the surface of the semiconductor.

The performance of $\quad \mathrm{Hg}_{1-\mathrm{x}} \mathrm{Cd}_{\mathrm{x}} \mathrm{Te}$ infrared photoconductors is strongly dependent on surface condition because of they has a highly reactive surface [1,2]. Surface recombination reduces the total number of steady state excess carriers by effectively reducing the average recombination time. A surface band bending in the semiconductor under certain conditions can lead to decrease the surface recombination and significantly increase its responsivity [3]. Surface-controlled photoconductivity has been demonstrated by Kinch [4] on photoconductive element $\sim 20 \mu \mathrm{~m}$ thick, using n-type $\mathrm{Hg}_{1-\mathrm{x}} \mathrm{Cd}_{\mathrm{x}} \mathrm{Te}$ with $x=0.2$ and $x=0.3$. In this MIS structure, the photosignal enhancement for $x=0.3$ composition is observed at 77 K on changing the gate voltage from accumulation to depletion condition. However, for $\mathrm{x}=0.2$ composition, photosignal decreases more than an order of magnitude. This may be relates with high density of surface states and low surface mobility [5].

Another effect, that limits responsivity, is sweep-out of minority carriers [6, 7] related with bipolarity of photoconductivity. At some applied voltage, when minority carriers can drift to ohmic contacts in a time short compared to recombination time, they are removed at an ohmic contact and the density of excess curriers in bulk reduces. This results in limiting the maximum applied voltage and reduction of responsivity.

However, in two-layer photoconductor (PC) in which the thin photoconductive layer is created on another layer with revers conductivity and separate from it by p-n junction, the both effects can be eliminated. In this case, like in p-n junction, the influence of surface recombination can be significantly reduced and as shown in [8], the presence of the quasi-neutral regions practically does not affect the responsivity of the structure and
photoconductivity is monopolar. Therefore, it is interesting experimentally to study of such two-layer structure based on $\mathrm{Hg}_{1-\mathrm{x}} \mathrm{Cd}_{\mathrm{x}} \mathrm{Te}$ and to establish the condition of achievement its high responsivity.

This paper presents the results of an experimental study of a thin n-type layer photoconductivity obtained by plasma treatment on the surface of $\mathrm{p}-\mathrm{Hg}_{1-\mathrm{x}} \mathrm{Cd}_{\mathrm{x}} \mathrm{Te}$ ( $x=0.24-0.3$ ) bulk. It is considered the plasma etching has a softer effect on the material, since midget ion energy (order of tens of eV or less) avoids the generation of radiation-induced defects [9]. This method allows obtain very high quality layers of n-type conductivity with the high charge carrier mobility and is used for the manufacture of photodiodes and photoconductors [9, 10].

## 2. METHOD OF EXPERIMENT

For sample preparation we used vacancy-doped and $\mathrm{Cu}, \mathrm{Au}$ doped p-type conductivity $\mathrm{Hg}_{1-\mathrm{x}} \mathrm{Cd}_{\mathrm{x}} \mathrm{Te}$ ( $\mathrm{x}=0.23-$ 0.3 ) single crystals with $\mathrm{N}_{\mathrm{A}^{-}} \mathrm{N}_{\mathrm{D}}=(0.5-2) \cdot 10^{16} \mathrm{~cm}^{-3}$ и $\mu_{\mathrm{p}}=$ (4-6) $\cdot 10^{2} \mathrm{~cm}^{2} / \mathrm{B} \cdot \mathrm{s}$ at $\mathrm{T}=80 \mathrm{~K}$. The $\mathrm{Hg}_{1-\mathrm{x}} \mathrm{Cd}_{\mathrm{x}} \mathrm{Te}$ slab was bonding using low- temperature epoxy on the substrate and thinned to of $0.1-0.3 \mathrm{~mm}$. The sample surface was mechanical polishing and then etching in a $4 \%$ solution of bromine in methanol and washing with methanol. The dimensions of the sensitive area were $5 \times 1 \mathrm{~mm}$ and 1 x 1 mm . As an ohmic contact to p-type chemical deposition of gold, and to the n-type the indium by vacuum thermal deposition was used. To avoid damages during wire bonding the metallisation continued on substrate as it is shown in fig.1. ZnS with the thickness of about 0.5 microns was used as passivation layer.

Plasma etching was carried out immediately after chemical etching in a vacuum chamber at $\mathrm{T}=300 \mathrm{~K}$ with a current density of high-frequency discharge (40 MHz ) plasma $6-10 \mu \mathrm{~A} / \mathrm{cm}^{-2}$ for 1-2 min. We assume the profile of the distribution of charge carriers in the depth, as it is well known [9,10], has a form which is characteristic for the n+-n-p structure (fig.2,).To determine the concentration of free electrons in the $n$ layer specifically mesa structured photodiode was prepared.


Fig.1. Schematic illustration of investigated photoconductor.


Fig.2. Impurity profile in the transverse cross section of twolayer photoconductor and corresponding it energy diagram in $\mathrm{p}-\mathrm{Hg}_{1-\mathrm{x}} \mathrm{Cd}_{\mathrm{x}} \mathrm{Te}$.

From C-V measurement is found that the n-layer is characterized by carrier concentration with an order of magnitude lower than the p-region of the sample, and the barrier height $\varphi_{b}=0.2-0.16 \mathrm{eV}$, depending on the composition and concentration of charge carriers. Photovoltage produced by background radiation reaches the value of 110 me , which indicates on high quality of the $n^{+}-n p$ junction.

Necessary for the analyses of photo effect the concentration and mobility of the majority charge carriers were determined based on measurements of the Hall effect and conductivity. Bulk lifetime $\tau_{\mathrm{v}}$ was determined by the method of compensation of PEM effect with photoconductivity [8]. Measurement of the photoconductivity spectra was carried out using a grating monochromator at 1.2 kHz modulation frequency of radiation from globar. Surface lifetime $\tau_{\mathrm{s}}$ determined from the decay of photoconductivity signal in pulsed illumination of the GaAs LED. To measure the absolute value of the photoconductivity signal the radiation from a blackbody with $T=500 \mathrm{~K}$ and calibrated amplifier with a gain of $10^{5}$ was used.

## 2. RESULTS AND DISCUSSION

The analysis of results we carry out by comparison the photoelectric properties of uniform p-type PC with that of two-layer PC fabricated by the formation on its surface a thin layer of n-type conductivity. In fig. 3 it is
shown the spectral dependence of the photoconductivity of the samples before and after the formation of n-layer at $T=80 \mathrm{~K}$. As it can be seen from the figure, the spectral dependence of two-layer PC increases in shortwavelength region, whereas the maximum sensitivity is shifted somewhat toward shorter wavelengths in comparison with the p-type PC. Its surface response time $\tau_{\mathrm{s}}$ decrease in comparison with the value of p-type PC. Despite this, the signal response of two- layer PC under total flux of the background radiation increases in 40-80 times. This is achieved mainly due to a significant increase of the bias voltage up to Joule heating, while for p-type PC the photo signal $U_{s}$ saturates at bias voltage $U_{b}=0,16-0.9 \mathrm{~V}$ due to extraction effect of excess carriers (fig.4). With reducing of background flux, using a cooled diaphragm, the surface response time $\tau_{\mathrm{s}}$ and thus photo signal increase more than tenfold, as it is shown in the fig. 4 .


Fig.3. The spectral dependence of the sensitivity of the $\mathrm{p}-\mathrm{Hg}_{1-\mathrm{x}} \mathrm{Cd}_{\mathrm{x}} \mathrm{Te}$ photoconductors before (1) and after (2) forming of a surface layer of n-type conductivity for $x=0.24$ (a) at $\mathrm{T}=80 \mathrm{~K}$.


Fig.4. The dependence of response signal on applied voltage for $\mathrm{p}-\mathrm{Hg}_{1-\mathrm{x}} \mathrm{Cd}_{\mathrm{x}} \mathrm{Te}(x=0.28) \mathrm{PC}(1,3)$ with $p_{0}=8 \cdot 10^{-15} \mathrm{~cm}^{-3}, \tau_{n}=1,2 \mu \mathrm{~s}$ (1) and two-layer PC $(2,3)$ under background radiation flux


The observed features are due to the presence of the p-n junction space charge region (SCR) in the interface region (fig.5). Field of SCR spatially separates generated electron-hole pairs and act as a potential barrier $\varphi_{b}$ for their recombination. The electrons generated by incident photon flux $\Phi$ within SCR and within the diffusion length of electron $L_{\mathrm{n}}$ from it in the p-region are accumulated at the boundary n-layer with SCR and cause compensation of acceptor's charge in it, while photoholes on the boundary of SCR and quasi-neutral p-type region. The width of SCR $a$ in this case is decreasing, while the quasi-neutral region of n-layer $d_{n}$ is increasing. Thus, the conductivity modulation of n-layer is done only by photoelectrons and therefore, the photoconductivity is unipolar.

The recombination rate of excess curriers determined by the response time constant $\tau_{b}=R_{d} C_{d}$, where $R_{d,}, C_{d}$ are differential resistance and a barrier capacity of the p-n junction, respectively. Under thermal equilibrium time constant is controlled by the dominant dark current source that is by the diffusion, depletion region, surface or tunnel current. Assuming the dominant mechanism is diffusion, response time may be determined by the formula [8] below:

$$
\begin{equation*}
\tau_{\mathrm{b}}=\frac{k T}{2 \varphi_{b}^{\prime}} \frac{N_{d} N_{a}}{N_{a}+N_{d}} \frac{a}{a+L} \frac{1}{g_{b}+v} \tag{1}
\end{equation*}
$$

where $k$ is Boltzmann's constant, $T$ is absolute temperature, $N_{a}, N_{d}$ are concentrations of acceptors and donors in the p and n-layers, respectively, $\varphi_{b}{ }^{r}$ is the potential barrier under background radiation, $v$ is the effective rate of heat generation in the quasi-neutral regions, $g_{b}=\eta \alpha \Phi_{\mathrm{b}}$ is the rate of generation of carriers background radiation $\Phi_{b}$ is photon flux density of the background radiation, $\eta$ is quantum efficiency, $\alpha$ is radiation absorption coefficient.

For the calculation of the voltage spectral responsivity of two-layer PC the expression obtained in [8] should be used:
$R_{v i}=\frac{\eta \lambda(a+L) \alpha \tau U_{n}}{h c A N_{d}}\left[d_{n}+\frac{a}{2}\left(\frac{\pi \cdot k T}{\varphi_{b}} \frac{N_{a}}{N_{a}+N_{d}}\right)^{1 / 2}\right]^{-1}$
where $d_{n}$ is the thickness of n -layer, $\lambda$-wavelength of the incident radiation, $h$-Planck's constant, $c$-is the speed of light, $A$ is the area of the sensitive area, $U_{n}$ is applied voltage.

The observed features of the spectral characteristics of responsivity are inherent to photodiodes and are well described by the formula $\eta=\eta_{0}\left(1-e^{-\alpha d_{n}} /(1+\alpha L)\right)$ [13], where $\eta_{o}$ - is the internal quantum efficiency. Here, to explain the response enhancement in the short wave region, we must prior to take account, that surface recombination is reduced by transvers field on the surface provided by $\mathrm{n}^{+}-\mathrm{n}$ accumulation layer [14]. If surface mobility of charge curriers is the same as in the bulk, so signal response enhancement at $h v>1,4 E g$ occurs due to increasing of $\eta_{o}$, as we assume.

With decreasing of $d$ less than the bipolar diffusion length $L$, begins to affect recombination of excess carriers on the back and front surfaces of the sample. Therefore, the optimal thickness of the experimental samples is taken $d \leq L$.

For uniform p-type PC the responsivity is expressed as [12]:

$$
\begin{equation*}
R_{v p}=\frac{\eta \lambda\left(\mu_{n} \tau_{n}+\mu_{p} \tau_{p}\right) \cdot U_{p}^{*}}{h c \cdot l \cdot w \cdot d \cdot\left(\mu_{n} n+\mu_{p} p\right)} \tag{4}
\end{equation*}
$$

here $\mu_{n}, \mu_{p}$-mobility of electrons and holes, and $\tau_{n}, \tau_{p^{-}}$ their lifetimes, respectively, $\eta=\eta_{0}\left(1-e^{-\alpha d}\right)$-for uniform photoconductors [14].

Since $\mu_{n} \tau_{n} » \mu_{p} \tau_{p}$, then in case of $\mu_{n} n \ll \mu_{p} p$, we have:

$$
\begin{equation*}
R_{v p}=\frac{\eta \lambda b \tau_{n} U_{p}^{*}}{h c \cdot l \cdot w \cdot d \cdot p} \tag{5}
\end{equation*}
$$

where $b=\mu_{n} / \mu_{h}$, from (3) and (5) we have a ratio for the maximum of responsivity:

$$
\begin{equation*}
\frac{R_{n}}{R_{p}}=\frac{p \cdot d}{b \cdot n_{n} \cdot d_{n}} \frac{\tau_{b}}{\tau_{n}} \frac{U_{n}}{U_{p}^{*}} \tag{6}
\end{equation*}
$$

Numerically evaluating this relationship, we note that in our case $p \cdot d / n_{n} \cdot d_{n} \approx 10^{3}$, and $\tau_{b} / \tau_{n} « 1$. The high intensity of the background radiation results in a significant lowering of the potential barrier height ( $\Delta \varphi_{b} \gg k T / q$ ), as a result of the rate of recombination of excess carriers in the SCR can exceed the rate of them recombination on the surface and in the bulk. In this case, $\tau_{b}$ is less than the bulk lifetime $\tau_{n}$. Calculation based on the formula (2) gives $\tau_{b}=(4-8) \cdot 10^{-8} \mathrm{~s}$, which is $10-30$ times less than $\tau_{n}$ for vacancy-doped and specially doped samples.


Fig.5. Energy diagram in $\mathrm{p}-\mathrm{Hg}_{1-\mathrm{x}} \mathrm{Cd}_{\mathrm{x}} \mathrm{Te}$.
Nevertheless, as result of $R_{n}\left(\lambda_{m}\right) / R_{p}\left(\lambda_{m}\right) » 1$. In accordance with formula (2), $\tau_{b}$ increases inversely proportional to the intensity of the background radiation. In this case, responsivity should also to grow, which is observed experimentally.


Fig.6. Dependence of responsivity $(1,2,3)$ and response time $\tau_{b}\left(2^{\prime}, 3^{\prime}\right)$ on the background radiation flux for $\mathrm{Hg}_{1-\mathrm{x}} \mathrm{Cd}_{\mathrm{x}} \mathrm{Te}$ photoconductors with $\mathrm{x}=0.28$ and sensitive area $1 \times 1 \mathrm{~mm}^{2}$ at $T=80 \mathrm{~K}$. (1) corresponds to the measured responsivity of uniform p-type PC with $\tau_{n}=1,2 \mu \mathrm{~s},\left(2,2^{\prime}\right)$ calculated and $\left(3,3^{\prime}\right)$ values for two-layer PC.

The measured and calculated responsivity and response time versus the background radiation flux for $\mathrm{Hg}_{1-\mathrm{x}} \mathrm{Cd}_{\mathrm{x}} \mathrm{Te}$ photoconductor with $x=0.28$ are shown in fig.6. As it is seen, the $R_{p}$ is not varied, while $R_{n}$ and $\tau_{b}$ increase with lowering of background radiation flux. However, for $\Phi_{b}<10^{14} \mathrm{~cm}^{-2} \mathrm{~s}^{-1}$ the $R_{n}$ and $\tau_{b}$ have constant
value. It is may be caused by surface leakage current due to non-passivated backside of sample that is limited $R_{d}$, hence $\tau_{b}$ and $R_{n}$. It is possible to achieve more high responsivity at low background radiation flux, probably, if to use epitaxial $\mathrm{Hg}_{1-\mathrm{x}} \mathrm{Cd}_{\mathrm{x}} \mathrm{Te}$ film passivated by CdTe or graded layer. For $\mathrm{Hg}_{1-\mathrm{x}} \mathrm{Cd}_{\mathrm{x}} \mathrm{Te}(x=0,28)$ two-layer PC with $1 \times 1 \mathrm{~mm}^{2}$ sensitive area at an field of view $\theta=50^{\circ}$ achieved the following parameters: $R_{v i}\left(\lambda_{m}\right)=4 \cdot 10^{6} \mathrm{~V} / \mathrm{W}$, $\tau_{s}=(0.8-1) \cdot 10^{-5} \mathrm{~s}$ at $T=80 \mathrm{~K}$.

## CONCLUSION

In a processing in the plasma of high-frequency discharge with surface of $\mathrm{p}-\mathrm{Hg}_{1-\mathrm{x}} \mathrm{Cd}_{\mathrm{x}} \mathrm{Te}(x=0.23-0.3)$, converted layers with thickness of $2-3 \mu \mathrm{~m}$ ave been obtained. The layers were characterized by a low concentration of charge carriers in comparison with their concentration in the p-region and form a high quality $\mathrm{n}+$ -$n-p$ junction. Due to the recombination potential barrier, this way obtained two-layer photoconductor have a high responsivity, which increases as the level of background radiation decreases. High responsivity, ease of manufacture and suitability for the production of lowerquality p-type material, allow us to consider it as an alternative to other types of photodetectors based on $\mathrm{Hg}_{1-\mathrm{x}} \mathrm{Cd}_{\mathrm{x}} \mathrm{Te}$.
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# PHASE TRANSITION IN ISING MAGNETIC HEXAGONAL NANOWIRES: EFFECTIVE- FIELD THEORY APPROACH 

V.A. TANRIVERDIYEV, V.S. TAGIYEV, G.G. KERIMOVA<br>Institute of Physics of the National Academy of Sciences of Azerbaijan, Baku Az-1143, Baku, H.Javid ave.33, E-mail: Vahid_tanriverdi @yahoo.com


#### Abstract

By means of the effective-field theory with correlations, the critical behavior of hexagonal magnetic nanowire is considered. The transition temperature $T_{c}$ for a spin- $1 / 2$ hexagonal Ising nanowires are calculated as a function of exchange constant by the transfer matrix method. The effects of surface modification are also studied numerically.


Keywords: Nanowires, effective-field theory, phase transition. PACS: 75.70. Ak

## 1. INTRODUCTION

In resent years, the number of theoretical and experimental investigations of various structures in the nanometer scale, such as nanowires, nanotubes, nanofilms, nanoparticles, nanobelts etc. have increased [1-4]. Studying the properties of these nanostructures provides considerable insight for possible applications. One of the potentially interesting aspects of nanophysics is related to magnetic phenomena. Nano-scale materials can be used in biomedical applications, nonlinear optics, magnetic recording media and electronic devices, sensors, environmental remediation and etc [5-7]. Resent advances in the microprocessing technology enable us to fabricate magnetic materials with various sample structures on nanometer scale. For example, Ebels and Wigen have created arrays of very long ferromagnetic nanowires of Ni , permalloy and Co, with diameters in the range of 35 to 500 nm and have carried out ferromagnetic resonance studies of their samples [8].

Different types of theoretical techniques, such as Green functions method, mean-field theory, effective field theory (EFT) with correlations, Monte Carlo simulations, transfer matrix formalism, recurrence relations technique have been used for the investigations of magnetic properties of nanomaterial [9-11]. On the other hand, various geometric configurations can be modeled as having a chosen shape and size cross section with a finite number spins arranged [12-13].

In comparison with bulk systems one finds unexpected and interesting properties in the various layered structures. The critical behavior of magnetic films and superlattice have been examined, either experimentally or theoretically [10-11]. It is well known that the bulk transition temperature is approximately proportional to the exchange coupling. The atoms at the surface are in different environment, and exchange constant between them may differ from those in the bulk. From the works devoted to the magnetic properties of surfaces, we can see that a magnetically ordered surface
can coexist with a magnetically disordered bulk phase [14-15].

In this paper, we are concerned with phase transition in hexagonal magnetic nanowire (HMN). We study them within the framework of the effective-field theory approach. In Section 2, we present the model of HMN and derive the equation that determines the transition temperatures. The equation is general one for arbitrary exchange interaction. Numerical results and discussion are given in section 3.

## 2. MODEL AND FORMALISM

The schematic representation of hexagonal magnetic nanowire (HMN) model with core/shell structure is shown in fig.1.
(Front view)

(Side view)


Fig. 1. Model of hexagonal ferromagnetic nanowires. The nanowires are infinite in the direction perpendicular to the axes z .

The exchange constant between two nearest-neighbor magnetic atoms at the surface shell and the core is denoted by $J$, and $J_{s}$ is exchange constants between spins at the surface shell in intralayer. On the other hand each magnetic atom connects to the two nearest-neighbor magnetic atoms along the wire, and corresponding exchange constants between spins at the surface shell and the core are $Y_{s}$ and $Y$, respectively.

The Ising Hamiltonian of the system can be written in the form

$$
\begin{equation*}
H=-\sum_{\substack{n, \tau, \tau^{\prime} \\\left(\tau \neq \tau^{\prime}\right)}} J_{n, n}^{\tau, \tau^{\prime}}\left(S_{n}^{\tau} S_{n}^{\tau^{\prime}}\right)-\sum_{n, \tau}\left(Y_{n, n-1}^{\tau, \tau}\left(S_{n}^{\tau} S_{n-1}^{\tau}\right)+Y_{n, n+1}^{\tau, \tau}\left(S_{n}^{\tau} S_{n+1}^{\tau}\right)\right) \tag{1}
\end{equation*}
$$

where the first term describes exchange interactions inside atomic layer, the second term describes exchange interactions between neighboring atomic layers. The external magnetic field is neglected for simplicity. Here, n is the index of atomic layer, $\tau$ describes the position of a
lattice site in this layer. The axis $z$ of the coordinate system is along the nanowires under study.

To evaluate the mean spin $m_{n}^{\tau}=\left\langle S_{n}^{\tau}\right\rangle \quad(\tau=1,2, \ldots 7)$, we start with the exact Callen identity [16],

$$
\begin{equation*}
m_{n}^{(\tau)}=\left\langle\tanh \left[\left(\sum_{\tau^{\prime}} J_{n, n}^{\tau, \tau^{\prime}} m_{n}^{\left(\tau^{\prime}\right)}+Y_{n, n+1}^{\tau, \tau} m_{n+1}^{(\tau)}+Y_{n, n-1}^{\tau, \tau} m_{n-1}^{(\tau)}\right) / k T\right]\right\rangle \tag{2}
\end{equation*}
$$

where k is Boltzman constant and T is temperature. According to the framework of EFT, the average atomic magnetization $m_{C}$ at the core and magnetization $m_{S}$ at the shell surface are given

$$
\begin{equation*}
m_{c}=\left.\left[\cosh (Y D)+m_{c} \sinh (Y D)\right]^{2} \cdot\left[\cosh (J D)+m_{s} \sinh h(J D)\right]^{6} \tanh (\beta x)\right|_{x=0} \tag{3a}
\end{equation*}
$$

$$
\begin{equation*}
m_{s}=\left.\left[\cosh \left(Y_{s} D\right)+m_{s} \sinh h\left(Y_{s} D\right)\right]^{2}\left[\cosh \left(J_{s} D\right)+m_{s} \sinh h\left(J_{s} D\right)\right]^{2}\left[\cosh h(J D)+m_{c} \sinh h(J D)\right] \tanh (\beta x)\right|_{x=0} \tag{3b}
\end{equation*}
$$

where $\beta=1 / k T, D=\partial / \partial x$ is differential operator and satisfies the relation

$$
\begin{equation*}
\exp (\alpha D) f(x)=f(x+\alpha) \tag{4}
\end{equation*}
$$

As the temperature becomes higher than the critical temperature $T_{c}$ the whole system becomes demagnetized and the average atomic magnetization approaches zero. Near the critical temperature $T_{c}$ mean spins $m_{C(S)}$ become small. Consequently, all terms of the order higher than linear in eqs. (3) can be neglected and eqs.(3) can be rewritten as follows:

$$
\begin{align*}
& m_{c}=\left.\left[\cosh ^{2}(Y D)+m_{c} \sinh (2 Y D)\right] \cdot\left[\cosh ^{6}(J D)+3 \cosh ^{4}(J D) \sinh (2 J D) m_{s}\right] \tanh (\beta x)\right|_{x=0}  \tag{5a}\\
& m_{s}=\left.\left[\cosh ^{2}\left(Y_{s} D\right)+m_{s} \sinh \left(2 Y_{s} D\right)\right] \cdot\left[\cosh ^{2}\left(J_{s} D\right)+m_{s} \sinh \left(2 J_{s} D\right)\right] \cdot\left[\cosh (J D)+m_{c} \sinh (J D)\right] \tanh (\beta x)\right|_{x=0} \tag{5b}
\end{align*}
$$

The set of equations (5) reduces to the secular equation

$$
\left\lvert\, \begin{array}{cc}
1-\lambda_{1} & -\lambda_{2}  \tag{6}\\
-\gamma_{2} & 1-\gamma_{1}
\end{array}=0\right.
$$

where the coefficients have the following form:

$$
\begin{aligned}
\lambda_{1}= & {[20 \tanh (2 Y \beta)+15\{\tanh (2 Y-2 J) \beta+\tanh (2 Y+2 J) \beta\}+6\{\tanh (2 Y-4 J) \beta+\tanh (2 Y+4 J) \beta\}+} \\
& +\tanh (2 Y-6 J) \beta+\tanh (2 Y+6 J) \beta] / 64 \\
\lambda_{2}= & {[30 \tanh (2 J \beta)+24 \tanh (4 J \beta)+6 \tanh (6 J \beta)+15\{\tanh (2 J-2 Y) \beta+\tanh (2 J+2 Y) \beta\}+} \\
& +12\{\tanh (4 J-2 Y) \beta+\tanh (4 J+2 Y) \beta\}+3\{\tanh (6 J-2 Y) \beta+\tanh (6 J+2 Y) \beta\}] / 64 \\
\gamma_{1}= & {\left[2 \tanh \left(2 Y_{s}-J\right) \beta+2 \tanh \left(2 Y_{s}+J\right) \beta+\tanh \left(2 Y_{s}-J-2 J_{s}\right) \beta+\tanh \left(2 Y_{s}-J+2 J_{s}\right) \beta+\tanh \left(2 Y_{s}+J-2 J_{s}\right) \beta+\right.} \\
& +\tanh \left(2 Y_{s}+J+2 J_{s}\right) \beta+2 \tanh \left(2 J_{s}-J\right) \beta+2 \tanh \left(2 J_{s}+J\right) \beta+\tanh \left(2 J_{s}-J-2 Y_{s}\right) \beta+\tanh \left(2 J_{s}-J+2 Y_{s}\right) \beta+ \\
& \left.+\tanh \left(2 J_{s}+J-2 Y_{s}\right) \beta+\tanh \left(2 J_{s}+J+2 Y_{s}\right) \beta\right] / 8 \\
\gamma_{2}= & {\left[4 \tanh (J \beta)+2 \tanh \left(J-2 Y_{s}\right) \beta+2 \tanh \left(J+2 Y_{s}\right) \beta+2 \tanh \left(J-2 J_{s}\right) \beta+2 \tanh h\left(J+2 J_{s}\right) \beta+\right.} \\
& \left.+\tanh \left(J-2 Y_{s}+2 J_{s}\right) \beta+\tanh \left(J+2 Y_{s}-2 J_{s}\right) \beta+\tanh \left(J-2 Y_{s}-2 J_{s}\right) \beta+\tanh \left(J+2 Y_{s}+2 J_{s}\right) \beta\right] / 16
\end{aligned}
$$

From the numerical calculation of secular equation (6) we can determine the transition temperature of the HMN as a function of exchange constants (fig. 2).


Fig. 2. Critical temperatures as a function of $Y / J_{a}$, and labeling curves corresponds to a $J_{s} / J=2.5, Y_{s} / J=1$; b, $J_{s} / J=1, Y_{s} / J=1 ; ~ с, ~ J_{s} / J=0.1, Y_{s} / J=1$.

## 3. CONCLUSION

The formalism of transition temperature derivation obtained above is universal and can be used for both ferromagnetic and antiferromagnetic cases. Hence, positive core-shell coupling $(J>0)$ and negative coreshell coupling $(J<0)$ correspond to ferromagnetic interfacial and antiferromagnetic one couplings, respectively. On the other hand, if $Y_{s}>0(Y>0)$ the neighboring spins belonging to different layers on the shell surface (core) are parallel and they show ferromagnetic behavior. If $Y_{s}<0(Y<0)$ their behavior is antiferromagnetic.

As numerically illustration, in Fig. 2, we show the results for the ferromagnetic hexagonal nanowires. The transition temperature (in unit $T=8 J / k$ ) is plotted as function of $Y / J$. The curve labeled b , corresponds to the case at which all exchange constants are equal to each other. When $J_{s}$ increases then the critical temperature increases (the curve labeled a), but when $J_{s}$ decreases (the curve labeled c) then it against decreases. Analysis shows that when the $J_{s}$ and $Y_{s}$ change transition temperatures are same. The cause of this is connection of each surface spin to the two nearest-neighbor magnetic atoms both along the wire $\left(Y_{s}\right)$ and intralayer $\left(J_{s}\right)$.
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# HIGGS BOSON PRODUCTION IN LEPTON COLLISIONS 

S.K. ABDULLAYEV, M.Sh. GOJAYEV, F.A. SADDIGH<br>Baku State University, Az-1148, Z. Khalilov str., 23<br>s_abdullayev@mail.ru, m_qocayev@mail.ru, f_seddig@yahoo.com

In the framework of Standard Model the process of scalar Higgs boson production in $e^{-} e^{+}$-collisions has been investigated: $e^{-} e^{+} \Rightarrow \mathrm{He}^{-} e^{+}$. It is shown that, the annihilation (scattering) diagram is defined by only four helicity amplitudes $F_{L L}^{(a)}, F_{L R}^{(a)}, F_{R L}^{(a)}, F_{R R}^{(a)}\left(F_{L R}^{(b)}, F_{R L}^{(b)}, F_{L L}^{(b)}, F_{R R}^{(b)}\right)$. A compact expressions for the cross sections of the Higgs-strahlung and $Z Z$ fusion mechanisms, including the interference terms, have been derived. Finally extensive numerical applications to $e^{-} e^{+} \Rightarrow \mathrm{He}^{-} e^{+}$reaction in the 500 GeV energy domain are presented.

Keywords: Higgs boson, left and right coupling constants, Weinberg's parameter, Higgs-strahlung mechanism, ZZ fusion mechanism.
PACS: 12.15.-y; 12.15.Mm; 14.70.Hp.

## INTRODUCTION

The Standard Model (SM) to describe the strong and electroweak interactions between quarks and leptons, is based on the gauge symmetry group $S U(3)_{C} \times S U(2)_{L} \times U(1)_{Y}$. A cornerstone of the $S M$ is the mechanism of spontaneous electroweak symmetry breaking. An $S U(2)$ doublet of complex scalar field is introduced and its neutral component develops a non-zero vacuum expectation value. As a consequence, the electroweak $S U(2)_{L} \times U(1)_{Y}$ symmetry is spontaneously broken to the electromagnetic $U(1)_{\mathrm{Q}}$ symmetry. Three of the four degrees of freedom of the doublet scalar field are absorbed by the $W^{ \pm}$and $Z$ weak vector bosons to form their longitudinal polarizations and to acquire masses. The remaining degree of freedom corresponds to a scalar particle, the Higgs boson.

The high-precision measurements carried out at SLC, LEP, Tevatron and established that the couplings of quarks and leptons to the electroweak gauge bosons and the trilinear couplings among vector bosons agree with those predicted by the SM. The only sector of the model which has not yet been probed in a satisfactory way is the scalar sector. Some experiments are carried out for the discovery of Higgs boson in different experimental labs. Finally in LHC new information are received concerning the existence of Higgs boson with the mass of 125 GeV [1-3]. So the channels which give rise to Higgs bosons have got more attensions [2-11].

In this work the annihilation of $e^{-} e^{+}\left(\mu^{-} \mu^{+}\right)$pair with longitudinal polarization is studied for the sake of production of Higgs boson and $e^{-} e^{+}\left(\mu^{-} \mu^{+}\right)$ pairs:

$$
\begin{equation*}
e^{-}+e^{+} \Rightarrow H+e^{-}+e^{+} \tag{1}
\end{equation*}
$$

## 1. The Higgs-strahlung mechanism.

The Feynman diagrams for the process (1) are shown in Fig. 1 (the momentum and helicity of the particles are shown in parentheses). First diagram is the Higgs-strahlung diagram i.e. $e^{-} e^{+}$-pairs first annihilate to $Z^{0}$ boson and $Z^{0}$ in turn transforms to $e^{-} e^{+}$-pair while emitting Higgs boson.

The helicity is conserved at high energy. The conservation of helicity imply that $e^{-}$and $e^{+}$colliding at the same vertex to have opposite helicities: $e_{L}^{-} e_{R}^{+}$or $e_{R}^{-} e_{L}^{+}$. So, four helicity amplitudes will correspond to the diagram a): $F_{L L}^{(a)}, F_{L R}^{(a)} F_{R L}^{(a)}$ and $F_{R R}^{(a)}$ (first and second indices indicate the initial and final helicity of electron). These helicity amplitudes are given by following expressions:

$$
\begin{array}{ll}
F_{L L}^{(a)}=D_{Z}(s) D_{Z}(x s) g_{L}^{2}, & F_{L R}^{(a)}=D_{Z}(s) D_{Z}(x s) g_{L} g_{R}  \tag{2}\\
F_{R L}^{(a)}=D_{Z}(s) D_{Z}(x s) g_{R} g_{L} & F_{R R}^{(a)}=D_{Z}(s) D_{Z}(x s) g_{R}^{2}
\end{array}
$$

Here

$$
\begin{equation*}
g_{L}=-\frac{1}{2}+\sin ^{2} \theta_{w}, g_{R}=\sin ^{2} \theta_{w} \tag{3}
\end{equation*}
$$

are the left and right coupling constants for interaction of electron with $Z^{0}$ boson, $\theta_{w}$ is the Weinberg angle,

$$
\begin{equation*}
D_{Z}(s)=\left(s-M_{Z}^{2}\right)^{-1}, \quad D_{Z}(x s)=\left(s x-H_{Z}^{2}+i M_{Z} \Gamma_{Z}\right)^{-1} \tag{4}
\end{equation*}
$$

$\sqrt{s}$ is the total energy of $e^{-} e^{+}$-pair in the center of mass system, $M_{Z}$ and $\Gamma_{Z}$ are the mass and total width of $Z$ boson,

$$
\begin{equation*}
x=1-\frac{2 \omega}{\sqrt{s}}+\frac{M_{H}^{2}}{s}, \tag{5}
\end{equation*}
$$

$\omega$ and $M_{H}$ are the energy and mass of Higgs boson.


Fig. 1. The Feynman diagrams for $e^{-} e^{+} \Rightarrow H e^{-} e^{+}$.
The transition amplitude for the diagram a) we can write as:

$$
\begin{gather*}
M_{a}\left(e^{-} e^{+} \Rightarrow H e^{-} e^{+}\right)=\left(\frac{e}{2 \sin \theta_{w} \cdot \cos \theta_{w}}\right)^{3} \times \\
\times M_{Z}\left\{F_{L L}^{(a)}\left[\bar{v}\left(p_{2}, \lambda_{2}\right) \gamma_{\mu}\left(1+\gamma_{5}\right) u\left(p_{1}, \lambda_{1}\right)\right]\left[\bar{u}\left(q_{1}, h_{1}\right) \gamma_{\mu}\left(1+\gamma_{5}\right) v\left(q_{2}, h_{2}\right)\right]+\right. \\
+F_{L R}^{(a)}\left[\bar{v}\left(p_{2}, \lambda_{2}\right) \gamma_{\mu}\left(1+\gamma_{5}\right) u\left(p_{1}, \lambda_{1}\right)\right]\left[\bar{u}\left(q_{1}, h_{1}\right) \gamma_{\mu}\left(1-\gamma_{5}\right) v\left(q_{2}, h_{2}\right)\right]+ \\
+F_{R L}^{(a)}\left[\bar{v}\left(p_{2}, \lambda_{2}\right) \gamma_{\mu}\left(1-\gamma_{5}\right) u\left(p_{1}, \lambda_{1}\right)\right]\left[\bar{u}\left(q_{1}, h_{1}\right) \gamma_{\mu}\left(1+\gamma_{5}\right) v\left(q_{2}, h_{2}\right)\right]+ \\
\left.+F_{R R}^{(a)}\left[\bar{v}\left(p_{2}, \lambda_{2}\right) \gamma_{\mu}\left(1-\gamma_{5}\right) u\left(p_{1}, \lambda_{1}\right)\right]\left[\bar{u}\left(q_{1}, h_{1}\right) \gamma_{\mu}\left(1-\gamma_{5}\right) v\left(q_{2}, h_{2}\right)\right]\right\} . \tag{6}
\end{gather*}
$$

Let's first calculate the square of amplitude

$$
\begin{align*}
& M_{a}\left(e^{-} e^{+} \Rightarrow H e^{-} e^{+}\right)_{I}=\left(\frac{e}{2 \sin \theta_{w} \cdot \cos \theta_{w}}\right)^{3} \cdot M_{Z} \cdot F_{L L}^{(a)} \times \\
& \times\left[\bar{v}\left(p_{2}, \lambda_{2}\right) \gamma_{\mu}\left(1+\gamma_{5}\right) u\left(p_{1}, \lambda_{1}\right)\right]\left[\bar{u}\left(q_{1}, h_{1}\right) \gamma_{\mu}\left(1+\gamma_{5}\right) v\left(q_{2}, h_{2}\right)\right],  \tag{7}\\
& \left|M_{a}\left(e^{-} e^{+} \Rightarrow H e^{-} e^{+}\right)_{I}\right|^{2}=\left(\frac{e^{2}}{4 x_{w}\left(1-x_{w}\right)}\right)^{3} M_{Z}^{2}\left|F_{L L}^{(a)}\right|^{2} \cdot T_{\mu \nu}^{(1)} \cdot T_{\mu \nu}^{(2)}, \tag{8}
\end{align*}
$$

where $x_{w}=\sin ^{2} \theta_{w}$ is the Weinberg's parameter, $T_{\mu \nu}^{(1)}$ and $T_{\mu \nu}^{(2)}$ are the tensors of 4-momentum and spiralities
for initial and final pair of $e^{-} e^{+}$:

$$
\begin{gather*}
T_{\mu v}^{(1)}=\operatorname{tr}\left[v\left(p_{2}, \lambda_{2}\right) \bar{v}\left(p_{2}, \lambda_{2}\right) \gamma_{\mu}\left(1+\gamma_{5}\right) u\left(p_{1}, \lambda_{1}\right) \bar{u}\left(p_{1}, \lambda_{1}\right) \gamma_{v}\left(1+\gamma_{5}\right)\right]= \\
=\operatorname{tr}\left[\frac{1+\lambda_{2} \gamma_{5}}{2} \hat{p}_{2} \gamma_{\mu}\left(1+\gamma_{5}\right) \cdot \frac{1-\lambda_{1} \gamma_{5}}{2} \hat{p}_{1} \gamma_{v}\left(1+\gamma_{5}\right)\right]= \\
=2\left(1-\lambda_{1}\right)\left(1+\lambda_{2}\right)\left[p_{1 \mu} p_{2 v}+p_{2 \mu} p_{1 v}-\left(p_{1} \cdot p_{2}\right) g_{\mu v}-i \varepsilon_{\mu v \rho \sigma} p_{1 \rho} p_{2 \sigma}\right],  \tag{9}\\
T_{\mu v}^{(2)}=\operatorname{tr}\left[u\left(q_{1}, h_{1}\right) \bar{u}\left(q_{1}, h_{1}\right) \gamma_{\mu}\left(1+\gamma_{5}\right) v\left(q_{2}, h_{2}\right) \bar{v}\left(q_{2}, h_{2}\right) \gamma_{v}\left(1+\gamma_{5}\right)\right]= \\
=\operatorname{tr}\left[\frac{1-h_{1} \gamma_{5}}{2} \hat{q}_{1} \gamma_{\mu}\left(1+\gamma_{5}\right) \cdot \frac{1+h_{2} \gamma_{5}}{2} \hat{q}_{2} \gamma_{v}\left(1+\gamma_{5}\right)\right]= \\
=2\left(1-h_{1}\right)\left(1+h_{2}\right)\left[q_{1 \mu} q_{2 v}+q_{2 \mu} q_{1 v}-\left(q_{1} \cdot q_{2}\right) g_{\mu v}+i \varepsilon_{\mu v \alpha \beta} q_{1 \alpha} q_{2 \beta}\right], \tag{10}
\end{gather*}
$$

The product of tensors $T_{\mu \nu}^{(1)}$ and $T_{\mu \nu}^{(2)}$ is a simple expression:

$$
\begin{equation*}
T_{\mu \nu}^{(1)} T_{\mu \nu}^{(2)}=2^{4}\left(1-\lambda_{1}\right)\left(1+\lambda_{2}\right)\left(1-h_{1}\right)\left(1+h_{2}\right)\left(p_{1} \cdot q_{2}\right)\left(p_{2} \cdot q_{1}\right) . \tag{11}
\end{equation*}
$$

The squared transition amplitude that we obtain is:

$$
\begin{aligned}
& \left|M_{a}\left(e^{-} e^{+} \Rightarrow H e^{-} e^{+}\right)_{I}\right|^{2}=\frac{1}{4}\left(\frac{e^{2}}{x_{w}\left(1-x_{w}\right)}\right)^{3} M_{Z}^{2}\left|F_{L L}^{(a)}\right|^{2} \times \\
& \quad \times\left(1-\lambda_{1}\right)\left(1+\lambda_{2}\right)\left(1-h_{1}\right)\left(1+h_{2}\right)\left(p_{1} \cdot q_{2}\right)\left(p_{2} \cdot q_{1}\right) .
\end{aligned}
$$

Because conservation of helicity no interference will happen between the of different spirality amplitudes. So, we easily will be able to calculate the square of amplitude:

$$
\begin{align*}
& \left|M_{a}\left(e^{-} e^{+} \Rightarrow H e^{-} e^{+}\right)\right|^{2}=\frac{1}{4}\left(\frac{e^{2}}{x_{w}\left(1-x_{w}\right)}\right)^{3} M_{Z}^{2}\left\{\left[\left(1-\lambda_{1}\right)\left(1+\lambda_{2}\right)\left(1-h_{1}\right)\left(1+h_{2}\right)\left|F_{L L}^{(a)}\right|^{2}+\right.\right. \\
& \left.+\left(1+\lambda_{1}\right)\left(1-\lambda_{2}\right)\left(1+h_{1}\right)\left(1-h_{2}\right)\left|F_{R R}^{(a)}\right|^{2}\right]\left(p_{1} \cdot q_{2}\right)\left(p_{2} \cdot q_{1}\right)+\left[\left(1-\lambda_{1}\right)\left(1+\lambda_{2}\right)\left(1+h_{1}\right) \times\right. \\
& \left.\quad \times\left(1-h_{2}\right)\left|F_{L R}^{(a)}\right|^{2}+\left(1+\lambda_{1}\right)\left(1-\lambda_{2}\right)\left(1-h_{1}\right)\left(1+h_{2}\right)\left|F_{R L}^{(a)}\right|^{2}\right]\left(p_{1} \cdot q_{1}\right)\left(p_{2} \cdot q_{2}\right) \tag{12}
\end{align*}
$$

The integration over $q_{1}$ and $q_{2}$ is conveniently performed by the invariant method [7]. Let's write the scalar product of 4-momentum in the form

$$
\left(p_{1} \cdot q_{1}\right)\left(p_{2} \cdot q_{2}\right)=p_{1 \mu} p_{2 v} \cdot q_{1 \mu} q_{2 v}
$$

Then the integral

$$
\begin{equation*}
I_{\mu v}=\int q_{1 \mu} q_{2 v} \frac{d \vec{q}_{1}}{\omega_{1}} \cdot \frac{d \vec{q}_{2}}{\omega_{2}} \delta\left(q-q_{1}-q_{2}\right) \tag{13}
\end{equation*}
$$

can be write as $\left(q=p_{1}+p_{2}-k\right)$ :

$$
\begin{equation*}
I_{\mu v}=\frac{\pi}{6}\left[q^{2} g_{\mu v}+2 q_{\mu} q_{v}\right] . \tag{14}
\end{equation*}
$$

In the center of initial $e^{-} e^{+}$mass frame we get the following expression for the $p_{1 \mu} p_{2 v}$ and $I_{\mu v}$ tensors product:

$$
\begin{equation*}
p_{1 \mu} p_{2 v} I_{\mu v}=\frac{\pi}{12} s^{2} f(\omega, \theta) \tag{15}
\end{equation*}
$$

where

$$
\begin{equation*}
f(\omega, \theta)=2 x+\frac{1}{s}\left(\omega^{2}-M_{H}^{2}\right) \sin ^{2} \theta \tag{16}
\end{equation*}
$$

$\theta$ is the angle between momentum of Higgs boson and initial electron. In the center of mass frame the cross section for the Higgs-strahlung process $e^{-} e^{+} \rightarrow H e^{-} e^{+}$is equal to $\left(k_{H}=\sqrt{\omega^{2}-M_{H}^{2}}\right.$ is the momentum of Higgs boson);

$$
\begin{gather*}
\frac{d \sigma_{a}\left(e^{-} e^{+} \Rightarrow H e^{-} e^{+}\right)}{d \omega d \cos \theta}=\frac{\alpha^{3} M_{Z}^{2}}{192 x_{w}^{3}\left(1-x_{w}\right)^{3}} k_{H} s f(\omega, \theta) \times \\
\times\left\{\left(1-\lambda_{1}\right)\left(1+\lambda_{2}\right)\left[\left(1-h_{1}\right)\left(1+h_{2}\right)\left|F_{L L}^{(a)}\right|^{2}+\left(1+h_{1}\right)\left(1-h_{2}\right)\left|F_{L R}^{(a)}\right|^{2}\right]+\right. \\
\left.+\left(1+\lambda_{1}\right)\left(1-\lambda_{2}\right)\left[\left(1-h_{1}\right)\left(1+h_{2}\right)\left|F_{R L}^{(a)}\right|^{2}+\left(1+h_{1}\right)\left(1-h_{2}\right)\left|F_{R R}^{(a)}\right|^{2}\right]\right\} \tag{17}
\end{gather*}
$$

We see from (17) that there are four helicity processes for the Higgs-strahlung diagram a):

1) initial and final electrons are polarized left $\left(\lambda_{1}=h_{1}=-1\right)$ while positrons are right $\left(\lambda_{2}=h_{2}=+1\right)$ :

$$
\begin{equation*}
\frac{d \sigma_{a}\left(e_{L}^{-} e_{R}^{+} \rightarrow H e_{L}^{-} e_{R}^{+}\right)}{d \omega d \cos \theta}=\frac{\alpha^{3} M_{Z}^{2}}{12 x_{w}^{3}\left(1-x_{w}\right)^{3}} \cdot k_{H} s\left|F_{L L}^{(a)}\right|^{2} f(\omega, \theta) \tag{18}
\end{equation*}
$$

2) unitial and final electrons are polarized right $\left(\lambda_{1}=h_{1}=+1\right)$ while positrons are left $\left(\lambda_{2}=h_{2}=-1\right)$ :

$$
\begin{equation*}
\frac{d \sigma_{a}\left(e_{R}^{-} e_{L}^{+} \rightarrow H e_{R}^{-} e_{L}^{+}\right)}{d \omega d \cos \theta}=\frac{\alpha^{3} M_{Z}^{2}}{12 x_{w}^{3}\left(1-x_{w}\right)^{3}} \cdot k_{H} s\left|F_{R R}^{(a)}\right|^{2} f(\omega, \theta) \tag{19}
\end{equation*}
$$

3) unitial (final) electron is polarized left (right) while positron is right (left):

$$
\begin{equation*}
\frac{d \sigma_{a}\left(e_{L}^{-} e_{R}^{+} \Rightarrow H e_{R}^{-} e_{L}^{+}\right)}{d \omega d \cos \theta}=\frac{\alpha^{3} M_{Z}^{2}}{12 x_{w}^{3}\left(1-x_{w}\right)^{3}} \cdot k_{H} s\left|F_{L R}^{(a)}\right|^{2} f(\omega, \theta) \tag{20}
\end{equation*}
$$

4) unitial (final) electron is polarized right (left) while positron is left (right):

$$
\begin{equation*}
\frac{d \sigma_{a}\left(e_{R}^{-} e_{L}^{+} \Rightarrow H e_{L}^{-} e_{R}^{+}\right)}{d \omega \cdot d \cos \theta}=\frac{\alpha^{3} M_{Z}^{2}}{12 x_{w}^{3}\left(1-x_{w}\right)^{3}} \cdot k_{H} s\left|F_{R L}^{(a)}\right|^{2} f(\omega, \theta) \tag{21}
\end{equation*}
$$

When the initial $e^{-} e^{+}$-pair are polarized longitudinally the differential cross section for Higgs-strahlung process will be written by the following form (the summation is carried over the final electron and positron spiralities):

$$
\begin{gather*}
\frac{d \sigma_{a}\left(\lambda_{1}, \lambda_{2}\right)}{d \omega d \cos \theta}=\frac{\alpha^{3} M_{Z}^{2} k_{H} s}{48 x_{w}^{3}\left(1-x_{w}\right)^{3}} \cdot \frac{g_{L}^{2}+g_{R}^{2}}{\left(s-M_{Z}^{2}\right)^{2}} \cdot \frac{f(\omega, \theta)}{\left(x s-M_{Z}^{2}\right)^{2}+M_{Z}^{2} \Gamma_{Z}^{2}} \times \\
\times\left[\left(1-\lambda_{1}\right)\left(1+\lambda_{2}\right) g_{L}^{2}+\left(1+\lambda_{1}\right)\left(1-\lambda_{2}\right) g_{R}^{2}\right] \tag{22}
\end{gather*}
$$

## 2. The $Z Z$ fusion mechanism.

The cross section that will be observed experimentally for the process $e^{-} e^{+} \rightarrow H e^{-} e^{+}$will not be due to the Higgs-strahlung process only, but part of it will come from the ZZ fusion process $e^{-}+e^{+} \rightarrow$ $\rightarrow Z^{*}+Z^{*}+e^{-}+e^{+} \rightarrow H+e^{-}+e^{+}$. We now analyze the diagram b ) corresponding ZZ bosons fusion. The transition amplitude of this diagram is given by:

$$
\begin{gather*}
M_{b}\left(e^{-} e^{+} \Rightarrow H e^{-} e^{+}\right)=-\left(\frac{e}{2 \sin \theta_{w} \cdot \cos \theta_{w}}\right)^{3} \times \\
\times M_{Z}\left\{F_{L L}^{(b)}\left[\bar{u}\left(q_{1}, h_{1}\right) \gamma_{\mu}\left(1+\gamma_{5}\right) u\left(p_{1}, \lambda_{1}\right)\right] \times\right. \\
\times\left[\bar{v}\left(p_{2}, \lambda_{2}\right) \gamma_{\mu}\left(1-\gamma_{5}\right) v\left(q_{2}, h_{2}\right)\right]+F_{R R}^{(b)}\left[\bar{u}\left(q_{1}, h_{1}\right) \gamma_{\mu}\left(1-\gamma_{5}\right) u\left(p_{1}, \lambda_{1}\right)\right] \times \\
\times\left[\bar{v}\left(p_{2}, \lambda_{2}\right) \gamma_{\mu}\left(1+\gamma_{5}\right) v\left(q_{2}, h_{2}\right)\right]+F_{L R}^{(b)}\left[\bar{u}\left(q_{1}, h_{1}\right) \gamma_{\mu}\left(1+\gamma_{5}\right) u\left(p_{1}, \lambda_{1}\right)\right] \times \\
\times\left[\bar{v}\left(p_{2}, \lambda_{2}\right) \gamma_{\mu}\left(1+\gamma_{5}\right) v\left(q_{2}, h_{2}\right)\right]+F_{R L}^{(b)}\left[\bar{u}\left(q_{1}, h_{1}\right) \gamma_{\mu}\left(1-\gamma_{5}\right) u\left(p_{1}, \lambda_{1}\right)\right] \times \\
\left.\times\left[\bar{v}\left(p_{2}, \lambda_{2}\right) \gamma_{\mu}\left(1-\gamma_{5}\right) v\left(q_{2}, h_{2}\right)\right]\right\}, \tag{23}
\end{gather*}
$$

where

$$
\begin{array}{ll}
F_{L L}^{(b)}=F_{R R}^{(b)}=D_{1} D_{2} g_{L} g_{R}, & \\
F_{L R}^{(b)}=D_{1} D_{2} g_{L}^{2}, & F_{R L}^{(b)}=D_{1} D_{2} g_{R}^{2} \tag{24}
\end{array}
$$

are the helicity amplitudes for the $Z Z$ fusion diagram, the first and second index indicate the spiralities of initial (or final) electron and positron, and

$$
\begin{equation*}
D_{1}=\left[\left(p_{1}-q_{1}\right)^{2}-M_{Z}^{2}\right]^{-1}, D_{2}=\left[\left(p_{2}-q_{2}\right)^{2}-M_{Z}^{2}\right]^{-1} \tag{25}
\end{equation*}
$$

Let's calculate the square of amplitude

$$
\begin{gather*}
M_{b}\left(e^{-} e^{+} \Rightarrow H e^{-} e^{+}\right)_{I I}=-\left(\frac{e}{2 \sin \theta_{w} \cdot \cos \theta_{w}}\right)^{3} M_{Z} F_{R R}^{(b)} \times \\
\times\left[\bar{u}\left(q_{1}, h_{1}\right) \gamma_{\mu}\left(1-\gamma_{5}\right) u\left(p_{1}, \lambda_{1}\right)\right] \cdot\left[\bar{v}\left(p_{2}, \lambda_{2}\right) \gamma_{\mu}\left(1+\gamma_{5}\right) v\left(q_{2}, h_{2}\right)\right] \\
\left|M_{b}\left(e^{-} e^{+} \rightarrow H e^{-} e^{+}\right)_{I I}\right|^{2}=\left(\frac{e^{2}}{4 x_{w}\left(1-x_{w}\right)}\right)^{3} M_{Z}^{2}\left(F_{R R}^{(b)}\right)^{2} X_{\mu v}^{(1)} X_{\mu v}^{(2)} \tag{26}
\end{gather*}
$$

where $X_{\mu \nu}^{(1)}$ and $X_{\mu \nu}^{(2)}$ are the tensors:

$$
\begin{gathered}
X_{\mu \nu}^{(1)}=\operatorname{tr}\left[u\left(q_{1}, h_{1}\right) \bar{u}\left(q_{1}, h_{1}\right) \gamma_{\mu}\left(1-\gamma_{5}\right) u\left(p_{1}, \lambda_{1}\right) \bar{u}\left(p_{1}, \lambda_{1}\right) \gamma_{v}\left(1-\gamma_{5}\right)\right]= \\
=\operatorname{tr}\left[\frac{1-h_{1} \gamma_{5}}{2} \hat{q}_{1} \gamma_{\mu}\left(1-\gamma_{5}\right) \cdot \frac{1-\lambda_{1} \gamma_{5}}{2} \hat{p}_{1} \gamma_{v}\left(1-\gamma_{5}\right)\right]= \\
=2\left(1+\lambda_{1}\right)\left(1+h_{1}\right)\left[q_{1 \mu} p_{1 v}+p_{1 \mu} q_{1 v}-\left(p_{1} \cdot q_{1}\right) g_{\mu v}-i \varepsilon_{\mu v \rho \sigma} q_{1 \rho} p_{2 \sigma}\right], \\
X_{\mu v}^{(2)}=\operatorname{tr}\left[v\left(p_{2}, \lambda_{2}\right) \bar{v}\left(p_{2}, \lambda_{2}\right) \gamma_{\mu}\left(1+\gamma_{5}\right) v\left(q_{2}, h_{2}\right) \bar{v}\left(q_{2}, h_{2}\right) \gamma_{v}\left(1+\gamma_{5}\right)\right]= \\
=\operatorname{tr}\left[\frac{1+\lambda_{2} \gamma_{5}}{2} \gamma_{\mu}\left(1+\gamma_{5}\right) \cdot \frac{1+h_{2} \gamma_{5}}{2} \gamma_{v}\left(1+\gamma_{5}\right)\right]= \\
=2\left(1+\lambda_{2}\right)\left(1+h_{2}\right)\left[p_{2 \mu} q_{2 v}+q_{2 \mu} p_{2 v}-\left(p_{2} \cdot q_{2}\right) g_{\mu v}+i \varepsilon_{\mu v \alpha \beta} p_{2 \alpha} q_{2 \beta}\right] .
\end{gathered}
$$

The product of tensors $X_{\mu \nu}^{(1)}$ and $X_{\mu \nu}^{(2)}$ gives:

$$
X_{\mu \nu}^{(1)} X_{\mu \nu}^{(2)}=2^{4}\left(1+\lambda_{1}\right)\left(1+\lambda_{2}\right)\left(1+h_{1}\right)\left(1+h_{2}\right)\left(p_{1} \cdot p_{2}\right)\left(q_{1} \cdot q_{2}\right)
$$

The expression for the squared matrix amplitude is:

$$
\begin{align*}
& \left|M_{b}\left(e^{-} e^{+} \Rightarrow H e^{-} e^{+}\right)_{I I}\right|^{2}=\frac{1}{4} \cdot\left(\frac{e^{2}}{x_{w}\left(1-x_{w}\right)}\right)^{3} M_{Z}^{2} \times \\
& \times\left|F_{R R}^{(b)}\right|^{2}\left(1+\lambda_{1}\right)\left(1+\lambda_{2}\right)\left(1+h_{1}\right)\left(1+h_{2}\right)\left(p_{1} \cdot p_{2}\right)\left(q_{1} \cdot q_{2}\right) \tag{27}
\end{align*}
$$

The integration over $q_{1}$ and $q_{2}$ is conveniently performed in the rest frame of the final leptons: $\vec{q}_{1}+\vec{q}_{2}=0$ (see Fig. 2). In this frame we obtains:

$$
\begin{align*}
& d \sigma_{a}\left(e^{-} e^{+} \Rightarrow H e^{-} e^{+}\right)_{I I}=\frac{1}{16 s(2 \pi)^{5}} \cdot \frac{d \vec{k}}{\omega} \int\left|M_{b}\left(e^{-} e^{+} \Rightarrow H e^{-} e^{+}\right)_{I I}\right|^{2} \times \\
& \times \delta\left(p_{1}+p_{2}-k-q_{1}-q_{2}\right) \frac{d \vec{q}_{1}}{\omega_{1}} \frac{d \vec{q}_{2}}{\omega_{2}}=\frac{1}{16 s} \cdot \frac{1}{(2 \pi)^{4}} k_{H} d \omega d \cos \theta \times \\
& \times \int\left|M_{b}\left(e^{-} e^{+} \Rightarrow H e^{-} e^{+}\right)_{I I}\right|^{2} \delta\left(E_{1}+E_{2}-\omega-2 \omega_{1}\right) d \omega_{1} d \cos \theta_{1} d \varphi_{1}= \\
& =\frac{1}{32 s} \cdot \frac{1}{(2 \pi)^{4}} k_{H} d \omega d \cos \theta \int_{-1}^{1} d \cos \theta_{1} \int_{0}^{2 \pi} d \varphi_{1}\left|M_{b}\left(e^{-} e^{+} \Rightarrow H e^{-} e^{+}\right)_{I I}\right|^{2} \tag{28}
\end{align*}
$$

where $\left|M_{b}\left(e^{-} e^{+} \Rightarrow H e^{-} e^{+}\right)_{I I}\right|^{2}$ can be written in the form:

$$
\begin{align*}
& \left|M_{b}\left(e^{-} e^{+} \Rightarrow H e^{-} e^{+}\right)_{I I}\right|^{2}=\frac{1}{4} \cdot\left(\frac{4 \pi \alpha}{x_{w}\left(-x_{w}\right)}\right)^{3} M_{Z}^{2} \cdot \frac{g_{L}^{2} g_{R}^{2}}{\left[2\left(p_{1} \cdot q_{1}\right)+M_{Z}^{2}\right]^{2}} \times \\
& \times \frac{s\left[s+M_{H}^{2}-2\left(k \cdot p_{1}\right)-\left(k \cdot p_{2}\right)\right]}{\left[s+M_{H}^{2}-2\left(k \cdot p_{2}\right)-2\left(p_{2} \cdot q_{1}\right)\right]^{2}}\left(1+\lambda_{1}\right)\left(1+\lambda_{2}\right)\left(1+h_{1}\right)\left(1+h_{2}\right) \tag{29}
\end{align*}
$$

$$
\left|M_{b}\left(e^{-} e^{+} \Rightarrow H e^{-} e^{+}\right)_{I I}\right|^{2} \text { depend on } \varphi_{1} \text { only through }\left(p_{2} \cdot q_{1}\right):
$$

$$
\begin{gathered}
\left(p_{1} \cdot q_{1}\right)=\frac{1}{4}\left[s-2\left(k \cdot p_{1}\right)\right]\left(1-\cos \theta_{1}\right) \\
\left(p_{2} \cdot q_{1}\right)=\frac{1}{4}\left[s-2\left(k \cdot p_{2}\right)\right]\left(1-\cos \theta_{1} \cos \chi-\sin \theta_{1} \sin \chi \cos \varphi_{1}\right)
\end{gathered}
$$

where

$$
\cos \chi=1-\frac{2 s\left[s+M_{H}^{2}-2\left(k \cdot p_{1}\right)-2\left(k \cdot p_{2}\right)\right]}{\left[s-2\left(k \cdot p_{1}\right)\right]\left[s-2\left(k \cdot p_{2}\right)\right]} .
$$

The integration over $\varphi_{1}$ and $\cos \theta_{1}$ can be analytically performed:

$$
\begin{gather*}
\frac{d \sigma_{b}\left(e^{-} e^{+} \Rightarrow H e^{-} e^{+}\right)}{d \omega d \cos \theta}=\frac{\alpha^{3} M_{Z}^{2}}{4 x_{w}^{3}\left(1-x_{w}\right)^{3}} \cdot \frac{k_{H}}{s} \cdot \frac{1}{s_{1} s_{2} r}\left\{\left[\left(1-\lambda_{1}\right)\left(1+\lambda_{2}\right) \times\right.\right. \\
\left.\cdot\left(1-h_{1}\right)\left(1+h_{2}\right) g_{L}^{4}+\left(1+\lambda_{1}\right)\left(1-\lambda_{2}\right)\left(1+h_{1}\right)\left(1-h_{2}\right) g_{R}^{4}\right] \times \\
\times\left[4\left(1+x_{1}\right)\left(1+x_{2}\right) F_{1}-F_{2}\right]+\left[\left(1-\lambda_{1}\right)\left(1-\lambda_{2}\right)\left(1-h_{1}\right)\left(1-h_{2}\right)+\right. \\
\left.\left.+\left(1+\lambda_{1}\right)\left(1+\lambda_{2}\right)\left(1+h_{1}\right)\left(1+h_{2}\right)\right] \cdot g_{L}^{2} g_{R}^{2} 2(1-\cos \chi) F_{1}\right\} \tag{30}
\end{gather*}
$$



Fig. 2. The rest frame of the final leptons.

$$
\begin{gather*}
F_{1}=\frac{1}{2 x_{1}\left(1+x_{1}\right)}+\frac{1}{2 x_{2}\left(1+x_{2}\right)}-\frac{6 \sin ^{2} \chi}{r}+\left(\frac{3 t_{1} t_{2}}{r}-\cos \chi\right) \frac{L}{\sqrt{r}}  \tag{31}\\
F_{2}=\frac{t_{1}}{x_{2}}+\frac{t_{2}}{x_{1}}+\left(t_{1}+t_{2}+\sin ^{2} \chi\right) \frac{L}{\sqrt{r}}  \tag{32}\\
s_{1}=\sqrt{s}\left(\sqrt{s}-\omega+k_{H} \cos \theta\right), \quad s_{2}=\sqrt{s}\left(\sqrt{s}-\omega-k_{H} \cos \theta\right), \\
t_{1}=1+2 x_{1}+\cos \chi\left(1+2 x_{2}\right), \quad t_{2}=1+2 x_{2}+\cos \chi\left(1+2 x_{1}\right), \\
\quad \cos \chi=1-\frac{2 x s}{x s+k_{H}^{2} \sin ^{2} \theta}, \quad \sin ^{2} \chi=1-\cos ^{2} \chi \\
r=\left(1+2 x_{1}\right)^{2}+\left(1+2 x_{2}\right)^{2}+2 \cos \chi\left(1+2 x_{1}\right)\left(1+2 x_{2}\right)-\sin ^{2} \chi \\
L=\ln \frac{\left(1+2 x_{1}\right)\left(1+2 x_{2}\right)+\cos \chi+\sqrt{r}}{\left(1+2 x_{1}\right)\left(1+2 x_{2}\right)+\cos \chi-\sqrt{r}}, \quad x_{1}=\frac{M_{Z}^{2}}{s_{1}}, \quad x_{2}=\frac{M_{Z}^{2}}{s_{2}}
\end{gather*}
$$

We see clearly from (23) and (30) that there are four helicity processes for the $Z Z$ fusion diagram b):

1) electrons are polarized left $\left(\lambda_{1}=h_{1}=-1\right)$ while positrons right $\left(\lambda_{2}=h_{2}=+1\right)$ :

$$
\begin{equation*}
\frac{d \sigma_{b}\left(e_{L}^{-} e_{R}^{+} \Rightarrow H e_{L}^{-} e_{R}^{+}\right)}{d \omega d \cos \theta}=\frac{4 \alpha^{3} M_{Z}^{2}}{x_{w}^{3}\left(1-x_{w}\right)^{3}} \cdot \frac{k_{H}}{s} \cdot \frac{g_{L}^{4}}{s_{1} s_{2} r}\left[4\left(1+x_{1}\right)\left(1+x_{2}\right) F_{1}-F_{2}\right] \tag{33}
\end{equation*}
$$

2) electrons are polarized right $\left(\lambda_{1}=h_{1}=+1\right)$ while positrons left $\left(\lambda_{2}=h_{2}=-1\right)$ :

$$
\begin{equation*}
\frac{d \sigma_{b}\left(e_{R}^{-} e_{L}^{+} \Rightarrow H e_{R}^{-} e_{L}^{+}\right)}{d \omega d \cos \theta}=\frac{4 \alpha^{3} M_{Z}^{2}}{x_{w}^{3}\left(1-x_{w}\right)^{3}} \cdot \frac{k_{H}}{s} \cdot \frac{g_{R}^{4}}{s_{1} s_{2} r}\left[4\left(1+x_{1}\right)\left(1+x_{2}\right) F_{1}-F_{2}\right] \tag{34}
\end{equation*}
$$

3) electrons and positrons are polarized left:

$$
\begin{equation*}
\frac{d \sigma_{b}\left(e_{L}^{-} e_{L}^{+} \Rightarrow H e_{L}^{-} e_{L}^{+}\right)}{d \omega d \cos \theta}=\frac{4 \alpha^{3} M_{Z}^{2}}{x_{w}^{3}\left(1-x_{w}\right)^{3}} \cdot \frac{k_{H}}{s} \cdot \frac{2 g_{L}^{2} g_{R}^{2}}{s_{1} s_{2} r} \cdot 2(1-\cos \chi) F_{1} \tag{35}
\end{equation*}
$$

4) electrons and positrons are polarized right:

$$
\begin{equation*}
\frac{d \sigma_{b}\left(e_{R}^{-} e_{R}^{+} \Rightarrow H e_{R}^{-} e_{R}^{+}\right)}{d \omega d \cos \theta}=\frac{4 \alpha^{3} M_{Z}^{2}}{x_{w}^{3}\left(1-x_{w}\right)^{3}} \cdot \frac{k_{H}}{s} \cdot \frac{2 g_{L}^{2} g_{R}^{2}}{s_{1} s_{2} r} \cdot 2(1-\cos \chi) F_{1} . \tag{36}
\end{equation*}
$$

When the initial $e^{-} e^{+}$-pair is polarized longitudinally the differential cross section for the $Z Z$ fusion process will be written as

$$
\begin{gather*}
\frac{d \sigma_{b}\left(\lambda_{1}, \lambda_{2}\right)}{d \omega d \cos \theta}=\frac{\alpha^{3} M_{Z}^{2}}{x_{w}^{3}\left(1-x_{w}\right)^{3}} \cdot \frac{k_{H}}{s} \cdot \frac{1}{s_{1} s_{2} r} \times \\
\times\left\{\left[\left(1-\lambda_{1}\right)\left(1+\lambda_{2}\right) g_{L}^{4}+\left(1+\lambda_{1}\right)\left(1-\lambda_{2}\right) g_{R}^{4}\right]\left[4\left(1+x_{1}\right)\left(1+x_{2}\right) F_{1}-F_{2}\right]+\right. \\
\left.+\left[\left(1-\lambda_{1}\right)\left(1-\lambda_{2}\right)+\left(1+\lambda_{1}\right)\left(1+\lambda_{2}\right)\right] g_{L}^{2} g_{R}^{2} \cdot 2(1-\cos \chi) F_{1}\right\} \tag{37}
\end{gather*}
$$

## 3. The interference between $\mathbf{a}$ ) and $\mathbf{b}$ ) diagrams.

It is interesting that the interference with a) and b) diagrams occur only between spirality processes $e_{L}^{-} e_{R}^{+} \rightarrow H e_{L}^{-} e_{R}^{+}$and $e_{R}^{-} e_{l}^{+} \rightarrow H e_{R}^{-} e_{L}^{+}$and we then have:

$$
\begin{align*}
\frac{d \sigma_{I}\left(e_{L}^{-} e_{R}^{+} \Rightarrow H e_{L}^{-} e_{R}^{+}\right)}{d \omega d \cos \theta} & =\frac{\alpha^{3} M_{Z}^{2}}{x_{w}^{3}\left(1-x_{w}\right)^{3}} \cdot \frac{k_{H}}{s} \cdot \frac{2 g_{L}^{4}}{\left(s-M_{Z}^{2}\right)\left[\left(x s-M_{Z}^{2}\right)^{2}+M_{Z}^{2} \Gamma_{Z}^{2}\right]} \cdot g_{I}  \tag{38}\\
\frac{d \sigma_{I}\left(e_{R}^{-} e_{L}^{+} \Rightarrow H e_{R}^{-} e_{L}^{+}\right)}{d \omega d \cos \theta}= & \frac{\alpha^{3} M_{Z}^{2}}{x_{w}^{3}\left(1-x_{w}\right)^{3}} \cdot \frac{k_{H}}{s} \cdot \frac{2 g_{R}^{4}}{\left(s-M_{Z}^{2}\right)\left[\left(x s-M_{Z}^{2}\right)^{2}+M_{Z}^{2} \Gamma_{Z}^{2}\right]} \cdot g_{I}  \tag{39}\\
\frac{d \sigma_{I}\left(\lambda_{1}, \lambda_{2}\right)}{d \omega d \cos \theta}= & \frac{\alpha^{3} M_{Z}^{2}}{4 x_{w}^{3}\left(1-x_{w}\right)^{3}} \cdot \frac{k_{H}}{s} \cdot \frac{2\left(x s-M_{Z}^{2}\right)}{\left(s-M_{Z}^{2}\right)\left[\left(x s-M_{Z}^{2}\right)^{2}+M_{Z}^{2} \Gamma_{Z}^{2}\right]} \times \\
& \times\left[\left(1-\lambda_{1}\right)\left(1+\lambda_{2}\right) g_{L}^{4}+\left(1+\lambda_{1}\right)\left(1-\lambda_{2}\right) g_{R}^{4}\right] \cdot g_{I} \tag{40}
\end{align*}
$$

where

$$
\begin{equation*}
g_{I}=2-2\left(1+x_{1}\right) \ln \frac{1+x_{1}}{x_{1}}-2\left(1+x_{2}\right) \ln \frac{1+x_{2}}{x_{2}}+4\left(1+x_{1}\right)\left(1+x_{2}\right) \frac{L}{\sqrt{r}} . \tag{41}
\end{equation*}
$$

## CONCLUSION

The overall cross section for the process $e^{-} e^{+} \Rightarrow \mathrm{He}^{-} e^{+}$receives contributions $G_{s}$ from Higgs-strahlung, $G_{Z}^{( \pm)}$from $Z Z$ fusion, and $G_{I}$ from the interference term between fusion and Higgs-strahlung:

$$
\begin{equation*}
\frac{d \sigma_{0}\left(e^{-} e^{+} \Rightarrow H e^{-} e^{+}\right)}{d \omega d \cos \theta}=\frac{\alpha^{3} M_{Z}^{2}}{4 x_{w}^{3}\left(1-x_{w}\right)^{3}} \cdot \frac{k_{H}}{s}\left[G_{s}+G_{Z}^{(+)}+G_{Z}^{(-)}+G_{I}\right] \tag{42}
\end{equation*}
$$

with

$$
\begin{align*}
& G_{s}=\frac{1}{12} \cdot \frac{\left(g_{L}^{2}+g_{R}^{2}\right) s\left(2 x s+k_{H}^{2} \sin ^{2} \theta\right)}{\left(s-M_{Z}^{2}\right)^{2}\left[\left(x s-M_{Z}^{2}\right)^{2}+M_{Z}^{2} \Gamma_{Z}^{2}\right]} \\
& G_{Z}^{(+)}=\frac{g_{L}^{4}+g_{R}^{4}}{s_{1} s_{2} r}\left[4\left(1+x_{1}\right)\left(1+x_{2}\right) F_{1}-F_{2}\right] \\
& G_{Z}^{(-)}=\frac{2 g_{L}^{2} g_{R}^{2}}{s_{1} s_{2} r} \cdot 2(1-\cos \chi) F_{1}  \tag{43}\\
& G_{I}=\frac{1}{2} \cdot \frac{\left(g_{L}^{4}+g_{R}^{4}\right)\left(x s-M_{Z}^{2}\right)}{\left(s-M_{Z}^{2}\right)\left[\left(x s-M_{Z}^{2}\right)^{2}+M_{Z}^{2} \Gamma_{Z}^{2}\right]} \cdot g_{I}
\end{align*}
$$

Denoting by $d \sigma_{L R}, d \sigma_{R L}, d \sigma_{L L}$ and $d \sigma_{R R}$ the cross sections for $e_{L}^{-} e_{R}^{+}, e_{R}^{-} e_{L}^{+}, e_{L}^{-} e_{L}^{+}$and $e_{R}^{-} e_{R}^{+}$polarized, respectively, we obtains:

$$
\begin{align*}
\frac{d \sigma_{L R}}{d \omega d \cos \theta} & =\frac{\alpha^{3} M_{Z}^{2}}{x_{w}^{3}\left(1-x_{w}\right)^{3}} \cdot \frac{k_{H}}{s}\left[\frac{g_{L}^{2}}{g_{L}^{2}+g_{R}^{2}} G_{s}+\frac{g_{L}^{4}}{g_{L}^{4}+g_{R}^{4}}\left(G_{Z}^{(+)}+G_{I}\right)\right] \\
\frac{d \sigma_{R L}}{d \omega d \cos \theta} & =\frac{\alpha^{3} M_{Z}^{2}}{x_{w}^{3}\left(1-x_{w}\right)^{3}} \cdot \frac{k_{H}}{s}\left[\frac{g_{R}^{2}}{g_{L}^{2}+g_{R}^{2}} G_{s}+\frac{g_{R}^{4}}{g_{L}^{4}+g_{R}^{4}}\left(G_{Z}^{(+)}+G_{I}\right)\right]  \tag{44}\\
\frac{d \sigma_{L L}}{d \omega d \cos \theta} & =\frac{d \sigma_{R R}}{d \omega d \cos \theta}=\frac{\alpha^{3} M_{Z}^{2}}{x_{w}^{3}\left(1-x_{w}\right)^{3}} \cdot \frac{k_{H}}{s} \cdot 2 G_{Z}^{(-)}
\end{align*}
$$

Since $g_{R} \approx-g_{L}$, the difference between $d \sigma_{L R}$ and $d \sigma_{R L}$ is however, strongly suppressed and we obtains;

$$
\begin{equation*}
\frac{d \sigma_{L R}}{d \omega d \cos \theta}=\frac{d \sigma_{R L}}{d \omega d \cos \theta}=\frac{\alpha^{3} M_{Z}^{2}}{x_{w}^{3}\left(1-x_{w}\right)^{3}} \cdot \frac{k_{H}}{s} \cdot 2\left(G_{s}+G_{Z}^{(+)}+G_{Z}^{(-)}\right) \tag{45}
\end{equation*}
$$

The distributions of Higgs boson over angles is depicted in Fig. 3 at the energy $\sqrt{s}=500 \mathrm{GeV}$, Weinberg parameter $x_{w}=0.232, \quad M_{H}=125 G e V$ and $\omega=250 \mathrm{GeV}$. We see from the Fig. 3a that as the angle of outgoing Higgs boson increase, the cross section also increase and reaches to its maximum at the value $\theta=90^{\circ}$. By further increase of angle, the cross section starts to decrease.

In the ZZ fusion mechanism, as the angle of Higgs bosons increase, the cross section is decrease and reaches to its maximum at the value $\theta=25^{\circ}$, by further increase of angle the cross section is decrease and reaches to its minimum at the angle $150^{\circ}$. Bu further increase of angle the cross section, also increase (see Fig. 3b).

One can that ZZ fusion cross section is dominant at a lower and at higher angles (the interference term is a very small in the over regions).
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Fig. 3. The distributions of Higgs boson over angles for $\sqrt{s}=500 \mathrm{GeV}, M_{H}=125 \mathrm{GeV}, \omega=250 \mathrm{GeV}$. The two components: Higgs-strahlung (Fig. 3a), ZZ fusion (Fig.3b).
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# POLYMORPHOUS TRANSFORMATIONS AND THERMAL EXPANSION OF CRYSTAL LATTICE PARAMETERS OF SEPARATE MODIFICATIONS IN 

$\mathrm{Ag}_{1.5} \mathbf{C u}_{0.5} \mathbf{S e}$ AND $\mathrm{Ag}_{0.4} \mathbf{C u}_{1.6} \mathbf{S e}$

U.G. ASADOV, A.G. BABAYEV, G.F. GANIZADE, B.I. ALIYEV<br>G.B. Abdullayev Institute of Physics of Azerbaijan NAS, Baku<br>AZ-1143, H. Javid, 131<br>E-mail: yusifasadov@rambler.ru

$\mathrm{Ag}_{1.5} \mathrm{Cu}_{0.5} \mathrm{Se}$ and $\mathrm{Ag}_{0.4} \mathrm{Cu}_{1.6} \mathrm{Se}$ are synthesized and the polymorphous transformations in them are investigated by method of high-temperature roentgenography. It is shown that FCC modification single crystals $\mathrm{Ag}_{1.5} \mathrm{Cu}_{0.5} \mathrm{Se}$ at temperature decrease lower 488 K decompose on $\mathrm{Ag}_{2} \mathrm{Se}$ and AgCuSe and $\mathrm{Ag}_{0.4} \mathrm{Cu}_{1.6} \mathrm{Se}$ lower than 540 K decompose on $\mathrm{Cu}_{2} \mathrm{Se}$ and AgCuSe .

The transformations in both compositions are reversible ones. From temperature dependence of lattice parameters of existing modifications the thermal expansion coefficients by main crystallographic directions are calculated.

Keywords: polymorphous transformations, roentgenography PACS: $62.20 . \mathrm{Fe}, 61.50 . \mathrm{Ks}$

## INTRODUCTION

AgCuSe compound forms at ratio $\mathrm{Cu}_{2} \mathrm{Se}: \mathrm{Ag}_{2} \mathrm{Se}=1: 1$ by peritectic reaction at temperature 1033K [1]. In [2] AgCuSe crystal structure is defined as tetragonal one with lattice parameters $a=4.083 \AA$, $\mathrm{c}=6.300 \AA \AA, \mathrm{Z}=2$, sp.gr. $D_{4 h}^{7}-$ Pnmm. Further, in [3] AgCuSe crystal structure is defined as rhombic one which is tetragonal lattice superstructure. The rhombic lattice parameter is equal to five parameters $\underline{b}$ of tetragonal lattice.

Ag atoms are in planes perpendicular to c axis in AgCuSe rhombic structure [3]. Four Ag atoms on distance $2.96 \AA$ and six Se atoms on distance $2.61 \AA$ $(4 \mathrm{Se}), 3.59 \AA(1 \mathrm{Se})$ and $3.64 \AA \AA(1 \mathrm{Se})$ locate round each of them. Se atoms form the prolate tetrahedrons in centers of which Cu atoms locate. The distance of $\mathrm{Se}-\mathrm{Se}=3.03 \AA, \mathrm{Cu}-\mathrm{Se}=2.06-2.50 \AA$ and the smallest distance of $\mathrm{Cu}-\mathrm{Ag}=2.98 \AA$.

It is shown [4] that rhombic modification at 504 K transforms into high-temperature FCC one with lattice parameter $\mathrm{a}=6.0823$ Á. In given work the polymorphous transformations in AgCuSe single crystals are studied by method of high-temperature roentgenography and stability temperature intervals of existing modification stability are obtained.

The equilibrium temperature in triple compound AgCuSe , i.e. $1_{2}\left(\mathrm{Cu}_{2} \mathrm{Se}, \mathrm{Ag}_{2} \mathrm{Se}\right)$ between modifications on 96 K higher than one in $\mathrm{Cu}_{2} \mathrm{Se}, \mathrm{Ag}_{2} \mathrm{Se}$ binary compounds.

It is important to note that lattice parameter values of low-temperature rhombic modification of AgCuSe approximately corresponds to lattice parameters of low-temperature rhombic modification of $\mathrm{Cu}_{2} \mathrm{Se}$. In $\mathrm{Cu}_{2} \mathrm{Se}$ crystal structure Cu atoms are statistically distributed in tetrahedral voids formed by Se atoms, in AgCuSe structure Ag atoms locate in planes perpendicular to c axis and Cu atoms as well as in $\mathrm{Cu}_{2} \mathrm{Se}$ locate in tetrahedron center formed by Se atoms. These structural differences and product additional bonds $\mathrm{Cu}-\mathrm{Ag}$ and $\mathrm{Ag}-\mathrm{Se}$ are also the reason of transformation temperature increase in AgCuSe ( $\mathrm{T}_{\mathrm{tr}}=504 \mathrm{~K}$ ) in comparison with $\mathrm{Cu}_{2} \mathrm{Se}\left(\mathrm{T}_{\mathrm{tr}}=407 \mathrm{~K}\right)$ and $\mathrm{Ag}_{2} \mathrm{Se}\left(\mathrm{T}_{\mathrm{tr}}=408 \mathrm{~K}\right)$.
$\mathrm{Cu}_{2} \mathrm{Se}$ compound on $\mathrm{Cu}-\mathrm{Se}$ state diagram exists in region $38,4 \mathrm{at} . \% \mathrm{Se}[5,6]$. The density of $\mathrm{Cu}_{2} \mathrm{Se}$ is $\rho=6.749 \mathrm{gr} / \mathrm{cm}^{3}$ and melting point is $\mathrm{T}_{\mathrm{m}}=1386 \mathrm{~K}$ [7].

The rhombic structure with lattice parameters $a=4.118 \AA ́, b=7.032 \AA ́, c=20.381 \AA\left(T_{\text {exp }}=293 \mathrm{~K}\right)$ for lowtemperature $\mathrm{Cu}_{2} \mathrm{Se}$ is supposed in [7].
$\alpha \rightleftharpoons \beta$ transformations in $\mathrm{Cu}_{2} \mathrm{Se}$ single crystals are investigated by roentgenographic and microscopic methods in [8-9]. It is established that low-temperature modification crystallizes in rhombic structure with lattice parameters $\mathrm{a}=4.119 \pm 0.001 \AA$ Á, $\mathrm{b}=7.028 \pm 0.002 \AA$, $c=20.394 \pm 0.003 \AA$ that confirms the investigation results of authors [7]. It is shown [8,9] that lowtemperature rhombic modification at 407 K transform into FCC one with lattice parameter $\mathrm{a}=5.840 \AA \hat{\AA}, \mathrm{Z}=4$, sp.gr. $\mathbf{O}_{\mathrm{h}}^{5}-\mathrm{Fm} 3 \mathrm{~m}, \rho=6.838 \mathrm{gr} / \mathrm{cm}^{3}$. The transformations are reversible ones and take place by single crystal single crystal type.

As it is mentioned in $[5,6]$ the silver with selenium form the one compound $\mathrm{Ag}_{2} \mathrm{Se}$ which consists of 26.79 weight\% $S \mathrm{e}$. The scientific data on crystal structure of low-temperature modification of $\alpha-\mathrm{Ag}_{2} \mathrm{Se}$ are contradictory ones. The cubic structure in [10], the tetragonal structure in $[11,12]$, the rhombic structure in $[13,15]$, the monoclinic structure in $[16,17]$ and triclinic structure in $[18,19]$ are supposed for lowtemperature modification.

The crystal structure of low-temperature modification is more detailed considered in [20,21]. The rhombic structure with lattice parameters $a=7.05 \AA$, $b=7.85 \AA \AA, \mathrm{c}=4.33 \AA \AA, \mathrm{Z}=4$, sp.gr. $\mathrm{P} 222_{1}$ is established in [20] by electronographic method for low-temperature modification of $\alpha-\mathrm{Ag}_{2} \mathrm{Se}$. The rhombic structure with lattice parameters $\mathrm{a}=4.333 \AA \AA, \quad b=7.062 \AA, \quad \mathrm{c}=7.764 \AA$, $\mathrm{Z}=4$, sp.gr. $\mathrm{P} 2_{1} 2_{1} 2_{1}$ for low-temperature modification of $\mathrm{Ag}_{2} \mathrm{Se}$ is supposed in [21]. In rhombic lattice $\mathrm{Ag}(\mathrm{I})$ is in tetrahedral surrounding of Se atoms and $\mathrm{Ag}(\mathrm{II})$ is in triangle surrounding of Se atoms. In sp.gr. $\mathrm{P} 222_{1}$ the damping conditions give the restricions only to reflection by (001) type where $l=2 n$ and in sp.gr. $\mathrm{P} 2_{1} 2_{1} 2_{1}$ the damping conditions are the following ones: $\quad(h k l)$ is unrestricted, (h00)-h=2n, (0k0) $-\kappa=2 n$, (00l) $-l=2 n$. According to [21] data the
lattice parameter of high-temperature VCC modification is a $=4.983 \AA \hat{A}, \mathrm{Z}=2$, sp.gr. $O_{h}^{5}-\mathrm{Fm} 3 \mathrm{~m}$. The polymorphous transformations in $\mathrm{Ag}_{2} \mathrm{Se}$ are investigated in detail and results are published in [24,25].

The structural changes at polymorphous transformations in compositions $\mathrm{Ag}_{1.5} \mathrm{Cu}_{0.5} \mathrm{Se}$ and $\mathrm{Ag}_{0.4} \mathrm{Cu}_{1.6} \mathrm{Se}$ where the cation number of Ag and Cu in AgCuSe are changed are studied in present work by method of high-temperature roentgenography.

## EXPERIMENTAL PART

## The synthesis of $\mathrm{Ag}_{1.5} \mathrm{Cu}_{0.5} S \mathrm{Se}$ and $\mathrm{Ag}_{0.4} \mathrm{Cu}_{1.6} \mathrm{Se}$.

The synthesis conditions don't differ from AgCuSe ones [26]. By roentgen-phase analysis, it is shown that at room temperature the both compositions are twophase ones. $\mathrm{Ag}_{1.5} \mathrm{Cu}_{0.5} \mathrm{Se}$ consists of AgCuSe and $\mathrm{Ag}_{2} \mathrm{Se}, \mathrm{Ag}_{0.4} \mathrm{Cu}_{1.6} \mathrm{Se}$ consists of AgCuSe and $\mathrm{Cu}_{2} \mathrm{Se}$, i.e. in both cases the high-temperature cubic phase decomposes in two phases at temperature lower than equilibrium one. By this reason, it is no possible to grow the low-temperature phases of these single crystals. The synthesized ingot in granular form is put in pointed ampoule, which provides the selection of high-temperature modification germs. The ampoules are evacuated up to pressure $10^{-3} \mathrm{~Pa}$ and located in upper furnace band and heated up to 1400 K after what they are put down through the temperature gradient band with velocity $2 \mathrm{~mm} / \mathrm{h}$. It is important to note that ampoule temperature becomes lower than melting temperature, the high-temperature modification crystals form and grow.

The low-temperature modification crystals form and grow with temperature decrease from hightemperature modification crystals. The density difference inside the matrix single crystal is the one from main factors influencing on new modification single crystallinity at growth of single crystals of new modification. The polymorphous substances can be divided on following three groups on density difference: a) the density of growing modification $\rho_{g}$ is less than matrix crystal density $\rho_{\mathrm{m}}$, i.e. $\rho_{\mathrm{g}}<\rho_{m} ; b$ ) the density of growing modification is bigger than matrix crystal density, i.e. $\rho_{g}>\rho_{m} ; c$ ) the densities of growing crystal and matrix crystal are either equal or insignificantly differ, i.e. $\rho_{g}=\rho_{m}, \rho_{g} \geq \rho_{m}$ or $\rho_{g} \leq \rho_{m}$.

The matrix crystal deforms in transformation process at $\rho_{\mathrm{g}}<\rho_{\mathrm{m}}$, often cracks and each formed crack becomes the source of formation of many crystallization centers. As a result, the single crystal of high-temperature modification transforms into polycrystal of low-temperature phase. In $\rho_{g}>\rho_{m}$ case the contact between growing crystal and crystalmedium weakens and the distance of surface interface becomes bigger than interatomic distance. Moreover, the new phase crystal growth stops. The transformation process continues because of formation of more and more new germs. In this case, the single crystal also transforms into polycrystal. From such polycrystal, it is impossible to grow up the new crystal. In case $\rho_{g} \geq \rho_{m}$, $\rho_{g} \leq \rho_{m}$ and $\rho_{g}=\rho_{m}$ the two transformation types single crystal $\rightleftharpoons$ single crystal and single crystal $\rightleftharpoons$ polycrystal
are usually observed. Here single crystal $\rightleftharpoons$ polycrystal takes place at transformation with formation of many crystallization centers and because of matrix crystal imperfection. The single crystal of given modification can be obtained from such polycrystal.

## The high-temperature diffractometric investigations of $\mathrm{Ag}_{1.5} \mathrm{Cu}_{0.5} S \mathrm{Se}$ and $\mathrm{Ag}_{0.4} \mathrm{Cu}_{1.6} \mathrm{Se}$ compounds.

The high-temperature investigations are carried out on diffractometer ДРОН-3M $\left(\mathrm{CuK}_{\alpha}\right.$ radiation, $\lambda_{\alpha}=1.5418 \AA$ and Ni is filter) with attachment URVT-2000, providing the vacuum $10^{-2} \mathrm{~Pa}$. The condition of recording resolution is $\sim 0.1^{\circ}$. The error of angle of reflection definition doesn't succeed $\Delta \theta= \pm 0.02^{\circ}$.

## 1. $\mathrm{Ag}_{1.5} \mathrm{Cu}_{0.5} \underline{S \mathrm{e} .}$

27 diffraction reflections (table 1) are fixed at room temperature from $\mathrm{Ag}_{1.5} \mathrm{Cu}_{0.5} \mathrm{Se}$ sample in the form of plane having sizes $4 \times 5 \times 1 \mathrm{~mm}$ in angle interval $10 \leq 2 \theta \leq 90^{\circ}$ at room temperature. For detail indexing of $\mathrm{Ag}_{1.5} \mathrm{Cu}_{0.5} \mathrm{Se}$ diffraction data the experimental values of interplanar spacings $d_{i}$ are compared with ones calculated on the base of crystal lattice parameters of $\mathrm{AgCuSe}, \quad \mathrm{Ag}_{2} \mathrm{Se}$ and $\mathrm{Cu}_{2} \mathrm{Se}$ low-temperature modifications.

As it is seen from table 1 experimental interplanar spacings $\mathrm{d}_{\mathrm{i}}$ of $\mathrm{Ag}_{1.5} \mathrm{Cu}_{0.5} \mathrm{Se}$ except of $\mathrm{d}=2.4812 \AA$ and $\mathrm{d}=1.8625 \AA$ satisfactory coincide with calculated values of interplanar spacings of $\mathrm{Ag}_{2} \mathrm{Se}$ with parameters $\mathrm{a}=4.333 \AA$ Á, $b=7.062 \AA, c=7.764 \AA$. The above mentioned two interplanar spacings and also the series of others are indicated on the base of lattice parameters of rhombic modification of AgCuSe where $\mathrm{a}=4.105 \AA \dot{\AA}, \mathrm{~b}=20.350 \AA$, $\mathrm{c}=6.310 \mathrm{~A}$. In diffraction patterns, the change doesn't take place in temperature interval 293-423 K. At 423 K in previous angle interval 14 reflections are fixed which also save diphase states. At temperature $488 \pm 1 \mathrm{~K}$ all reflections disappear and in previous angle interval the four new reflections with (200), (220), (311) and (400) indexes are fixed which belong to high-temperature FCC modifications with lattice parameter $\mathrm{a}=6.107 \AA$ Á.

The temperature dependences of lattice parameter dependences of existing phases of $\mathrm{Ag}_{1.5} \mathrm{Cu}_{0.5} \mathrm{Se}$ are given in fig.1. As it is seen from fig. 1 the parameter values $\underline{a}$, $\underline{c}$ of $\mathrm{Ag}_{2} \mathrm{Se}$ and $\underline{a}$ of AgCuSe increase linearly in dependence on temperature and parameter $\underline{b}$ of $\mathrm{Ag}_{2} \mathrm{Se}$, parameters $\underline{b}$ and $\underline{c}$ of AgCuSe deviate from linearity.

## 2. $\mathrm{Ag}_{0.4} \mathrm{Cu}_{1.6} \mathrm{Se}_{\text {. }}$

The sample by $2 \times 4 \times 6 \mathrm{~mm}$ size is cut from $\mathrm{Ag}_{0.4} \mathrm{Cu}_{1.6} \mathrm{Se}$ composition at room temperature. 18 sharp diffraction reflections (table 2) are fixed from this sample in angle interval $10^{\circ} \leq 26 \leq 110^{\circ}$. As it is seen from table 2, 15 from 18 reflections are indicated on the base of AgCuSe rhombic modification parameters and 11 from 15 are indicated on the base of $\mathrm{Cu}_{2} \mathrm{Se}$ rhombic modification parameters. It is followed that $\mathrm{Ag}_{0.4} \mathrm{Cu}_{1.6} \mathrm{Se}$ composition is diphase one as well as $\mathrm{Ag}_{1.5} \mathrm{Cu}_{0.5} \mathrm{Se}$ composition at room temperature.

Table 1.
$\mathrm{Ag}_{1.5} \mathrm{Cu}_{0.5} \mathrm{Se}$ diffractogram calculation described at different temperatures.
Radiation $\mathrm{CuK}_{\alpha}\left(\lambda_{\alpha}=1,5418 \AA\right)$, $\mathrm{N} i$ is filter, mode: $35 \kappa \mathrm{~V}, 10 \mathrm{~mA}$.

| $\mathrm{T}_{\text {exp }}, \mathrm{K}$ | $\theta$ | $\mathrm{I} / \mathrm{I}_{0}$ | $\mathrm{D}_{\text {exp }}, \AA$ | $\mathrm{Ag}_{2} \mathrm{Se}$ |  | AgCuSe |  | Crystal lattice parameters |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  | $\mathrm{D}_{\text {calc }}$, Á | h к 1 | $\mathrm{D}_{\text {calc }}$, £́ | h к 1 |  |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 295 | $11^{\circ} 27^{\prime}$ | 30 | 3.882 | 3.8820 | 002 |  |  |  |
|  | $11^{\circ} 46^{\prime}$ | 20 | 3.781 | 3.7836 | 101 |  |  |  |
|  | $13^{\circ} 22^{\prime}$ | 20 | 3.336 | 3.3351 | 111 |  |  |  |
|  | $13^{\circ} 52^{\prime}$ | 10 | 3.217 | 3.2142 | 021 |  |  |  |
|  | $16^{\circ} 22^{\prime}$ | 30 | 2.737 | 2.7372 | 120 |  |  |  |
|  | $16^{\circ} 45^{\prime}$ | 90 | 2.675 | 2.6758 | 112 |  |  | $\mathrm{Ag}_{2} \mathrm{Se}$ |
|  | $17^{\circ} 09^{\prime}$ | 90 | 2.614 | 2.6121 | 022 |  |  | Orthorhombic |
|  | $17^{\circ} 23^{\prime}$ | 100 | 2.581 | 2.5815 | 121 |  |  | $\mathrm{a}=4.333 \AA$ |
|  | $18^{\circ} 06^{\prime}$ | 60 | 2.481 | - | - | 2.4828 | 112 | $\mathrm{b}=7.062 \AA$ |
|  | $18^{\circ} 30^{\prime}$ | 40 | 2.430 | 2.4300 | 013 |  |  | $\mathrm{c}=7.764 \AA$ |
|  | $20^{\circ} 09^{\prime}$ | 30 | 2.238 | 2.2370 | 122 |  |  | $\mathrm{Z}=4$ |
|  | $21^{\circ} 20^{\prime}$ | 80 | 2.119 | 2.1194 | 113 |  |  | sp.gr. $\mathrm{P} 2_{1} 2_{1} 2_{1}$ |
|  | $21^{\circ} 51^{\prime}$ | 20 | 2.071 | 2.0712 | 210 |  |  | $\rho=8.237 \mathrm{gr} / \mathrm{cm}^{3}$ |
|  | $21^{\circ} 53$ ' | 30 | 2.068 | 2.0685 | 130 |  |  |  |
|  | $22^{\circ} 31^{\prime}$ | 30 | 2.013 | 2.0128 | 032 | 2.0120 | 220 | AgCuSe |
|  | $22^{\circ} 39^{\prime}$ | 45 | 2.002 | 2.0012 | 211 |  |  | Orthorhombic |
|  | $24^{\circ} 27^{\prime}$ | 20 | 1.863 | - | - | 1.8640 | 113 | $a=4.105 \AA$ |
|  | $25^{\circ} 03$ ' | 5 | 1.821 | 1.8255 | 132 | 1.8223 | 241 | $\mathrm{b}=20.350 \AA$ |
|  | $25^{\circ} 33^{\prime}$ | 10 | 1.787 | 1.7875 | 041 | 1.7875 | 063 | $\mathrm{c}=6.310 \AA$ |
|  | $26^{\circ} 39^{\prime}$ | 10 | 1.719 | 1.7182 | 114 | 1.7205 | 202 | $\mathrm{Z}=10$ |
|  | $29^{\circ} 39^{\prime}$ | 10 | 1.558 | 1.5615 | 231 | 1.5589 | 024 | sp.gr. P4/nmm |
|  | $31^{\circ} 45^{\prime}$ | 15 | 1.465 | 1.4618 | 105 | 1.4625 | 0.10.3 | $\rho=7.885 \mathrm{gr} / \mathrm{cm}^{3}$ |
|  | $32^{\circ} 57^{\prime}$ | 10 | 1.417 | 1.4163 | 214 | 1.4113 | 243 |  |
|  | $33^{\circ} 54{ }^{\prime}$ | 20 | 1.382 | 1.3823 | 143 | 1.3847 | 154 |  |
|  | $38^{\circ} 21^{\prime}$ | 10 | 1.242 | 1.2424 | 215 | 1.2468 | 0.10.4 |  |
|  | $39^{\circ} 35^{\prime}$ | 20 | 1.210 | 1.2099 | 243 | 1.2042 | 115 |  |
|  | $40^{\circ} 16^{\prime}$ | 20 | 1.193 | 1.1920 | 153 | 1.1911 | 2.10 .3 |  |
| 373 | $11^{\circ} 25^{\prime}$ | 30 | 3.893 | 3.8934 | 002 |  |  |  |
|  | $11^{\circ} 44^{\prime}$ | 20 | 3.791 | 3.7905 | 101 |  |  |  |
|  | $13^{\circ} 20^{\prime}$ | 20 | 3.343 | 3.3426 | 111 |  |  | $\mathrm{Ag}_{2} \mathrm{Se}$ |
|  | $13^{\circ} 50^{\prime}$ | 10 | 3.224 | 3.2241 | 021 |  |  | Orthorhombic |
|  | $16^{\circ} 20^{\prime}$ | 30 | 2.744 | 2.7441 | 120 |  |  | $\mathrm{a}=4.3396 \AA$ |
|  | $16^{\circ} 42^{\prime}$ | 90 | 2.682 | 2.6822 | 112 |  |  | $\mathrm{b}=7.0844 \AA$ |
|  | $17^{\circ} 06^{\prime}$ | 90 | 2.622 | 2.6198 | 022 |  |  | $\mathrm{c}=7.7868 \AA$ |
|  | $17^{\circ} 20^{\prime}$ | 100 | 2.587 | 2.5880 | 121 |  |  | $\mathrm{Z}=4$ |
|  | $18^{\circ} 03^{\prime}$ | 60 | 2.488 | - | - | 2.4838 | 112 | $\rho=8.175 \mathrm{gr} / \mathrm{cm}^{3}$ |
|  | $18^{\circ} 28^{\prime}$ | 40 | 2.434 | 2.4376 | 013 |  |  |  |
|  | $20^{\circ} 07^{\prime}$ | 30 | 2.241 | 2.2428 | 122 |  |  |  |
|  | $21^{\circ} 18^{\prime}$ | 80 | 2.122 | 2.1253 | 113 |  |  |  |
|  | $21^{\circ} 49^{\prime}$ | 20 | 2.074 | 2.0748 | 210 |  |  |  |
|  | $21^{\circ} 51$, | 30 | 2.071 | 2.0743 | 130 |  |  |  |


| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 373 | $22^{\circ}{ }^{\prime}{ }^{\prime}$ | 30 | 2.017 | 2.0191 | 032 | 2.0150 | 220 |  |
|  | $22^{\circ} 37^{\prime}$ | 45 | 2.004 | 2.0048 | 211 | - | - |  |
|  | $24^{\circ} 24^{\prime}$ | 20 | 1.866 | - | - | 1.8640 | 113 |  |
|  | $25^{\circ} 00^{\prime}$ | 5 | 1.824 | 1.8306 | 132 | 1.8257 | 241 | AgCuSe |
|  | $25^{\circ} 51$ | 10 | 1.768 | 1.7625 | 400 | - | - | Orthorhombic |
|  | $26^{\circ} 36^{\prime}$ | 10 | 1.722 | 1.7229 | 114 | 1.7216 | 202 | $\mathrm{a}=4.1100 \AA$ |
|  | $29^{\circ} 34^{\prime}$ | 10 | 1.562 | 1.5652 | 231 | 1.5585 | 024 | $\mathrm{b}=20.4808 \AA$ |
|  | $31^{\circ} 42$ ' | 20 | 1.467 | 1.4658 | 105 | 1.4669 | 0.10.3 | $\mathrm{c}=6.3069$ A |
|  | $32^{\circ} 55^{\prime}$ | 10 | 1.417 | 1.4196 | 214 | 1.4120 | 243 | $\mathrm{Z}=10$ |
|  | $33^{\circ} 52^{\prime}$ | 20 | 1.384 | 1.3864 | 143 | 1.3834 | 154 | $\rho=7.829 \mathrm{gr} / \mathrm{cm}^{3}$ |
|  | $38^{\circ} 18^{\prime}$ | 10 | 1.244 | 1.2455 | 215 | 1.2481 | 0.10.4 |  |
|  | $39^{\circ} 32^{\prime}$ | 20 | 1.211 | 1.2130 | 243 | 1.2037 | 115 |  |
|  | $40^{\circ} 14^{\prime}$ | 20 | 1.196 | 1.1956 | 153 | 1.1936 | 2.10 .3 |  |
| 423 | $14^{\circ} 08^{\prime}$ | 20 | 3.157 | - |  | 3.1585 | 002 | $\mathrm{Ag}_{2} \mathrm{Se}$ |
|  | $15^{\circ} 20^{\prime}$ | 60 | 2.915 | - | - | 2.9148 | 150 | Orthorhombic |
|  | $17^{\circ} 03^{\prime}$ | 80 | 2.629 | 2.6288 | 022 | - |  | $\mathrm{a}=4.3540 \AA$ |
|  | $18^{\circ} 06^{\prime}$ | 70 | 2.482 | 2.6288 | 22 | 2.4815 | 112 | $5=7.0675 \AA$ |
|  | $18^{\circ} 16^{\prime}$ | 80 | 2.459 | 2.4589 | 013 | - |  | $\mathrm{c}=7.8688 \AA$ |
|  | $21^{\circ} 07$ | 90 | 2.140 | 2.1408 | 113 | 2.1423 | 152 | $\mathrm{Z}=4$ |
|  | $21^{\circ} 45^{\prime}$ | 20 | 2.081 | 2.0806 | 210 | - |  | $\rho=8.119 \mathrm{gr} / \mathrm{cm}^{3}$ |
|  | $22^{\circ} 25^{\prime}$ | 60 | 2.021 | 2.0211 | 032 |  |  | AgCuSe |
|  | $22^{\circ} 33^{\prime}$ | 100 | 2.0-10 | 2.0113 | 211 | - |  | Orthorhombic |
|  | $24^{\circ} 21^{\prime}$ | 20 | 1.870 |  | - | 1.8644 | 113 | $\mathrm{a}=4.0850 \AA$ |
|  | $26^{\circ} 21^{\prime}$ | 10 | 1.737 | 1.7376 | 114 |  |  | $\mathrm{b}=20.7973 \AA$ |
|  | $29^{\circ} 31^{\prime}$ | 10 | 1.565 | 1.5667 | 231 | 1.5614 | 024 | $\mathrm{c}=6.3170 \AA$ |
|  | $31^{\circ} 24^{\prime}$ | 10 | 1.480 | 1.4799 | 105 | 1.4797 | 0.10 .3 | $\mathrm{Z}=10$ |
|  | $35^{\circ} 38^{\prime}$ | 10 | 1.323 | 1.3233 | 321 | 1.3233 | 2.10 .2 | $\rho=7.744 \mathrm{gr} / \mathrm{cm}^{3}$ |
| 473 | $14^{\circ} 07^{\prime}$ | 20 | 3.165 | - | - | 3.1647 | 002 | $\mathrm{Ag}_{2} \mathrm{Se}$ |
|  | $15^{\circ} 18^{\prime}$ | 60 | 2.921 |  | - | 2.9161 | 150 | Orthorhombic |
|  | $17^{\circ} 00^{\prime}$ | 80 | 2.637 | 2.6361 | 022 | 2.6481 | 151 | $\mathrm{a}=4.3643 \AA$ |
|  | $18^{\circ} 04^{\prime}$ | 70 | 2.486 | - | - | 2.4853 | 112 | $\mathrm{b}=7.0781 \AA$ |
|  | $18^{\circ} 14^{\prime}$ | 80 | 2.464 | 2.4678 | 013 |  |  | $\mathrm{c}=7.8995 \AA$ |
|  | $21^{\circ} 05^{\prime}$ | 80 | 2.143 | 2.1482 | 113 | 2.1447 | 152 | $\mathrm{Z}=4, \rho=8.019 \mathrm{gr} / \mathrm{cm}^{3}$ |
|  | $21^{\circ} 42^{\prime}$ | 20 | 2.085 | 2.0851 | 210 | - |  | AgCuSe |
|  | $22^{\circ} 22^{\prime}$ | 60 | 2.026 | 2.0257 | 032 | - | - | Orthorhombic |
|  | $22^{\circ} 31^{\prime}$ | 100 | 2.013 | 2.0161 | 211 |  |  | $\mathrm{a}=4.0902 \AA$ |
|  | $24^{\circ} 18^{\prime}$ | 20 | 1.874 |  | - | 1.8676 | 113 | $\mathrm{b}=20.7928 \AA$ |
|  | $26^{\circ} 19^{\prime}$ | 10 | 1.739 | 1.7437. | 114 |  |  | $\mathrm{c}=6.3296 \AA$ |
|  | $29^{\circ} 28^{\prime}$ | 10 | 1.567 | 1.5702 | 231 | 1.5642 | 024 | $\mathrm{Z}=10$ |
|  | $31^{\circ} 22^{\prime}$ | 10 | 1.481 | 1.4856 | 105 | 1.4810 | 0.10 .3 | $\rho=7.721 \mathrm{gr} / \mathrm{cm}^{3}$ |
|  | $35^{\circ} 36^{\prime}$ | 10 | 1.324 | 1.3268 | 321 | 1.3243 | 2.10 .2 |  |
| 523 | $14^{\circ} 38^{\prime}$ | 60 | 3.053 | 3.0534 | 200 |  |  | HCC |
|  | $20^{\circ} 55^{\prime}$ | 80 | 2.159 | 2.1591 | 220 |  |  | $\mathrm{a}=6.1068 \AA$ |
|  | $24^{\circ} 45^{\prime}$ | 100 | 1.841 | 1.8413 | 311 |  |  | $\mathrm{Z}=4$, sp.gr.Fm3m |
|  | $30^{\circ} 19^{\prime}$ | 40 | 1.527 | 1.5267 | 400 |  |  | $\rho=7.95 \mathrm{gr} / \mathrm{cm}^{3}$ |
| 573 | $26^{\circ} 21^{\prime}$ | 60 | 3.058 | 3.0592 | 200 |  |  | HCC |
|  | $29^{\circ} 31^{\prime}$ | 80 | 2.164 | 2.1632 | 220 |  |  | $a=6.1184 \AA$ |
|  | $31^{\circ} 24^{\prime}$ | 100 | 1.845 | 1.8448 | 311 |  |  | $\mathrm{Z}=4$, sp.gr.Fm3m |
|  | $35^{\circ} 38^{\prime}$ | 40 | 1.530 | 1.5296 | 400 |  |  | $\rho=7.90 \mathrm{gr} / \mathrm{cm}^{3}$ |



Fig.1. The temperature dependence of crystal lattice parameters and modification density of $\mathrm{Ag}_{1,5} \mathrm{Cu}_{0,5} \mathrm{Se}$.

- are a,b,c parameters of crystal lattice and density of $\mathrm{Ag}_{1,5} \mathrm{Cu}_{0,5} \mathrm{Se}$
- are a,b,c parameters of crystal lattice and density of $\mathrm{Ag}_{2} \mathrm{Se}$
o are a parameter and $\rho_{x}$ density of FCC modification of $\mathrm{Ag}_{1,5} \mathrm{Cu}_{0,5} \mathrm{Se}$.

The furnace is switched on after recording of diffraction reflections at room temperature not changing the sample orientation and every each 50 K the control diffraction recordings are carried out. The sample temperature before the beginning of each recording is kept constant during 50 minutes. As it is seen from table 3 in temperature interval 293-523 K numbers and intensities of diffraction reflection changes don't change. At 573 K all diffraction reflections disappear and in previous angle interval 7 new reflections belonging to high-temperature FCC modification with elementary cell parameter $\mathrm{a}=5.896 \AA$ are fixed.

The equilibrium temperature between modifications is equal to $540 \pm 1 \mathrm{~K}$. The transformations are reversible ones and cubic modification decomposes on AgCuSe and $\mathrm{Cu}_{2} \mathrm{Se}$ at temperature less than equilibrium one; both compositions have rhombic structure. The temperature dependences of lattice parameters of rhombic and FCC modifications of $\mathrm{Ag}_{0.4} \mathrm{Cu}_{1.6} S \mathrm{e}$ are given in fig.2. As it is seen from fig.2. the parameters $\underline{a}$ and $\underline{b}$ of AgCuSe at 473 K deviate from linearity and parameter $\underline{a}$ of $\mathrm{Cu}_{2} \mathrm{Se}$ strongly increases up to temperature 373 K and further increases linearly up to transformation temperature. The parameter deviation from linearity of both rhombic phases mainly is connected with redistribution of
cation two types. The density temperature dependences of existing modifications are also shown in fig. 2. The density difference presence of existing phases is the one of the instability reasons of compositions under consideration.


Fig.2. The temperature dependence of lattice parameters, volume and density of orthorhombic and FCC modifications of $\mathrm{Ag}_{0.4} \mathrm{Cu}_{1.6} \mathrm{Se}$

- are a,b,c parameters of crystal lattice and FCC modifications of AgCuSe
- are $\mathrm{a}, \mathrm{b}, \mathrm{c}$ parameters of crystal lattice and $\mathrm{Cu}_{2} \mathrm{Se}$ density
o are a parameter and $\rho_{\mathrm{x}}$ density of FCC modification of $\mathrm{Ag}_{0,4} \mathrm{Cu}_{1,6} \mathrm{Se}$.


## THERMAL EXPANSION OF LATTICE PARAMETERS OF POLYMORPHOUS MODIFICATIONS OF $\mathrm{Ag}_{1.5} \mathbf{C u}_{0.5} \mathrm{Se} \quad$ AND $\mathbf{A g}_{0.4} \mathbf{C u}_{1.6} \mathbf{S e}$.

The study of thermal expansion of pure chemical compounds by methods of high-temperature roentgenography is enough trivial task because the same questions are solved using dilatometric method by less difficulties and more accuracy. However, the possibility of investigation on micro-sample that is especially valuable at study of structural transformations is the advantage of high-temperature roentgenography method.

The study of thermal expansion anisotropy not only on single crystal samples but on polycrystalline ones and also the measurement of thermal expansion coefficient (TEC) in phase mixture can be carried out with the help of high-temperature roentgenography.
$\mathrm{Ag}_{0.4} \mathrm{Cu}_{1.6} \mathrm{Se}$ diffractogram calculation described at different temperatures.
Radiation $\mathrm{CuK}_{\alpha}\left(\lambda_{\alpha}=1,5418 \AA\right.$ ), $\mathrm{N} i$ is filter, mode: $35 \mathrm{KV}, 10 \mathrm{~mA}$.

| $\mathrm{T}_{\text {exp }}, \mathrm{K}$ | $\theta$ | $\mathrm{I} / \mathrm{I}_{0}$ | $\mathrm{D}_{\text {exp }}$, $\AA$ Í | CuAgSe |  | $\mathrm{Cu}_{2} \mathrm{Se}$ |  | Crystal lattice parameters |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  | $\mathrm{D}_{\text {calc }}$, , | hкl | $\mathrm{D}_{\text {calc }}$, Á | hкl |  |
| 1 | $\underline{2}$ | 3 | 4 | 5 | $\underline{6}$ | 7 | 8 | 9 |
| 293 | $13^{\circ} 08^{\prime}$ | 60 | 3.3916 | 3.3917 | 060 | - | - | AgCuSe |
|  | $15^{\circ} 28^{\prime}$ | 40 | 2.8916 | 2.8902 | 150 | 2.8939 | 024 | Orthorhombic |
|  | $16^{\circ} 54$ | 50 | 2.6518 | - | - | 2.6512 | $\underline{121}$ | $a=4.102 \AA$ |
|  | $18^{\circ} 05^{\prime}$ | 40 | 2.4836 | 2.4828 | $\underline{112}$ | 2.4881 | 123 | $\mathrm{b}=0.362 \AA$ |
|  | $20^{\circ} 19^{\prime}$ | 80 | 2.2203 | 2.2207 | 171 | 2.2158 | 033 | $\mathrm{c}=6.292 \AA$ |
|  | $\underline{21}{ }^{\circ} \underline{12}$ | 40 | 2.1296 | 2.1284 | $\underline{112}$ | 2.1295 | 034 | $\mathrm{Z}=10$ |
|  | $22^{\circ} 15^{\prime}$ | $\underline{100}$ | 2.0362 | 2.0350 | $\underline{0} \underline{10.0}$ | 2.0371 | 130 | sp.gr. P4/nmm |
|  | $24^{\circ} 39^{\prime}$ | $\underline{10}$ | 1.8484 | - | - | 1.8423 | 214 | $\rho=7.909 \mathrm{gr} / \mathrm{cm}$ |
|  | $26^{\circ} 03$ ' | 90 | 1.7554 | 1.7560 | 260 | 1.7580 | 040 |  |
|  | $29^{\circ} 31^{\prime}$ | $\underline{10}$ | 1.5728 | 1.5739 | 173 | 1.5729 | 143 | $\mathrm{Cu}_{2} \mathrm{Se}$ |
|  | $30^{\circ} 40^{\prime}$ | $\underline{10}$ | 1.5122 | - | - | 1.5083 | 233 | Oprthorhombic |
|  | $31^{\circ} 51^{\prime}$ | 30 | 1.4609 | 1.4625 | 0.10.3 |  | - | $\mathrm{a}=4.137 \AA$ |
|  | $35^{\circ} 09^{\prime}$ | $\underline{10}$ | 1.3390 | 1.3406 | 084,311 | 1.3370 | 240 | $\mathrm{b}=7.022 \AA$ |
|  | $39^{\circ} 57^{\prime}$ | $\underline{20}$ | 1.2006 | 1.2042 | 115,352 | - | - | $\mathrm{c}=20.390 \AA$ |
|  | $40^{\circ} 27^{\prime}$ | $\underline{20}$ | 1.1882 | 1.1876 | 135 | 1.1845 | 330 | $\mathrm{Z}=12$ |
|  | $42^{\circ} 39^{\prime}$ | $\underline{10}$ | 1.1378 | 1.1309 | 333 | 1.1374 | 335 | sp.gr. P222 ${ }_{1}$ |
|  | $\begin{aligned} & 48^{\circ} 21^{\prime} \\ & 51^{\circ} 33^{\prime} \end{aligned}$ | $\frac{10}{10}$ | $\begin{aligned} & 1.0317 \\ & 0.9844 \end{aligned}$ | $\begin{aligned} & 1.0323 \\ & 0.9823 \end{aligned}$ | $\begin{aligned} & 314 \\ & 460 \end{aligned}$ | $0.9834$ | $422$ | $\rho=6.930 \mathrm{gr} / \mathrm{cm}^{3}$ |
|  | $51^{\circ} 33^{\prime}$ |  | 0.9844 | 0.9823 |  | 0.9834 |  |  |
| 373 | $13^{\circ} 06^{\prime}$ | 60 | 3.4005 | 3.3993 | 060 | - | - | AgCuSe <br> Orthorhombic $\mathrm{a}=4.106 \AA$ <br> $\mathrm{b}=20.389 \AA$ $\mathrm{c}=6.295 \AA$ <br> $\mathrm{Z}=10$ sp.gr. $\mathrm{P} 4 / \mathrm{nmm}$ $\rho=7.886 \mathrm{gr} / \mathrm{cm}^{3}$ |
|  | $15^{\circ} 26^{\prime}$ | 40 | 2.8959 | 2.8940 | 150 | 2.8939 | 024 |  |
|  | $16^{\circ} 52^{\prime}$ | 50 | 2.6574 | - | - | 2.6512 | $\underline{121}$ |  |
|  | $18^{\circ} 03$ ' | 40 | 2.4884 | 2.4853 | $\underline{112}$ | 2.4881 | $\overline{123}$ |  |
|  | $\underline{20}{ }^{\circ} 16^{\prime}$ | 80 | 2.2255 | 2.2239 | 171 | 2.2158 | 033 |  |
|  | $\underline{21}^{\circ} 19^{\prime}$ | 40 | $\underline{2.1202}$ | - | $\underline{112}$ | 2.1295 | 034 |  |
|  | $22^{\circ} 13$, | $\underline{100}$ | 2.0389 | 2.0396 | $\underline{0} \underline{10.0}$ | 2.0371 | 130 |  |
|  | $24^{\circ} 37{ }^{\prime}$ | $\underline{10}$ | 1.8505 | - | - | 1.8423 | 214 |  |
|  | $26^{\circ} \underline{01}{ }^{\prime}$ | 90 | 1.7572 | 1.7571 | 260 | 1.7580 | 040 | $\mathrm{Cu}_{2} \mathrm{Se}$$\begin{gathered} \text { Orthorhombic } \\ \mathrm{a}=4.139 \AA \\ \mathrm{~b}=7.029 \AA \\ \mathrm{c}=20.434 \AA \\ \mathrm{Z}=12 \text { sp.gr. P} 222_{1} \\ \rho=6.904 \mathrm{gr} / \mathrm{cm}^{3} \end{gathered}$ |
|  | $29^{\circ}{ }^{\circ}{ }^{\prime}$ | $\underline{10}$ | 1.5742 | 1.5760 | 173 | 1.5729 | 143 |  |
|  | $30^{\circ} 38^{\prime}$ | $\frac{10}{30}$ | 1.5131 | 1.4651 | 0.10.3 | 1.5083 | 233 |  |
|  | $31^{\circ} 49^{\prime}$ | $\frac{10}{30}$ | 1.4623 | - | - | - | - |  |
|  | $35^{\circ} 07^{\prime}$ | $\underline{10}$ | 1.3402 | 1.3428 | 084,311 | 1.3370 | 240 |  |
|  | $39^{\circ} 54^{\prime}$ | $\underline{20}$ | 1.2019 | 1.2056 | 115,352 | - | - |  |
|  | $40^{\circ} 25^{\prime}$ | $\underline{20}$ | 1.1891 | 1.1891 | 135 | 1.1845 | $330$ |  |
|  | $42^{\circ} 36^{\prime}$ | $\underline{10}$ | 1.1389 | 1.1313 | 333 | 1.1374 | 335 |  |
|  | $40^{\circ} 25^{\prime}$ | $\underline{10}$ | 1.0323 | 1.0329 | 314 | - | - |  |
|  | $42^{\circ} 36^{\prime}$ | $\underline{10}$ | 0.9848 | 0.9840 | 460 | 0.9834 | 422 |  |


| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 473 | $13^{\circ} 03^{\prime}$ | 60 | 3.4141 | 3.4088 | 060 | - |  | AgCuSe |
|  | $15^{\circ} 23^{\prime}$ | 40 | 2.9058 | 2.9025 | 150 | 2.8939 | 024 | Orthorhombic |
|  | $16^{\circ} 50$, | 50 | 2.6619 | - | - | 2.6512 | 121 | $\mathrm{a}=4.114$ £́ |
|  | $18^{\circ} 00^{\prime}$ | 40 | 2.4948 | 2.4845 | 112 | 2.4881 | 123 | $\mathrm{b}=20.421$ Á |
|  | $20^{\circ} 14^{\prime}$ | 80 | 2.2293 | 2.2294 | 171 | 2.2158 | 033 | $\mathrm{c}=6.300$ Á |
|  | $21^{\circ} 16^{\prime}$ | 40 | 2.1254 | - | 112 | 2.1295 | 034 | $\mathrm{Z}=10$ |
|  | $22^{\circ} 11^{\prime}$ | 100 | 2.0421 | 2.0453 | 0.10.0 | 2.0371 | 130 | sp.gr. P4/nmm |
|  | $24^{\circ} 35^{\prime}$ | 10 | 1.8531 | - | - | 1.8423 | 214 | $\rho=7.851 \mathrm{gr} / \mathrm{cm}^{3}$ |
|  | $25^{\circ} 58^{\prime}$ | 90 | 1.7604 | 1.7631 | 260 | 1.7580 | 040 |  |
|  | $29^{\circ} 16^{\prime}$ | 10 | 1.5768 | 1.5758 | 173 | 1.5729 | 143 | $\begin{gathered} \mathrm{Cu}_{2} \mathrm{Se} \\ \text { Orthorhombic, } \mathrm{a}=4.147 \AA \dot{\AA} \mathrm{~A}=7.042 \AA \\ \mathrm{c}=20.572 \AA \\ \mathrm{Z}=12 \mathrm{sp} . \mathrm{gr} . \mathrm{P} 222_{1} \\ \rho=6.832 \mathrm{gr} / \mathrm{cm}^{3} \end{gathered}$ |
|  | $30^{\circ} 35^{\prime}$ | 10 | 1.5154 | - | - | 1.5083 | 233 |  |
|  | $31^{\circ} 46^{\prime}$ | 30 | 1.4642 | 1.4652 | 0.10.3 | - |  |  |
|  | $35^{\circ} 05^{\prime}$ | 10 | 1.3412 | 1.3411 | 084,311 | 1.3370 | 240 |  |
|  | $39^{\circ} 51$, | 20 | 1.2032 | 1.2030 | 115,352 | 45 | - |  |
|  | $40^{\circ} 22^{\prime}$ | 20 | 1.1911 | 1.1867 | 135 | 1.1845 | 330 |  |
|  | $42^{\circ} 34^{\prime}$ | 10 | 1.1395 | 1.1334 | 333 | 1.1374 | 335 |  |
|  | $48^{\circ} 16^{\prime}$ | 10 | 1.0331 | 1.0338 | 314 | - | - |  |
|  | $51^{\circ} 28^{\prime}$ | 10 | 0.9854 | 0.9854 | 460 | 0.9834 | 422 |  |
| 523 | $13^{\circ} 01^{\prime}$ | 60 | 3.4217 | 3.4221 | 060 | - |  | AgCuSe Orthorhombic, $a=4.121 \AA$ Á $\mathrm{b}=20.432$ Á $\mathrm{c}=6.309$ Á $\mathrm{Z}=10$ <br> sp.gr. P4/nmm $\rho=7.822 \mathrm{gr} / \mathrm{cm}^{3}$ <br> $\mathrm{Cu}_{2} \mathrm{Se}$ <br> Orthorhombic , $a=4.154 \AA$ b=7.052 Á $\mathrm{c}=20.666$ £́ $\mathrm{Z}=12$ <br> sp.gr. P222 ${ }_{1}$ $\rho=6.780 \mathrm{gr} / \mathrm{cm}^{3}$ |
|  | $15^{\circ} 21^{\prime}$ | 40 | 2.9124 | 2.9198 | 150 | 2.8939 | 024 |  |
|  | $16^{\circ} 49^{\prime}$ | 50 | 2.6647 | - | - | 2.6512 | 121 |  |
|  | 17 ${ }^{\circ} 58^{\prime}$ | 40 | 2.4989 | 2.4942 | 112 | 2.4881 | 123 |  |
|  | $20^{\circ} 12^{\prime}$ | 80 | 2.2326 | 2.2398 | 171 | 2.2158 | 033 |  |
|  | $21^{\circ} 14^{\prime}$ | 40 | 2.1290 | - | 112 0.10.0 | 2.1295 |  |  |
|  | $22^{\circ} 10^{\prime}$ | 100 | 2.0432 | 2.0530 | - | 2.0371 | 130 |  |
|  |  |  |  | - | 260 | 1.8423 | 214 |  |
|  | $24^{\circ} 10^{\prime}$ | 10 | 1.8830 | 1.7630 | 173 | 1.7580 | 040 |  |
|  | $25^{\circ} 56$, | 90 | 1.7629 | 1.5809 | - | 1.5729 | 143 |  |
|  | $29^{\circ} 14^{\prime}$ | 10 | 1.5784 | - | 0.10.3 | 1.5083 | 233 |  |
|  | $30^{\circ} 33^{\prime}$ | 10 | 1.5166 | 1.4695 | 084,311 | 1.3370 | 20 |  |
|  | $31^{\circ} 44^{\prime}$ | 30 | 1.4656 | 1.3443 | 115, 352 | 1.3370 | 240 |  |
|  | $35^{\circ} 03$, | 10 | 1.3423 | 1.2057 | 135333 | 1.1845 |  |  |
|  | $39^{\circ} 49^{\prime}$ | 20 | 1.2040 | 1.1895 | 314460 | 1.1374 | 330 |  |
|  | $40^{\circ} 20^{\prime}$ | 20 | 1.1930 | 1.1403 1.0392 |  |  | 335 |  |
|  | $42^{\circ} 32^{\prime}$ | 10 | 1.1540 | 1.0392 0.9935 |  |  | $422$ |  |
|  | $5^{5} 0^{\circ} 11^{\prime}$, | 10 10 | 1.0521 |  |  |  |  |  |
| 573 | $15^{\circ} 10^{\prime}$ | 50 | 2.9469 | 2.9479 | 200 |  |  | $\begin{gathered} \text { FCC } \\ \mathrm{a}=5.8257 \AA \\ \mathrm{Z}=4 \\ \text { sp.gr. Fm3m } \\ \rho=7.258 \mathrm{~g} / \mathrm{cm}^{3} \end{gathered}$ |
|  | $21^{\circ} 42$, | 30 | 2.0852 | 2.0845 | 220 |  |  |  |
|  | $25^{\circ} 42^{\prime}$ | 45 | 1.7775 | 1.7777 | 311 |  |  |  |
|  | $26^{\circ} 56^{\prime}$ | 100 | 1.7021 | 1.7020 | 222 |  |  |  |
|  | $31^{\circ} 32^{\prime}$ | 60 | 1.4740 | 1.4740 | 400 |  |  |  |
|  | $34^{\circ} 45^{\prime}$ | 40 | 1.3525 | 1.3526 | 331 |  |  |  |
|  | $35^{\circ} 47^{\prime}$ | 60 | 1.3182 | 1.3184 | 420 |  |  |  |
| 673 | $15^{\circ} 07$ ' | 50 | 2.9559 | 2.9516 | 200 |  |  | $\begin{gathered} \text { FCC } \\ \mathrm{a}=5.9063 \AA \\ \mathrm{Z}=4 \\ \text { sp.gr. Fm } 3 \mathrm{~m} \\ \rho=7.211 \mathrm{gr} / \mathrm{cm}^{3} \end{gathered}$ |
|  | $21^{\circ} 39^{\prime}$ | 30 | 2.0897 | 2.0871 | 220 |  |  |  |
|  | $25^{\circ} 40^{\prime}$ | 45 | 1.7795 | 1.7799 | 311 |  |  |  |
|  | $26^{\circ} 54$ ' | 100 | 1.7040 | 1.7041 | 222 |  |  |  |
|  | $31^{\circ} 30^{\prime}$ | 60 | 1.4754 | 1.4758 | 400 |  |  |  |
|  | $34^{\circ} 42^{\prime}$ | 40 | 1.3541 | 1.3543 | 331 |  |  |  |
|  | $35^{\circ} 45^{\prime}$ | 60 | 1.3196 | 1.3200 | 420 |  |  |  |

TEC obtaining is made by differentiation (analytic or graphic) of equation for temperature dependence of parameters: $a=f(T)$ for cubic crystal lattice, $a=f(T)$ and $c=f(T)$ for hexagonal, tetragonal and rhombic ones, $a=f(T), b=f(T), \quad c=f(T)$ for orthorhombic and etc. The crystal thermal expansion in given work is calculated from temperature dependence of elementary cell parameters in temperature interval enveloping all possible structural changes. The crystal elementary cell parameters change at increase of its temperature on $\Delta T$. Let's designate the crystal elementary cell parameters by primed letters at change of its temperature on $\Delta T$ :

$$
\begin{aligned}
& a^{\prime}=a\left(1+\alpha_{1} \Delta T\right) \\
& b^{\prime}=b\left(1+\alpha_{2} \Delta T\right) \\
& c^{\prime}=c\left(1+\alpha_{3} \Delta T\right)
\end{aligned}
$$

From these equations TEC by main crystallographic directions is as follows:

$$
\begin{gathered}
\alpha_{[100]}=\frac{a^{1}-a}{a\left(T_{2}-T_{1}\right)} \\
\alpha_{[010]}=\frac{b^{1}-b}{b\left(T_{2}-T_{1}\right)}, \alpha_{[001]}=\frac{c^{1}-c}{c\left(T_{2}-T_{1}\right)}, \quad \mathrm{T}_{2}>\mathrm{T}_{1}
\end{gathered}
$$

Calculations of $\mathrm{Ag}_{1.5} \mathrm{Cu}_{0.5} \mathrm{Se}$ diffractogram in temperature interval $295-573 \mathrm{~K}$ enveloping all possible structural changes are given in table 1. TECs, which are given in table, are calculated from temperature dependence of lattice parameters of both rhombic and cubic phases. The anisotropy of thermal expansion on main crystallographic directions is the one of main reasons of temperature instability of crystal structure in which structure transformation with low symmetry into cubic structure having more high symmetry takes place and transformations are carried out by single crystal polycrystal type. The crystal lattice parameters (table 2) of existing phases in composition $\mathrm{Ag}_{0.4} \mathrm{Cu}_{1.6} \mathrm{Se}$ of thermal expansion coefficient calculated from temperature dependence are given in table 4 . As it is seen from table 4, thermal expansion on crystallographic directions [100] and [010] is more strong than in [001] direction in AgCuSe structure. The strong anisotropy on main crystallographic directions is also one of the main reasons of temperature instability of crystal structure.

Table 3.
The thermal expansion coefficients of crystal $\mathrm{Ag}_{1.5} \mathrm{Cu}_{0.5} \mathbf{S e}\left(\times 10^{6} \mathrm{~K}^{-1}\right)$

| Modification | $\mathrm{T}, \mathrm{K}$ | $\alpha_{[100]}$ | $\alpha_{[010]}$ | $\alpha_{[001]}$ | $\overline{\boldsymbol{a}}=\frac{\alpha_{[100]}+\alpha_{[010]}+\alpha_{[001]}}{3}$ | $\beta=\alpha_{[100]}+\alpha_{[010]}+\alpha_{[001]}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $295-373$ | 19.04 | 39.65 | 36.71 | 31.80 | 95.40 |
|  | $295-473$ | 37.28 | 5.99 | 103.83 | 49.03 | 147.10 |
|  | $295-473$ | 40.13 | 12.67 | 96.96 | 49.92 | 149.76 |
| AgCuSe | $295-373$ | 15.23 | 80.34 | -6.14 | 29.81 | 89.43 |
|  | $295-423$ | 37.48 | 169.08 | 8.53 | 71.70 | 215.09 |
|  | $295-473$ | 33.56 | 120.88 | 17.26 | 57.23 | 171.70 |
| FCC | $523-573$ | 37.99 |  |  | 37.99 | 113.97 |

Table 4.
The thermal expansion of orthorhombic and FCC phase of $\mathrm{Ag}_{0.4} \mathrm{Cu}_{1.6} \mathrm{Se}\left(\times 10^{6} \mathrm{~K}^{1}\right)$ composition

| Modification | $\mathrm{T}, \mathrm{K}$ | $\alpha_{[100]}$ | $\alpha_{[010]}$ | $\alpha_{[001]}$ | $\overline{\boldsymbol{a}}=\frac{\alpha_{[100]}+\alpha_{[010]}+\alpha_{[001]}}{3}$ | $\beta=\alpha_{[100]}+\alpha_{[010]}+\alpha_{[001]}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Orthorhombic | $293-373$ | 20.194 | 47.791 | 1.610 | 23.198 | 69.595 |
| AgCuSe | $293-473$ | 35.900 | 50.348 | 6.440 | 30.896 | 95.686 |
|  | $293-523$ | 91.311 | 67.723 | -2.800 | 52.078 | 156.234 |
| Orthorhombic | $293-373$ | 6.043 | 12.460 | 26.974 | 15.159 | 45.477 |
| $\mathrm{Cu}_{2} \mathrm{Se}$ | $293-473$ | 13.428 | 15.823 | 49.589 | 26.28 | 78.840 |
|  | $293-523$ | 1.866 | 19.809 | 58.852 | 32.10 | 96.519 |
| FCC | $573-673$ | 17.979 |  |  | 17.979 | 53.937 |
| $\mathrm{Ag}_{0.4} \mathrm{Cu} 1.6 \mathrm{Se}$ |  |  |  |  |  |  |

## CONCLUSION

In conclusion let's note that Ag cation number in $\mathrm{Ag}_{1.5} \mathrm{Cu}_{0.5} \mathrm{Se}$ compositions is more than Cu one, that's why the high-temperature FCC modification decomposes on $\mathrm{Ag}_{2} \mathrm{Cu}$ and $\mathrm{AgCuSe}\left(\mathrm{T}_{0}=488 \mathrm{~K}\right)$ at temperature lower equilibrium temperature. The Cu cation number in $\mathrm{Ag}_{0.4} \mathrm{Cu}_{1.6} \mathrm{Se}$ composition is more
than Ag one, that's why high-temperature FCC modification ( $\mathrm{T}_{0}=540 \mathrm{~K}$ ) also decomposes on $\mathrm{Cu}_{2} \mathrm{Se}$ and AgCuSe at temperature lower equilibrium temperature. The strong anisotropy of thermal expansion is also one of the main reasons of temperature instability of crystal structure in both compositions.
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# THE INFLUENCE OF TEMPERATURE AND EXCITATION LEVEL ON PHOTOLUMINESCENCE SPECTRA OF Ca(AI $\left.\mathbf{0 . 1}^{1} \mathbf{G a}_{0.9}\right)_{2} \mathbf{S}_{4}: \mathbf{E u}^{2+}$ 

B.G. TAGIYEV ${ }^{1,3}$, O.B. TAGIYEV ${ }^{1,2}$, S.A. ABUSHOV ${ }^{\mathbf{1}}$, E.G. ASADOV ${ }^{\mathbf{1}}$<br>${ }^{l}$ National Space Academy, Bina, Baku, AZ1045,25km<br>${ }^{2}$ The branch of MSU named by M.V.Lomonosov, Baku<br>${ }^{3}$ Institute of Physics of Azerbaijan NAS, AZ1143, Baku Azerbaijan<br>E-mail:elsenesedov@gmail.com


#### Abstract

The dependences of photoluminescence ( PhL ) spectrum intensity of $\mathrm{Ca}\left(\mathrm{Al}_{0.1} \mathrm{Ga}_{0.9}\right)_{2} \mathrm{~S}_{4}: \mathrm{Eu}^{2+}$ crystals on temperature and excitation power are investigated. It is shown that PhL spectrum intensity decreases with temperature increase and it linearly increases in interval $2-10 \mathrm{~mW} / \mathrm{cm}^{2}$ at temperatures 22 and 300 K with increase of exciting radiation power.


Keywords: solid solutions, radiation spectrum, excitation, $\mathrm{Eu}^{2+}$ ions, power
PACS: 76.30.,78.55.,78.60.

## EXPERIMENT TECHNIQUE INTRODUCTION

The perspective of creation of new class optoelectronic devices based on semiconductors doped by europium ions stimulates the intensive work in this direction in series of semiconductor centers. That's why investigation of europium ion photoluminescence in more perspective semiconductor matrixes for optoelectronic applications is the actual problem. The efficiency of optoelectronic devices based on semiconductor matrix doped by europium is defined firstly by energy transition efficiency on semiconductor matrix charge carriers into internal europium ion 4f-shell [1].

The study of luminescent properties of rare-earth elements (REE) in semiconductors and dielectrics gives the information on REE nearest surrounding, centers of symmetry of PhL and crystal field. The ternary alkaliearth chalcogenide semiconductors of $\mathrm{II}-\mathrm{III}_{2}-\mathrm{VI}_{4}(\mathrm{II}-\mathrm{Ba}$, $\mathrm{Sr}, \mathrm{Ca}$; III - Ga, Al; VI - S, Se, O) type activated by REE ions ( $\mathrm{Eu}, \mathrm{Ce}, \mathrm{Er}, \mathrm{Yb}, \mathrm{Pr}, \mathrm{Sm}$ ) are perspective ones for use them in the capacity of luminophors [2-5].

The tiogallates of barium, strontium and calcium activated by $\mathrm{Eu}^{2+}$ ions are effective luminescent materials radiating in blue-green spectrum region caused by transitions $4 \mathrm{f}^{6} 5 \mathrm{~d} \rightarrow 4 \mathrm{f}^{7}$ [6-11]. Last time the investigations of optical properties of mixed compounds $\mathrm{MGa}_{2} \mathrm{~S}_{4}{ }^{-}$ $\mathrm{M}^{\prime} \mathrm{Ga}_{2} \mathrm{~S}_{4}\left(\mathrm{M}, \mathrm{M}^{\prime}=\mathrm{Ba}, \mathrm{Sr}, \mathrm{Ca}\right.$ are alkali-earth elements) activated by REE ions in which matrix composition variation leads to shift of luminescence spectrum in visible region are carried out [12-14]. Such mixed compounds are new ones and their luminescence properties aren't investigated enough. The obtaining of mixed compound $\mathrm{Ca}\left(\mathrm{Al}_{0,1} \mathrm{Ga}_{0,9}\right)_{2} \mathrm{~S}_{4}: \mathrm{Eu}^{2+}$ and investigation of temperature influence and exciting radiation power on spectra of its photoluminescence are the aim of present work.

## EXPERIMENT TECHNIQUE

The chalcogenide wide-band semiconductors $\mathrm{Ca}\left(\mathrm{Al}_{\mathrm{x}} \mathrm{Ga}_{1-\mathrm{x}}\right)_{2} \mathrm{~S}_{4}: \mathrm{Eu}^{2+}(\mathbf{x}=\mathbf{0 . 1})$ are obtained by solid-phase reactions from binary compounds $\mathrm{CaS}, \mathrm{BaS}$ and $\mathrm{Al}_{2} \mathrm{~S}_{3}$ taken in stoichiometric ratios. The activation by $\mathrm{Eu}^{2+}$ ions
up to $7 \mathrm{at} \%$ is carried out by introduction into $\mathrm{EuF}_{3}$ initial batch. The initial mixture of binary components is put into quartz ampoule evacuated up to $10^{-4}$ millimeter of mercury. The synthesis is carried out at $1100^{\circ} \mathrm{C}$ during one hour with following 4-hour annealing at $800^{\circ} \mathrm{C}$.

The luminescence spectra are taken on spectrometer HR-460 (Jobin-Ivon SpectrometerHR 460). The continuous argon laser with power $10 \mathrm{~mW}\left(\lambda_{\mathrm{ex}}=488 \mathrm{~nm}\right)$ is used in the capacity of exciting radiation source. The synthesized samples are subjected by X-ray diffraction investigations on X-ray diffractometer D8 Advance (Bruker). The analysis of X-ray diffraction of compound $\mathrm{Ca}\left(\mathrm{Al}_{0,1} \mathrm{Ga}_{0,9}\right)_{2} \mathrm{~S}_{4}$ shows that it has the orthorhombic structure with space group $D_{2 h}^{24}-F d d d$.

## RESULTS AND DISCUSSION

$\mathrm{Ca}\left(\mathrm{Al}_{0.1} \mathrm{Ga}_{0.9}\right)_{2} \mathrm{~S}_{4}: \mathrm{Eu}^{2+}: 7 \%$ solid solutions doped by europium ions have the intensive luminescence in green spectral region. Its PhL spectrum measured in temperature range $10-300 \mathrm{~K}$ presents itself the wide band including the range of wave length $525-625 \mathrm{~nm}$ with maximum on 556 nm (fig.1) and caused by electron transitions $4 f^{6} 5 d \rightarrow 4 f^{8}\left(S_{7 / 2}\right)$ of $\mathrm{Eu}^{2+}$ ion.

The intensity of PhL spectra of $\mathrm{Ca}\left(\mathrm{Al}_{0.1} \mathrm{Ga}_{0.9}\right)_{2} \mathrm{~S}_{4}: \mathrm{Eu}^{2+}$ decreases with temperature increasing in $10-300 \mathrm{~K}$ interval, the half-width increases om law $\Gamma(T) \sim f\left(T^{1 / 2}\right)$. At temperature 10 K the maximum of wide-band spectrum takes place at 556 nm and at temperature 300 K it takes place at 554 nm , i.e. the spectrum maximum shifts to the short-wave region with temperature increasing.

The temperature dependence of radiation band intensity with maximum on 556 nm of $\mathrm{Ca}\left(\mathrm{Al}_{0.1} \mathrm{Ga}_{0.9}\right)_{2} \mathrm{~S}_{4}$ : Eu: $7 \%$ crystals in coordinates $\lg (I)$ and $10^{3} / T$ is shown in fig.2.

It is seen that in region $10-70 \mathrm{~K}$ the intensity weakly depends on temperature and after 70 K the intensity strongly decreases. $\lg (I) \sim 10^{3} / T$ dependence in this temperature region is linear one. The activation energy of temperature damping of PhL which is equal to $0,03 \mathrm{eV}$ is defined by inclination of this dependence.


Fig. 1. The temperature dependence of PhL spectra intensity of mixed compound $\mathrm{Ca}\left(\mathrm{Al}_{0.1} \mathrm{Ga}_{0.9}\right)_{2} \mathrm{~S}_{4}: \mathrm{Eu}^{2+}$.


Fig. 2 The temperature dependence of luminescence intensity of mixed compound $\mathrm{Ca}\left(\mathrm{Al}_{0.1} \mathrm{Ga}_{0.9}\right)_{2} \mathrm{~S}_{4}: \mathrm{Eu}^{2+}$.


Fig.3a. The intensity dependence of PhL spectra of mixed compound $\mathrm{Ca}\left(\mathrm{Al}_{0.1} \mathrm{Ga}_{0.9}\right)_{2} \mathrm{~S}_{4}: \mathrm{Eu}^{2+}$ on excitation power at $\mathrm{T}=22 \mathrm{~K}$.


Fig. 3b. The intensity dependence of PhL spectra of mixed compound $\mathrm{Ca}\left(\mathrm{Al}_{0.1} \mathrm{Ga}_{0.9}\right)_{2} \mathrm{~S}_{4}: \mathrm{Eu}^{2+}$ on excitation power at $\mathrm{T}=300 \mathrm{~K}$.


Fig. 4. The temperature dependence of luminescence intensity of $\mathrm{Ca}\left(\mathrm{Al}_{0.1} \mathrm{Ga}_{0.9}\right)_{2} \mathrm{~S}_{4}: \mathrm{Eu}^{2+}$ mixed compound on excitation power.

The intensity dependences of PhL spectra on excitation luminecsence power $\mathrm{Ca}\left(\mathrm{Al}_{0.1} \mathrm{Ga}_{0.9}\right)_{2} \mathrm{~S}_{4}: \mathrm{Eu}: 7 \%$ in $2-10 \mathrm{~mW} / \mathrm{cm}^{2}$ are investigated at 20 K and 300 K temperatures. PhL spectra at 22 K (fig.3a) and 300 K (fig.3b) at different values of exciting radiation power are shown in fig.3. As it seen from the figure the radiation band intensities increase and energy positions of its maxima don't change at exciting radiation power increasing.

The intensity dependences of bands on exciting radiation power in double logarithmic scale is shown in fig.4. As it is seen from figure, the luminescence intensity linearly depends on excitation power [15].

## CONCLUSION

The activating of mixed compound $\mathrm{Ca}\left(\mathrm{Al}_{0.1} \mathrm{Ga}_{0.9}\right)_{2} \mathrm{~S}_{4}$ by $\mathrm{Eu}^{2+}$ ions leads to wide-band intensive photoluminescence in spectrum green region which caused by transition $4 f^{6} 5 d \rightarrow 4 f^{7}\left(S_{7 / 2}\right)$ of $\mathrm{Eu}^{2+}$ ion. The linear dependence of PhL spectrum intensity on excitation level is caused by thin solubility of europium ions in matrix and formation of isolated radiated centers.

The given work was supported by Science Development Foundation under the President of the Republic of Azerbaijan - Grant N - EIF -BGM-2 -BRFTF-1 2012/2013-07/02/1.
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# NANOSTRUCTURED HYBRID OF PHOTOVOLTAIC SOLAR CELL WITH SUPERCAPACITOR AND ITS REALIZATION 

SH.O. EMINOV ${ }^{1}$, A.SH. ALIYEV ${ }^{2}$, KH.D. JALILOVA ${ }^{1}$, I. S. HASANOV ${ }^{1}$, A.A. RAJABLI ${ }^{1}$, N.J., ISMAYILOV ${ }^{1}$, G.KH. MAMEDOVA ${ }^{1}$, J.A. GULIYEV ${ }^{\mathbf{1}}$, I.I. GURBANOV ${ }^{\mathbf{1}}$<br>Institute of Physics of NAS Azerbaijan ${ }^{1}$, H.Javid ave., 33 AZ1143, Baku,Azerbaijan<br>Institute of Catalysis and Inorganic Chemistry of NAS Azerbaijan ${ }^{2}$, H.Javid ave.,31, AZ1143,<br>Baku, Azerbaijan<br>e-mail shikhamirem@gmail.ru


#### Abstract

The construction of the novel hybrid device comprises PV-cell and nanocapacitor which disposed on front and back sides on common glass substrate as well as the flow chart of the device's fabrication procedures are presented. For realizing the proposed device the anodic aluminum oxidation (AAO ) nanostructures on basis of glass-ITO-Ti-Al thin film structure were synthesized. The method of electrochemical deposition of CdS thin film on ITO covered glass substrates. was developed. The optical microphotograph, SEM imaging, EDX spectra, optical transmission and Raman scattering data are presented.


Keywords : PVsolar cells, CdS, thin films, anodic aluminum oxide( AAO), electrodeposition, hybrid device nanostructures. PACS: 81.05.Rm, 81.16.Pr, 81.07-b, 82.45.Cc.

## 1. INTRODUCTION

Solar energy represents one of the most abundant and yet least harvested sources of renewable energy. Because intermittent nature of solar energy, typical photovoltaic solar energy harvesting system includes both Photovoltaic (PV) cells which are often electrically connected and encapsulated as module and energy storage systems such as batteries or electrochemical capacitors (ECs).

In practice nearly all photovoltaic energy conversion uses semiconductor materials in the form of p-n- and hetero-junctions. Second generation solar cells are based on heterojunctions of thin layers of different semiconductor among which $\mathrm{CdS} / \mathrm{Cu}_{2} \mathrm{~S}$, $\mathrm{CdS} / \mathrm{CdTe}$, $\mathrm{CdS} /$ $\mathrm{CuInSe}_{2}$ (or CIS) combinations are the most promising solar cells are developed so far [1-4]. In such cells CdS -n-type semiconductor with band gap of $\sim 2.5 \mathrm{eV}$ is commonly used as a window layer, while CdTe was found to be a very suitable absorbing layer for solar cells due to its direct band gap of $\sim 1.5 \mathrm{eV}$ close to the optimum band gap for PVs. The CdS/CdTe based solar cells have reached an efficiency of $16.5 \%$ which is close to the predicted efficiency limit of $17.5 \%$. This kind of solar cells has been used for a long time and still being widely used nowadays. However, due to a lot issues associated with the fabrication procedures of $\mathrm{CdTe}-\mathrm{CdS}$ solar cells they are not much more efficient than silicon solar cells as we might expect.

Electrochemical capacitors that are also designated supercapacitors [5-9] derive their energy storage capacity from interaction between electrode and electrolyte at the interfacial region. Supercapacitors are currently a prominent area of research for energy storage devices as they have high power density, long cycling life, and short charging time [2-4]. Moreover, they have higher energy density than conventional dielectric capacitors . Supercapacitors can be used either alone as a primary power source or as an auxiliary one with rechargeable
batteries for high-power applications, such as industrial mobile equipment and hybrid/electric vehicles.

In recent years, the novel characteristics of nanostructures such as nanowires, nanorods (NRs) and nanotubes (NTs) have attracted great attention from researchers in many fields such as electronics, optoelectronics and magnetism. In particular, the nanostructured PV-cells and nanocapacitor arrays have been intensively studied for the last generation of both energy harvesting and storage devices, sensors and optoelectronics [10,11].

As one of the most promising fabricating methods of nanowire arrays, the porous nanostructure templates including anodic alumina (AAO) templates are used widely. It's well known that during anodization of Al in certain acidic media ( $\mathrm{H}_{2} \mathrm{SO}_{4}, \mathrm{C}_{2} \mathrm{H}_{2} \mathrm{O}_{4}$ or $\mathrm{H}_{3} \mathrm{PO}_{4}$ ) a self organized, highly ordered array of cylindrical shaped pores can be produced in AAO film with controllable pore diameters, periodicity and ultrahigh density $\left(\sim 10^{10}\right.$ $\mathrm{cm}^{-2}$ ) distribution.

Vertically oriented NWs (or nanopillars, NTs) of CdS and CdTe , grown within templates of porous anodic alumina oxide (AAO) replaced the traditional thin film of those semiconductor materials in nanostructured PV-cells $[12,13]$

## 2. CONSTRUCTION AND FABRICATING STAGES OF THE HYBRID DEVICE

Almost all main fabrication steps used for manufacturing of nanostructured PV-cells and nanocapacitors are similar. Moreover, some of these steps are carried out under the same technological process conditions. Using a such a similarity of fabrication steps make we developed novel single hybrid device through combining PV-cell with the nanocapacitor by manufacturing them simultaneously on front and back sides of common glass substrate.


Fig. 1. Shcheme of hybrid device.


Fig. 2. Fabrication stages of hybrid device.

The hybrid device comprises PV-cell and nanocapacitor which disposed on front and back sides on common glass substrate (1) covered with ITO layer (2) from front and back sides. The PV-cell part comprises of free standing CdS nanopillars (3) embedded in CdTe or CIS thin layer (4), transparent ZnO front layer (5), front and back current leads (6 and 7). The capacitor side comprises of free standing NiO nanotubes (positive electrode) (8) embedded in electrolyte (9), lead (10) to the positive electrode, activated carbon (negative electrode) (11) and electrolyte (12), porous separator between positive and negative electrodes (13) and lead (14) to the negative electrode. The flow chart of the device's fabrication procedures comprises the following stages: (Fig. 2, a, b, c)

Stage 1: fabrication Al-ITO-Glass-ITO-Al structure on both sides of glass wafer by magnetron sputtering.

Stage 2: Fabrication of AAO templates simultaneously on the both sides by Al anodic oxidation in electrochemical cell in oxalic or phosphorus or sulphuric acid;

The mechanism behind anodizing Al on substrates (particularly Si ) is well documented. Briefly an Al-coated substrate (the anode) and an inert electrode (the cathode,e.g., Pt-mesh) are placed opposite to each other in a dilute acid and a constant electrical voltage is applied across the electrodes to effect anodization . Sulphuric,oxalic and phosphoric acids and voltages ranging from $25-200 \mathrm{~V}$ are routinely employed depending on the pore dimensions and spacing desired. As $\mathrm{O}_{-2}$ and OH ions diffuse to the Al surface, an $\mathrm{Al}_{2} \mathrm{O}_{3}$
anodization front is created. Because the $\mathrm{Al}_{2} \mathrm{O}_{3}$ at the anodization front is not perfectly smooth, the electric field in the sample concentrates at depressions in the $\mathrm{Al}_{2} \mathrm{O}_{3}$ layer. Due to higher local electric field and temperature, the $\mathrm{Al}_{2} \mathrm{O}_{3}$ formed at the depressions is preferentially dissolved resulting in the formation of pore channels as the anodization proceeds (Fig. 1(b)). When the anodization reaches the substrate, a thin inverted $U$ shaped barrier layer is formed (Fig. 1(c)).

Because the barrier layer is usually much thinner than the AAO pore walls, immersing the substrate in dilute phosphoric acid readily dissolves the barrier layer allowing connectivity to the substrate and also simultaneously enlarges the pore channels

Stage 3: Electrochemical growth of CdS nanorods and Ni nanotubes inside AAO templates.

Creating array of free standing CdS and Ninanopillars on front and back sides simultaneously by etching of AAO templates in $5 \% \mathrm{NaOH}$ solution;

Annealing of whole structure at $450^{\circ} \mathrm{C}$ in air;
Stage 4: Deposition of p -CdTe or p - CuInGaSe thin film with thickness of about 2-5 mkm on PV-cell side either by magnetron sputtering or electrochemically for embedding CdS nano-columns within absorber layer.filing of the array of free standing NiO nanopillars (positive electrode) with electrolyte, installation of separation layer, installation of carbon nanoporous (negative) electrode and encapsulation; Deposition of ZnO front layer to to PV-cell; Fabrication of electrical contacts to the PV cell and to the electrodes of nanocapacitor;

In the PV-cell side of the proposed hybrid device the traditional thin film CdS window layer will be replaced by vertically aligned nanowire array of CdS. This array will be grown inside AAO template by electrodepositing. The positive electrode of the electrochemical capacitor will be a NiO nanostructure, whereas the negative one will be activated carbon. Non-aqueous electrolytes will chosen in order to push the range of voltage beyond 1 V . This kind design of the device allows to combine several fabrication steps which usually applied for creation of an each device separately in one.

It is expected that the combination of fabrication processes steps would reduce the manufacturing costs of solar energy harvesting system. At the same time disposition of capacitor on the same substrate with PVcell will lead to compactness of the whole system.

## 3. EXPERIMENTAL PROCEDURES AND CHARACTERIZATION

For realize the proposed device we synthesized AAO nanostructures on basis of glass-ITO-Ti-Al thin film structure by anodic oxidation in oxalic acid as well as developed method of electrochemical deposition of CdS thin film on ITO covered glass substrates.

Commercial glass slides covered by ITO layer sputtered by magnetron deposition used as working electrode, were ultrasonically cleaned in acetone. The
electrolyte for CdS deposition was composed of 0.055 M CdCl 2 and 0.19 M elemental sulfur, dissolved in 50 mL dimethyl sulfoxide (DMSO).

The schematic diagram, optical microphotograph , plain-view SEM imaging, as well as EDX spectra of such structure are presented in Fig.3.

SEM images of a CdS thin film as well as EDX spectra of CdS deposited on the glass/ITO substrate are shown on the Fig.4a and Fig.4b, respectively. Optical analysis of CdS film samples with different thickness deposited over glass during different deposition duration was performed using optical transmittance spectra ( Specord 210) at room temperature and at a the region from 1.0 to 4.0 eV .

The UV-visible spectrum and CdS thin film with thickness of 500 nm grown on glass/ITO substrate catholically deposited on glass/ITO substrate are shown in Fig. 5. We have determined the band gap of our samples by Tauc's formula to be as 2.42 eV which coincided with the dates reported earlier.

Raman spectrum of CdS thin film obtained in backscattering geometry by using confocal measurement system at room temperature [14] is shown on the Fig. 5. The sample is exhibit relatively sharp crystal-like peaks at $300 \mathrm{~cm}^{-1}$ and $600 \mathrm{~cm}^{-1}$ corresponding to the $1 \mathrm{LO}-$ and 2LO phonon modes, correspondently . The FWHM (full-width half-maxima) of Raman peak at the 1 LO phonons was estimated to be $40 \mathrm{~cm}^{-1}$.


Fig. 3. The schematic diagram (a), microphotograph (b), SEM imaging(c) and EDX spectra (d) of AAO film CdS thin films were characterized by various techniques like SEM, EDX, optical transmission and Raman spectroscopy.


Fig. 4. SEM image of a CdS thin film cross-section (a) and EDX spectra of CdS deposited on the glass/ITO substrate (b).


Fig 5. The UV-visible spectrum of CdS thin film.


Fig.6. Raman scattering spectrum of CdS thin film.

## 4. CONCLUSION

In summary, the both proposed construction of the novel hybrid device comprises nanostructured solar cell and supercapacitor and the flow chart of the device's fabrication have been presented.

For realize the proposed device we synthesized AAO nanostructures on basis of glass-ITO-Ti-Al thin film structure by anodic oxidation in oxalic acid as well as developed the method of catholically deposition of

CdS thin films on ITO covered glass substrates. The synthesized structures were characterized by using SEM, EDX, optical transmission, Raman spectroscopy .

Acknowledgment : This work was supported by the Science Development Foundation under the President of the Republic of Azerbaijan, grant № EIF-2014-9(24) KETL-14/04/4.
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# PHYSICAL PROCESSES IN WATER AT THERMAL AND ELECTRIC BREAKDOWN 

E.J. GURBANOV<br>"Azersu" Open Joint Stock Company, Baku, Moscow av.67, Azerbaijan, KurbanovEJ_mpei@mail.ru


#### Abstract

Article to electronic and ion treatment of drinking water and sewage at impact of high-voltage pulses of various polarity and amplitudes for disinfecting from pathogenic microbes is devoted. It is shown that depending on amplitude of influencing pulse the vesiculate and electric breakdown of water with formation of high conductivity leader channels are observed. The physical processes happening in channel at its formation and collapse lead to death of bacteria and microbes containing in water medium. This technology can be partially or completely replace the existing chlorination process at inactivation of drinking water and sewage.


Keywords: water medium, microorganism, high-voltage installation, pulse front, cell, nanosecond pulse, process, leader channel, vesiculate, thermal, electric breakdown, amplitude, electrode system, shock wave, ultra-violet radiation
PACS: $52.80 . \mathrm{Wq}$

## INTRODUCTION

Methods of electronic and ion treatment of various mediums for their activation and improvement of properties gain the highest interest in connection with the most real providing (with the smallest power losses) of the effective energy on activation processes recently. In this sense the choice of water medium has the certain advantages [1-4]. Water is the unique medium for transformation of one look in energy in another. In this context transformation of high electric energy in water in mechanical and use of this property in technologies of water purification from microorganisms is represented very tempting [5-8]. In this direction enough articles is published and uniqueness of physical processes in water at impact on medium of high voltage is shown. Application for this purpose of microsecond high voltage leads to development of various physical processes with the finishing breakdown of the medium [9-13].

The present article to the physical and mathematical description of the processes happening in water medium at influence of microsecond pulse tensions is devoted.

## EXPERIMENTAL METHODS

As electrode system the "pin - plane" configuration was chosen. As the generator of pulse tensions the generator by Arkadyev-Marx's scheme with output voltage $10-100 \mathrm{kV}$ was elaborated. Depending on tension amplitude, in interval between electrodes it was observed the vesiculate, thermal and electric processes of the water breakdown. Everyone them has the features and is applicable depending on characteristics of the treated medium and a problem definition. At first we will consider the physical processes happening in water at influence of microsecond pulses of low amplitude (less than 25 kV ). In article will be considered discharge processes in water medium at impact on containing microorganisms by microsecond pulses. At voltage up to 25 kV , irrespective of its polarity, thermal processes, liquid boiling up, formation of gas inclusions with leader channels and thermal breakdown of discharge interval are observed. Thermal breakdown time $-\mathrm{t}_{\mathrm{br} 1}$ will consist of several components:

$$
\begin{equation*}
t_{b r 1}=t_{d}+t_{i}+t_{l}+t_{f}+t_{r} \tag{1}
\end{equation*}
$$

where $t_{d}$ - delay time; $t_{i}$ - ionization time; $t_{l}$ - leader's formation time; $\mathrm{t}_{\mathrm{f}}$ - time of leader's final jump to opposite electrode; $t_{r}$ - time of reverse discharge. As $t_{f}$ and $t_{r}$ are less than other parameters in (1), they can be neglected. At short interelectrode distance breakdown time only by delay time - $\mathrm{t}_{\mathrm{d}}$ will be defined. Delay time $-\mathrm{t}_{\mathrm{d}}$ will depend on tension polarity on potential "pin" electrode. At negative polarity and electric field intensity ( $<85 \mathrm{kV} / \mathrm{cm}$ ) delay time is much less than at positive one. It will be decreased from $900 \mu \mathrm{~s}$ at $\mathrm{U}=10 \mathrm{kV}$ up to $2 \mu \mathrm{~s}$ at $\mathrm{U}=100 \mathrm{kV}$. Change of tension polarity on potential electrode and field intensity in discharge interval influences also on leader's distribution speed. At negative polarity it is less than sound speed in water and makes ~ $5 * 10^{4} \mathrm{~cm} / \mathrm{s}$. By increase of field intensity (up to $350 \mathrm{kV} / \mathrm{cm}$ ) at positive tension polarity on potential electrode an opposite situation is observed. The leader's distribution speed becomes more than sound speed in water and makes $\sim 5^{*} 10^{6} \mathrm{~cm} / \mathrm{s}$. Delay time of leaders appearance is decreased from $700 \mu \mathrm{~s}$ at $\mathrm{U}=10 \mathrm{kV}$ up to $0,5 \mu \mathrm{~s}$ at $\mathrm{U}=100 \mathrm{kV}$ in distance between electrodes $-\mathrm{l}=1$ 20 cm and radius of curvature of the "pin" electrode $\mathrm{r}=0,2 \mathrm{~cm}$.

At voltage over 25 kV thermal breakdown of water medium is replaced by electric one. At this moment spark discharge with followed leader channels and powerful mechanical compression waves are developing.

Will note that electric breakdown of water medium at both tension polarities on "pin" electrode comes to the end by crossing of leader channels the all interelectrode distance. In this case temperature and pressure in leader channel are reached up to $(3-4) \times 10^{4} \mathrm{~K}$ and $(2-3) \times 10^{4}$ atm respectively.
In technological installations better to use a positive voltage polarity on potential electrode for creation of powerful mechanical compression waves and dispersing liquid streams in water. The formula for definition of average breakdown time is given below:

$$
\begin{equation*}
t_{b r 2}=\frac{a l}{\left(U-U_{\min }\right)^{2}} \tag{2}
\end{equation*}
$$

where U - voltage between electrodes, a - constant coefficient ( $\mathrm{a}=3.6 \times 10^{5} \mathrm{~V}^{2} \mathrm{~s} / \mathrm{m}$ ) on electric water conductivity - $\sigma=2.5 \times 10^{-4}(\mathrm{Sm} / \mathrm{cm})$; 1 - interelectrode distance ( cm ), $\mathrm{U}_{\text {min }}=18 \times 10^{3} \times \mathrm{r} \times \ln (41 / \mathrm{r})-$ minimum voltage, when leader is aroused and developed (kV); r radius of curvature of "pin" electrode (mm).

Dependence of dissipated energy in discharge gap from distance between the electrodes- 1 is shown, that with increase in distance between electrodes the energy consumed from source is grow too.

Dependences of emitted energy in discharge gap from the radius of curvature and naked surface of potential "pin" - electrode is shown, that with increase of geometrical parameters of "pin" - electrode an emitted energy in discharge gap is grow too.

For determination of the energy losses and other parameters during breakdown process in discharge gap at positive tension polarity on the "pin" electrode the following expression is used:
$W_{l}=\left[C U_{1}^{2}\left(1-\frac{U_{b r}^{2}}{U_{1}^{2}}\right) / a b \omega+4 \pi S / b^{2}\right]^{1 / 2}-2^{\sqrt{\pi S}} / b$
where C - capacity of condenser battery; $\mathrm{U}_{1}$ - charging voltage of condenser; $\mathrm{U}_{\mathrm{br}}$ - breakdown voltage; S surface of naked electrode in water; $b=2 * 10^{-4} U_{1}$.

Maximal length between electrodes -1 , on which the energy losses are minimal can be defined from the following expression:

$$
\begin{equation*}
l=8 * 10^{-9} * U_{b r}^{3 / 2} *\left(\frac{C}{L}\right)^{0,25} \tag{4}
\end{equation*}
$$

where $U_{b r}$ - brealdown voltage, $C$ - capacity of condenser battery, L-inductance of the discharge circuit.

## RESULTS AND DISCUSSION

Thus, results of our researches testify to interference of the main parameters of high-voltage installation of technological appointment at each other. Depending on tension amplitude and intensity of electric field in discharge interval thermal and electric breakdown of water medium can be observed.

At voltage less 25 kV thermal processes, followed by boiling of water, formation of gas inclusions and leader channels there are taken place. Temperature and pressure in gas inclusions are very high and leads to their expansion and cooling. At the moment when pressure inside of inclusion is less than surrounding hydrostatic one, it collapses and promotes formation of weak mechanical compression waves in medium. Physical processes of formation and collapse of gas inclusions at influence of high pulse electric fields are repeated with a
certain frequency, thereby perniciously influencing activity of microorganisms there. It should be noted, that more notable reduction of delay time at negative tension polarity on potential "pin" electrode is related with prevalence of ionization processes around it as a result of increase of electric field intensity.

At voltage over 25 kV breakdown process is also begun with water boiling up, discharges in gas inclusions and formation of the high conductivity leader channels. Difference of these processes from described above is that breakdown of discharge interval in this case happens due to short circuit of the distance between electrodes by leader channels, i.e. the spark discharge. As a result of expansion and collapse processes in gas inclusions under influence of high pressure and temperature, the powerful shock waves and a bright ultra-violet luminescence are formed in water, which are also perniciously influencing on microorganisms.

At "pin-pin" electrode system in discharge interval a crown discharge is arousing and gives rise to the origin and development of the negative high conductivity leader channel, moving to an opposite "pin" electrode. After some time at opposite "pin" electrode the positive crown discharge is arousing. Breakdown of discharge interval comes to the end with meeting of the negative leader channels and positive crown. At further increase in tension near anode positive leader channels are formed (besides a crown) and breakdown between electrodes comes to the end with a meeting of opposite directed leaders.

## CONCLUSIONS

Thus, in article the physical processes happening at thermal and electric breakdown of water medium are described, the main dependence ratios of the unit electric parameters on medium characteristics and parameters of electrode system are given. It is shown, that at elaboration of high-voltage pulse installations the accounting of the pulsed generator parameters and a discharge interval is necessary.

It is revealed, that depending on pulse amplitude are possible thermal (vesiculate) or electric breakdown of the medium. In both cases there is breakdown of interelectrode distance be followed by some physical processes (formation of shock mechanical compression waves, ultra-violet radiation, thermo ionization and etc.), perniciously influencing on activity of the microorganisms containing there.

Considering that recently the huge attention to development of ecologically safe technologies, this method of disinfecting drinking water is paid and sewage can successfully replace (partially or completely) chlorination process for disinfecting of the noted mediums.
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# SYNTHESIS AND CHARACTERIZATION OF MULTIWALL CARBON NANOTUBE HEXAMETHYLENEDIAMINE - MALEIC ANHYDRIDE - 1-HEPTENE NANOCOMPOSITE 

E.Y. MALIKOV* ${ }^{*}$ O.H. AKPEROV, M.B. MURADOV, G.M. EYVAZOVA<br>Baku State University, Z.Khalilov str.,23, Baku, Azerbaijan AZ - 1148, *E-mail: bsuc@hotmail.com


#### Abstract

The multiwalled carbon nanotubes synthesized by Chemical Vapor Deposition over an $\mathrm{Fe}-\mathrm{Co} /$ alumina catalyst were oxidized and grafted with maleic anhydride-1-heptene copolymer via the "grafting to" approach using hexamethylenediamine bridge. The obtained nanocomposite was characterized by Raman spectroscopy, XRD, FTIR, SEM and TEM methods. FTIR confirmed the presence of the characteristic peaks of the anticipated zwitterion and amine-amide conversion. The completion of the grafting process was also confirmed by XRD and Raman spectroscopy. Microstructure images of the nanocomposite obtained by TEM and SEM revealed that the nanotubes are uniformly covered with the polymer which shows the effectiveness of the method. Whole the process proceeds at room conditions which is the main advantage of this method.


Keywords: Carbon nanotubes; Polymer nanocomposites; Grafting to; Scanning/Transmission electron microscopy. PACS: 81.05.Qk; 81.07.-b; 81.07.De; 81.16.Be; 82.35.Np

## 1. INTRODUCTION

Carbon nanotubes (CNTs) have received considerable attention recently owing to their unique electronic and mechanical properties that are expected to lead to breakthrough industrial applications. They can be synthesized by chemical vapor deposition (CVD) [2-4], laser ablation [2,5-7] and d.c. arc discharge [2,6-8]. Among these techniques, CVD has inherent advantages such as better control over process parameters and good scalability [9].

CNTs exhibit a well-known tendency to form agglomerates due to van der Waals forces, which makes them extremely difficult to disperse and align in a polymer matrix. Thus, a significant challenge in developing high performance polymer/CNTs composites is to introduce the individual CNTs into a polymer matrix in order to achieve better dispersion and alignment, promote strong interfacial interactions and improve load transfer across the CNT-polymer matrix interface. The functionalization of CNTs is an effective way to prevent nanotube aggregation, which helps in dispersing and stabilizing carbon nanotubes within a polymer matrix. There are several approaches towards CNT functionalization including defect functionalization, covalent functionalization and non-covalent functionalization [10, 11].

The functionalization of carbon nanotubes can improve their solubility as well as dispersion properties in solvents and in polymers. Covalent functionalization can be carried out either by the modification of surface-bound carboxylic acid groups or by directly attacking the sidewalls of nanotubes. Usually, functional groups such as -COOH or -OH are formed on the CNTs during oxidation by oxygen, air, concentrated sulfuric acid, nitric acid or aqueous hydrogen peroxide [12,13]. Acid treated multiwall carbon nanotubes (MWCNTs) have defects in the carbon-carbon bonds. The number of functional groups on the nanotube surface depends on acid treatment temperature and time, increasing with increasing temperature [14]. Nanotube end caps can be opened as the result of oxidation process [11]. The presence of
carboxylic groups on the CNT surface is advantageous from the synthetic chemistry point of view because a variety of chemical reactions can be conducted with this group. The -COOH and -OH groups on the nanotube surface help the attachment of organic or inorganic materials, which is important for solubilizing nanotubes [15,16]. Functionalization of CNTs with polymer molecules (polymer grafting) is particularly important for obtaining polymer/CNT nanocomposites [17,18].

The two main pathways suggested for the covalent grafting of polymers to CNTs are the "grafting from" and the "grafting to" approaches. In the "grafting from" approach, the polymer is bound to the CNT surface by insitu polymerization of monomers in the presence of reactive nanotubes or CNT-supported initiators. In this process the polymer-CNT nanocomposites can be prepared with high grafting density $[11,19]$.

The "grafting to" approach is based on the attachment of as-prepared or commercially available polymer molecules to the CNT surface by chemical reactions, such as amidation, esterification, radical coupling, etc. The polymer macromolecule must possess adequate reactive functional groups for this approach to work $[11,20,21]$. This method was used in functionalization of MWCNTs with poly(vinyl alcohol) (PVA) via Fischer esterification reaction. FTIR confirmed the presence of the characteristic peaks of the anticipated ester group. The formation of polymer nanocomposites based on PVA and MWCNTs was confirmed by SEM and TEM. High resolution electron micrographs revealed that the primary binding sites for PVA grafting are the sidewall defects of the nanotubes [22].

In this paper the "grafting to" approach was used to graft maleic anhydride-1-heptene copolymer (MAHP) to oxidized-MWCNTs using hexamethylenediamine (HMDA) bridge. First of all HMDA was added to the oxidized-MWCNTs to form a salt. Then this salt was reacted with MAHP to form a grafted structure. The solubility of the MWCNTs was improved by the functionalization because, grafting MWCNTs to MAHP helps in reducing the nanotube-nanotube adhesion and the tendency to form entangled stacks, which generally make

MWCNTs unusable for manufacturing advanced plastic materials. The obtained material can be a precursor for the manufacturing the advanced plastic composite materials or an additive to construction materials for strengthening purposes.

The novelty of this work is that MAHP macromolecules are attached to oxidized-MWCNT using HMDA bridge via the "grafting to" approach for the first time at room conditions. The long copolymer chains in the resulting material are able to screen and protect the nanotubes from entanglement during dispersion.

## 2. EXPERIMENTAL

### 2.1. Materials and methods

All chemicals were of analytical reagent grades. Transmission Electron Microscopy images were taken with a FEI TECNAI G2 20 X-TWIN Transmission Electron Microscope using 200 kV acceleration voltage. The TEM specimens were prepared by dripping the droplets of sonicated solutions of the samples onto carbon coated copper grids. Scanning Electron Microscopy images were recorded using a Hitachi S-4700 SEM instrument operated at 10 kV acceleration voltage in secondary electron imaging mode. Powder XRD patterns were recorded on a Rigaku MiniFlex desktop X-ray diffractometer. X-ray diffraction measurements were performed using $\mathrm{Cu} \mathrm{K}_{\alpha}$ radiation (1.5418 $\AA$ ). FTIR spectra were recorded on a BRUKER Vertex 70 IR spectrometer. Raman investigations were done using Thermo Scientific DXR Raman Microscope using a 532 nm laser for excitation at 10 mW laser power.

### 2.2. Synthesis and purification of MWCNT

MWCNTs were synthesized by the CVD method. The experimental set-up used for this process consists of a Lenton LTF 14/75/610 type horizontal furnace, a quartz tube and gas flow meters. An $\mathrm{Fe}-\mathrm{Co} /$ alumina catalyst was used in the process. It was prepared from $\mathrm{Al}(\mathrm{OH})_{3}$, $\mathrm{Fe}\left(\mathrm{NO}_{3}\right)_{3} \times 9 \mathrm{H}_{2} \mathrm{O}$ and $\mathrm{Co}\left(\mathrm{NO}_{3}\right)_{2} \times 6 \mathrm{H}_{2} \mathrm{O}$ and alcohol solvent under ultrasonic agitation. After the catalyst preparation the solvent was evaporated in vacuum and the catalyst was dried in air.

MWCNT synthesis on the catalyst was performed using acetylene (acetylene purity: 3.0 [>=99.9\%]) (acetylene flow rate $=30 \mathrm{ml} / \mathrm{min}$ ) as the carbon source and nitrogen (nitrogen flow rate $=300$ $\mathrm{ml} / \mathrm{min}$ ) as inert gas. In a typical synthesis MWCNT growth was run over 1 gram of catalyst for 2 hours at $650{ }^{\circ} \mathrm{C}$. After the synthesis, the concentration of the catalyst in the raw product powder was $2.8 \%$ (according to the EDS results). Therefore it was subjected to purification for removing the remnant catalyst particles from the system. The as-synthesized MWCNT product mixture was mixed with concentrated aqueous HCl solution ( $36 \%$ ) and the mixture was boiled under reflux for 16 hours. The product was filtered, washed to pH 7 with deionized water and then boiled under reflux for 16
additional hours in 10 M aqueous NaOH solution. The obtained catalyst-free MWCNT product was then filtered, washed to pH 7 again and dried in air.

### 2.3. Oxidation of MWCNTs

Since our chosen purification procedure did not involve any oxidizing agents (e.g. nitric acid), it was necessary to add an additional oxidation step to initiate the formation of -COOH functionalities on the MWCNTs surface. Purified MWCNTs were mixed with 0.1 M aqueous $\mathrm{KMnO}_{4}$ solution and stirred at $80^{\circ} \mathrm{C}$ for 3 hours. Oxygen bubble formation observable throughout the process confirmed the progress of the reaction. The final product was a mixture of MWCNTs with diverse oxygencontaining functionalities (carboxyl, hydroxyl, aldehyde, anhydride etc.) dominated by -COOH groups.

### 2.4. Formation of the HMDA salt of oxidizedMWCNT (ox-MWCNT-HMDA).

$0.3 \mathrm{~g}(0.0025 \mathrm{~mol})$ HMDA was added to the 100 ml solvent in a beaker and mixed on a magnetic stirrer for 15 minutes. The solvent used in this process is the mixture of ethanol and water in $3: 1$ ratio, respectively. Then 0.24 g $(0.005 \mathrm{~mol})$ oxidized MWCNTs were added to the solution and homogenized by stirring 15 more minutes. This process is exothermic and does not need the external energy. It proceeds without heating with release of the heat which can be observed with warming of the beaker during the last stage of the process. The beaker was placed into the refrigerator and cooled to temperatures under zero for 30 minutes in order to accelerate the process. Then the product was precipitated, washed and filtered. Scheme 1 represents this process.

### 2.5. Grafting of the ox-MWCNT-HMDA to MAHP.

0.024 g MAHP was dissolved in dimethylformamide on a magnetic stirrer. Then 0.04 g ox-MWCNT-HMDA was added to the solution and stirred for 15 minutes. The obtained mixture was washed, filtered and dried. The final product is the MAHP grafted ox-MWCNT-MAHP (ox-MWCNT-HMDA-MAHP). This process proceeds at room conditions because the amine groups easily brakes the anhydride group cycle at room conditions. This process can be visually shown by the scheme 2 .

## 3. RESULTS AND DISCUSSION <br> 3.1. FTIR investigation

FTIR spectra of pristine-MWCNT (a), oxidizedMWCNT (b), ox-MWCNT-HMDA (c) and ox-MWCNT-HMDA-MAHP (d) samples are shown in fig. 1. The aromatic $\mathrm{C}=\mathrm{C}$ stretching peaks at $1539 \mathrm{~cm}^{-1}, 1541 \mathrm{~cm}^{-1}$ and $1558 \mathrm{~cm}^{-1}$ as well as $\mathrm{C}-\mathrm{C}$ vibrations at $1456 \mathrm{~cm}^{-1}$ and $1506 \mathrm{~cm}^{-1}$ characterize the pristine MWCNTs [23-25]. The same peaks can be observed in the spectrum of oxidized MWCNT (fig.1b) sample, however, the


Scheme 1. Formation of the ox-MWCNT-HMDA .


Scheme 2. Grafting of the ox-MWCNT-HMDA to maleic anhydride-1-heptene copolymer.


Fig. 1. FTIR spectra of pristine-MWCNT (a), oxidizedMWCNT (b), ox-MWCNT-HMDA (c) and ox-MWCNT-HMDA-MAHP (d) samples.
decreased intensities of the $\mathrm{C}=\mathrm{C}$ peaks at $1539 \mathrm{~cm}^{-1}, 1541$ $\mathrm{cm}^{-1}$ and $1558 \mathrm{~cm}^{-1}$ indicate defect formation via oxidation. Oxidation is also confirmed by the appearance of the $\mathrm{C}=\mathrm{O}$ (at $1635 \mathrm{~cm}^{-1}$ and $1697 \mathrm{~cm}^{-1}$ ) and $\mathrm{C}-\mathrm{O}$ (at $1163 \mathrm{~cm}^{-1}$ and $\left.1295 \mathrm{~cm}^{-1}\right)$ bands. The broad band with a maximum at $3381 \mathrm{~cm}^{-1}$ can be assigned as the $\mathrm{O}-\mathrm{H}$ stretching peak of the carboxylic group formed by the oxidative treatment [26].

The spectrum changes considerably upon addition of HMDA and MAHP copolymer addition. The addition of the HMDA causes the appearance of new characteristic peaks of amine groups at $1353 \mathrm{~cm}^{-1}$ and $3180-3676 \mathrm{~cm}^{-1}$ region. Moreover, the peak at $1525 \mathrm{~cm}^{-1}$ assigned to zwitterions also appears with this addition (fig. 1c). We can see the peak of Amine groups at $1359 \mathrm{~cm}^{-1}$ and the


Fig. 2. XRD patterns of pristine-MWCNT (a), oxidizedMWCNT (b), ox-MWCNT-HMDA (c) and ox-MWCNT-HMDA-MAHP (d) samples.
peak of the zwitterions at $1525 \mathrm{~cm}^{-1}$ even after the addition of the MAHP copolymer to the system. In addition to these peaks the peak at $1643 \mathrm{~cm}^{-1}$ is appeared which can be assigned to $\mathrm{N}-\mathrm{H}$ bend of amide groups (fig. 1d). The broad peak at $3055-3676 \mathrm{~cm}^{-1}$ region is the asymmetric and symmetric (associated) $\mathrm{N}-\mathrm{H}$ stretching. This peak is the mixed peak of amide and amine groups [27,28].

### 3.2. XRD

Fig. 2 shows the X-ray diffraction patterns of pristine-MWCNT (a), oxidized-MWCNT (b), ox-MWCNT-HMDA (c) and ox-MWCNT-HMDA-MAHP
(d) samples. The peaks at $26.34^{\circ}, 44.82^{\circ}$ and $77.58^{\circ}$ can be assigned to reflections from the (002), (101) and (110) crystallographic planes of multiwall carbon nanotubes, respectively (PDF no: 00-001-0640). These peaks are observable in the patterns of the other three samples as well. However, slight differences in peak widths and intensities indicate that the oxidation and functionalization processes have affected the ordering of the graphitic layers to some extent.

The average coherence length $\left(\mathrm{L}_{\mathrm{c}}\right)$ or mean crystalline size along the c -axis (the crystallographic caxis is the one perpendicular to the long axis of the MWCNTs) was estimated by the Scherrer`s formula [29]:

$$
L_{h k l}=(0.9 \times \lambda) /(\beta x \cos \theta)
$$

where $\lambda$ corresponds to the $X$-ray wavelength, $\theta$ is the Bragg angle and $\beta$ is the half-peak width in radians. The (002) Bragg peak was used to calculate $\mathrm{L}_{\mathrm{c}}$. The results were about 10.5 nm (pristine-MWCNT), 6.2 nm (oxidized-MWCNT), 3.4 nm (ox-MWCNT-HMDA) and 2.9 nm (ox-MWCNT-HMDA-MAHP). These values represent an average stacking height of graphitic planes in the MWCNT walls. It can be seen from the results that the value of $\mathrm{L}_{\mathrm{c}}$ decreases from pristine MWCNT to ox-MWCNT-HMDA-MAHP. The reason behind this is that oxidation by $\mathrm{KMnO}_{4}$ results in the partial loss of the outermost graphitic layers and the introduction of defects, which reduce the symmetry of the plane. Binding the HMDA and MAHP molecules to the defects amplifies this effect, resulting in the further reduction of the $L_{c}$ value.

### 3.3. Raman spectroscopy

Raman spectra of pristine-MWCNT (1), oxidizedMWCNT (2), ox-MWCNT-HMDA (3) and ox-MWCNT-HMDA-MAHP (4) samples are depicted in fig. 3. The Raman spectrum of MWCNTs contains 3 major peaks: the D band, G band and $\mathrm{G}^{`}$ band [30]. The D band which is observed at $\sim 1342 \mathrm{~cm}^{-1}$ is a disorder induced peak corresponding to scattering from defects and amorphous carbon impurities present in the MWCNTs samples. The G band peak ( $\sim 1579 \mathrm{~cm}^{-1}$ ) is the result of ordered highfrequency in-plane stretching of the C-C bonds. The G` band ( $\sim 2682 \mathrm{~cm}^{-1}$ ) is the result of double resonance process. This band does not require an elastic defectrelated scattering process and is observable also for defect-free $\mathrm{sp}^{2}$ carbons. The ratio between the intensities of $D$ and $G$ bands $\left(I_{D} / I_{G}\right)$ is proportional with the extent of defect concentration, thus it can be used to quantify oxidation and functionalization. As it can be seen from fig. 3, the $\mathrm{I}_{\mathrm{D}} / \mathrm{I}_{\mathrm{G}}$ ratios for pristine MWCNTs, oxidized MWCNTs, ox-MWCNT-HMDA and ox-MWCNT-HMDA-MAHP are $0.86,0.95,0.87$ and 0.72 respectively. An increase in the $I_{D} / I_{G}$ ratio indicates an increase in the number of defects on the sidewalls of MWCNTs. These values suggest that while oxidation has increased the number of sidewall defects in the MWCNTs to some extent, the subsequent grafting steps did not alter the $\mathrm{sp} 3 / \mathrm{sp} 2$ carbon ratio of the oxidized nanotube wall structure any further.

### 3.4. Microscopic investigations <br> 3.4.1. TEM investigation

Fig. 4 shows the TEM images of pristine-MWCNT (a), oxidized-MWCNT (b), ox-MWCNT-HMDA (c) and ox-MWCNT-HMDA-MAHP (d) samples.

These micrographs are evidences of the completion of "grafting to" process. Pristine MWCNTs (fig. 4a) are more TEM-transparent than oxidized (fig. 4b) and grafted ones (fig. 4d). This is because the sidewalls of pristineMWCNTs are smooth, whereas the oxidized and defected walls visible in fig. 4b-d have more electron scattering power. The outer layers of the sidewalls of these MWCNTs are exfoliated due to the strong oxidation effect of oxidation agent and have changed their shape partly to a graphene-like structure (fig. 4b). The average diameter of the pristine-MWCNTs is $16.5 \pm 2.5 \mathrm{~nm}$ according to the fig. 4a. After the purification and oxidation processes (fig. 4b) the exfoliation of the outer layers of the MWCNTs changes the apparent diameter of the tubes to $19.8 \pm 1.7 \mathrm{~nm}$. The exfoliation of the outer layers of the tubes can be easily seen in fig. 4b. But the fig. 4d shows different view. In this picture the MWCNTs are arranged in ordered manner and covered by thin polymeric layers which can be seen as the shadows on the tubes. The average thickness of the copolymer cover layer is $7.8 \pm 1.4 \mathrm{~nm}$.

### 3.4.2. SEM investigation

Characteristic SEM micrographs of pristineMWCNT (a), oxidized-MWCNT (b), ox-MWCNTHMDA (c) and ox-MWCNT-HMDA-MAHP (d) samples


Fig. 3. Raman spectra of pristine-MWCNT (1), oxidizedMWCNT (2), ox-MWCNT-HMDA (3) and ox-MWCNT-HMDA-MAHP (4)


Fig. 4. TEM images of pristine-MWCNT (a), oxidized-MWCNT (b), ox-MWCNT-HMDA (c) and ox-MWCNT-HMDA-MAHP (d)


Fig. 5. SEM images of pristine-MWCNT (a), oxidized-MWCNT (b), ox-MWCNT-HMDA (c) and ox-MWCNT-HMDA-MAHP (d)
are depicted in fig. 5. The unmodified, smooth surface of pristine MWCNTs visible in fig. 5a confirms the TEM-
derived diameter estimation. In contrast, the surface of the oxidized-MWCNTs looks rough because of the defected regions created by oxidation (fig. 5b). The image of the intermediate ox-MWCNT-HMDA sample also shows the visible defects (fig. 5c). The polymer coating of the tubes can be observed in fig. 5d. The maleic anhydride-1heptene copolymer macromolecules were attached to the defect-activated regions of the MWCNTs by the "grafting to" method using HMDA bridge and cover the whole nanotube surface. This is the surface polymer layer that keeps CNTs apart, makes them soluble in hydrophilic solvents and prevents their entanglement and agglomeration.

## 4. CONCLUSION

Multiwall carbon nanotubes synthesized by CVD from acetylene over an $\mathrm{Fe}, \mathrm{Co} /$ alumina catalyst were oxidized by $\mathrm{KMnO}_{4}$ solution to form functionalities on
wall defects and end caps. The oxidized MWCNTs were grafted with maleic anhydride-1-heptene copolymer via the "grafting to" approach using hexamethylenediamine bridge. The proof of completion of the "grafting to" process was obtained by XRD, Raman and FTIR methods. FTIR also confirmed the presence of the characteristic peaks of the anticipated zwitterion and amine-amide conversion. TEM and SEM revealed that the nanotubes are uniformly covered with the polymer which shows the effectiveness of the method. The suggested process was carried out at room conditions and therefore it can be considered as a feasible alternative for carbon nanotube functionalization targeted at polymer composite applications.

## ACKNOWLEDGEMENTS

This work was supported by EC FP7 program "NAPEP" (Grant agreement number: 266600).
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# ELECTRON-CONFORMATIONAL PROPERTIES AND MOLECULAR DYNAMICS OF THE CREKA MOLECULE 

G.D. ABBASOVA, E.Z. ALIYEV<br>Baku State University, Az-1148, Z. Khalilov str., 23


#### Abstract

The spatial and electron structure of CREKA molecule, the new drug with antitumor activity was investigated by the methods of theoretical conformational analysis, quantum chemistry and molecular dynamics. The geometrical parameters and energy contributions of various types of interatomic interactions in stabilization of the molecule stable conformations are calculated, the quantitative evaluation of the change limits of dihedral angles in main and side chains of amino-acid residuals is carried out. The electron and conformational properties of CREKA molecule are studied by semi-empirical methods of quantum chemistry CNDO/2 and MNDO using AM1 and PM3 calculation schemes. The comparative analyze of the calculation results carried out by the different methods is done.


Keywords: CREKA, peptide, conformational analysis, electron structure, molecular dynamics.
PACS: 31.15; 33.15

## INTRODUCTION

The investigation of processes of controlled transport of drugs and diagnostic agents realized with the help of nano-particles is the one of actual directions of nano-bio-technology. The nano-particles loaded by drug molecules, are able to deliver the chemical compounds directly to injured cells without essential influence on healthy ones of different organs and tissues. In spite of the fact that the more than thirty thousands of different drugs are registered in the world, the search of compounds having the clearly expressed selective action effect has been continued up to nowadays. The new compounds are synthesized and their modified analogues are investigated. The compound consisting on five amino-acid residuals Cys, Arg, Glu, Lys, Ala and called CREKA is related to number of such drugs applied in antitumor therapy with the use of nano-particles. CREKA drug having the antitumoral effect at prostate cancer had been firstly synthesized in 2006 by American scientists [1]. Later, its pharmacological properties had been investigated [2-7]. However, the numerical biological tests are carried out without knowing of its space structure, conformational mobility and electron properties necessary for revealing of molecular bases of drug action mechanism and intentional search of more effective analogues of CREKA molecule.

The geometric and energy parameters defining the molecule stable conformational states are calculated by theoretic methods with use of computing programs in the present work with the aim of reporting on conformational mobility and electron-conformational properties of CREKA molecule.

## CALCULATION METHODS

The low-energy conformational states of CREKA molecules are found by method of theoretical conformational analysis in approximation of atom mechanic model by technique described in detail in [8]. The potential function parameters used in present work describing the different types of atom-atom interactions: electrostatic, non-valent (including hydrogen bonds forming with participation of hydrogen atom of functional
groups $\mathrm{OH},-\mathrm{NH}$ and SH and oxygen heteroatom) and torsion potentials are taken from [8]. The calculations are carried out for conditions modeling the water surrounding and dielectric constant value is taken equal to 10 .

Electron structure of CREKA molecule is investigated by semi-empirical methods of quantum chemistry CNDO/2 and MNDO with the use of parameterized calculation schemes AM1 and PM3.

The demonstrated version of HyperChem 7.5 program of site of corporation Hypercube (http://www.hyper.com/) is used for calculation. The equilibrium nuclear configurations corresponding to geometry of low-energy conformations calculated by method of theoretical conformational analysis are taken in the capacity of zero approximations at optimization of molecule electron energy. It is known that these semiempirical methods decrease the barrier value of peptide bond rotation that's why the structure correction by molecular dynamics method is carried out before calculation beginning.

The calculations by molecular dynamics method are carried out under conditions of implicit water molecules with medium dielectric constant ( $\varepsilon$ ) under consideration. It is known that change of dielectric constant influences on balance of functional groups of amino-acid residuals in peptide molecules and essentially influences on formation of hydrogen bonds and its number. In all cases, the calculated equilibrium geometry is used in the capacity of initial one for molecular-dynamic calculation carried out in potentials of semi-empirical method MM+ without taking into consideration the symmetry. The optimization of molecule geometry is carried out with convergence parameter 0.01 .

## RESULTS AND DISCUSSION

The stable conformational states of CREKA molecule are obtained on the base of stage-by-stage approach including the calculation of fragment lowenergy states according to scheme given in fig.1. The acceptable values of dihedral angles in main and side chains of amino-acid residuals including in CREKA molecule composition are used in the capacity of zero approximations. 800 starting conformations included in
procedure of minimization of total conformation energy being the additive sum of energy depositions of nonvalent, electrostatic, torsion interactions and energy of hydrogen bond formation, are chosen.


Fig.1. The scheme of step-by-step calculation of CREKA molecule.

The calculation results are generalized in tables 1-3 and in fig. 2 where the low-energy conformational states of CREKA molecule are given. According to
investigation results, the peptide molecule can realize 12 stable conformational states divided by not high potential barrier. The conformations with both unfolded form of main chain (conformations 1,5-11, fig.2) and conformation with folded form of peptide frame (conformations 2-4 and 12, fig.2) are related to them. The conformation 3 , in which the distance between $\mathrm{C}^{\alpha}$-atoms of first and last residuals is minimum one and it is equal to $4.5 \AA$, is the more compact one. The tail residuals in 3,4 and 12 conformations (table 1) are space-conciliated. The difference in conformational energy value of calculated structures doesn't exceed $3,4 \mathrm{kcal} / \mathrm{mol}$ (table 1), i.e. the molecule is conformationally mobile and the choice of concrete structure will depend on real surrounding of peptide molecule. The interactions of valence-unbound atoms make the main stabilizing contribution into energy of calculated structures. The destabilizing contribution of electric interactions varies in limits $2.6 \div 8.4 \mathrm{kcal} / \mathrm{mol}$.

Table 1.
The contributions of different interaction types in low-energy conformation CREKA molecule ( $\mathrm{kcal} / \mathrm{mol}$ ).

| Conformation | $\mathrm{E}_{\text {nv }}$ | $\mathrm{E}_{\text {el }}$ | $\mathrm{E}_{\text {tors }}$ | $\mathrm{E}_{\text {tot }}$ | $\mathrm{E}_{\text {rel }}$ | $\mathrm{C}^{\alpha}$-atoms of Cys1 and Ala5 ( $\AA$ ) <br> residuals |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | -16.0 | 2.8 | 1.9 | -11.3 | 0.0 | 11.1 |
| 2 | -17.4 | 4.8 | 2.5 | -10.0 | 0.3 | 9.5 |
| 3 | -17.1 | 4.1 | 2.0 | -10.9 | 0.3 | 4.5 |
| 4 | -16.5 | 2.6 | 3.1 | -10.7 | 0.5 | 6.0 |
| 5 | -15.6 | 2.9 | 2.3 | -10.4 | 0.9 | 6.1 |
| 6 | -19.8 | 7.4 | 2.2 | -10.2 | 1.0 | 12.3 |
| 7 | -18.6 | 5.6 | 2.7 | -10.2 | 1.1 | 8.5 |
| 8 | -20.5 | 8.4 | 2.1 | -10.0 | 1.2 | 11.4 |
| 9 | -14.8 | 2.8 | 2.0 | -9.8 | 1.5 | 11.3 |
| 10 | -17.4 | 6.3 | 2.6 | -8.5 | 2.8 | 11.0 |
| 11 | -17.9 | 7.7 | 1.9 | -8.4 | 2.2 | 12.2 |
| 12 | -15.6 | 4.3 | 3.4 | -7.8 | 3.4 | 6.4 |

Table 2.
Hydrogen bonds in low-energy conformations of CREKA molecule.

| *Conformation | Hydrogen bond | Hydrogen bond length, $\AA$ | Hydrogen bond energy, $\mathrm{kcal} / \mathrm{mol}$ |
| :---: | :---: | :---: | :---: |
| 1 | $\mathrm{N}^{8} \mathrm{H}$ (Arg2) ...COO(Glu3) | 2.7 | -0.18 |
| 2 | NH (Glu3)...COO(Glu3) | 2.5 | -0.34 |
|  | CO (Glu3) ...NH(Ala5) | 2.7 | -0.18 |
| 3 | $\mathrm{N}^{\mathrm{d}} \mathrm{H}$ (Arg2) ...COO(Glu3) | 2.3 | -0.54 |
| 4 | $\mathrm{N}^{\mathbf{d}} \mathrm{H}$ (Arg2) ...COO(Glu3) | 2.9 | -0.11 |
| 5 | $\mathrm{N}^{\delta} \mathrm{H}$ (Arg2) ...COO(Glu3) | 2.8 | -0.15 |
| 6 | NH(Cys1)...COO(Glu3) | 1.9 | -1.25 |
|  | NH(Arg2)...COO(Glu3) | 2.2 | -0.76 |
| 7 | NH(Cys1)...COO(Glu3) | 2.1 | -1.05 |
| 8 | NH(Cys1)...COO(Glu3) | 2.1 | -1.05 |
|  | NH(Arg2)...COO(Glu3) | 2.0 | -0.94 |
| 9 | $\mathrm{N}^{\mathbf{\delta}} \mathrm{H}$ (Arg2) ...COO(Glu3) | 2.4 | -0.42 |
| 11 | NH(Arg2)...COO(Glu3) | 2.3 | -0.50 |

*Note: Conformation numbers correspond to table 1.

Table 3.
Dihedral angles in low-energy conformations of CREKA molecule on data of conformational analysis.

| Conformation | Amino-acid residuals |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | Cys1 | Arg2 | Glu3 | Lys4 | Ala5 |
| 1 | $\begin{gathered} -73,- \\ 55,180, \\ 176 \\ \hline \end{gathered}$ | $\begin{gathered} -104,-59,178, \\ 177,185,176,181 \end{gathered}$ | $\begin{aligned} & -99,137,185, \\ & -54,-69,166 \end{aligned}$ | $\begin{gathered} -117,-61,181 \\ -61,179,179,179,180 \end{gathered}$ | $\begin{gathered} -88,-52,178, \\ 180 \end{gathered}$ |
| 2 | $\begin{gathered} \hline-76,- \\ 52,180, \\ 179 \end{gathered}$ | $\begin{gathered} \hline-92,-56,178, \\ 178,182,178,181 \end{gathered}$ | $\begin{gathered} 147,173,180, \\ 43,60,67 \\ \hline \end{gathered}$ | $\begin{gathered} -90,95,180, \\ -60,181,181,181,180 \end{gathered}$ | $\begin{gathered} \hline-84,-55,179, \\ 180 \end{gathered}$ |
| 3 | $\begin{gathered} \hline-83,72,181, \\ 178 \\ \hline \end{gathered}$ | $\begin{gathered} \hline-116,-63,177, \\ 175,187,171,180 \\ \hline \end{gathered}$ | $\begin{aligned} & \hline-96,-52,183, \\ & -55,-66,154 \\ & \hline \end{aligned}$ | $\begin{gathered} \hline-114,123,175, \\ 180,179,180,180,180 \\ \hline \end{gathered}$ | $\begin{gathered} \hline-83,-54,180, \\ 181 \\ \hline \end{gathered}$ |
| 4 | $\begin{gathered} \hline-83,76,181, \\ 180 \end{gathered}$ | $\begin{gathered} -119,-63,179, \\ 179,185,177,181 \end{gathered}$ | $\begin{array}{r} -94,140,187, \\ -56,-70,167 \end{array}$ | $\begin{gathered} 54,65,184, \\ -57,179,181,180,180 \end{gathered}$ | $\begin{gathered} \hline 50,56,188, \\ -59 \end{gathered}$ |
| 5 | $\begin{gathered} -77,- \\ 57,179, \\ 176 \end{gathered}$ | $\begin{gathered} \hline-108,-61,178, \\ 177,183,177,181 \end{gathered}$ | $\begin{aligned} & -98,143,186, \\ & -55,-70,168 \end{aligned}$ | $\begin{gathered} 55,68,181 \\ -57,180,180,180,180 \end{gathered}$ | $\begin{gathered} 113,141,183 \\ 61 \end{gathered}$ |
| 6 | $\begin{aligned} & -87,- \\ & 62,180, \\ & -57 \end{aligned}$ | $\begin{gathered} -136,-63,180, \\ -67,179,182,179 \end{gathered}$ | $\begin{aligned} & 53,62,183, \\ & -60,75,228 \end{aligned}$ | $\begin{gathered} -117,96,182 \\ -57,179,182,180,180 \end{gathered}$ | $\begin{gathered} -89,-56,180, \\ 180 \end{gathered}$ |
| 7 | $\begin{gathered} -88,- \\ 63,180, \\ -62 \end{gathered}$ | $\begin{gathered} -137,-62,180, \\ -72,181,180,180 \end{gathered}$ | $\begin{aligned} & \hline 53,68,183, \\ & -61,74,230 \end{aligned}$ | $\begin{gathered} 60,68,183 \\ -54,179,181,179,180 \end{gathered}$ | $\begin{gathered} 111,141,177, \\ 59 \end{gathered}$ |
| 8 | $\begin{gathered} \hline-89,- \\ 62,180, \\ -63 \end{gathered}$ | $\begin{gathered} \hline-138,-63,179, \\ -67,179,182,179 \end{gathered}$ | $\begin{aligned} & \hline 53,59,183, \\ & -60,74,234 \end{aligned}$ | $\begin{gathered} \hline-113,-61,182, \\ -58,179,182,180,180 \end{gathered}$ | $\begin{gathered} \hline-86,-54,179, \\ 180 \end{gathered}$ |
| 9 | $\begin{gathered} 82,179,181 \\ 85 \end{gathered}$ | $\begin{gathered} \hline-105,-62,179, \\ 176,186,174,181 \end{gathered}$ | $\begin{gathered} -98,139,188, \\ -56,-68,163 \end{gathered}$ | $\begin{gathered} \hline-116,-60,181, \\ -59,179,180,180,180 \end{gathered}$ | $\begin{gathered} \hline-87,-52,178, \\ 180 \end{gathered}$ |
| 10 | $\begin{gathered} 79,181,181, \\ 84 \\ \hline \end{gathered}$ | $\begin{gathered} \hline-103,101,181, \\ -61,179,180,179 \end{gathered}$ | $\begin{array}{r} 107,167,189, \\ -51,-56,124 \end{array}$ | $\begin{gathered} \hline-83,-53,177, \\ -60,179,181,179,180 \end{gathered}$ | $\begin{gathered} \hline-83,-53,176, \\ 180 \end{gathered}$ |
| 11 | $\begin{gathered} 79,180,181 \\ 83 \end{gathered}$ | $\begin{gathered} \hline-113,-62,180, \\ -60,178,182,178 \end{gathered}$ | $\begin{aligned} & \hline 50,62,179, \\ & -62,72,234 \end{aligned}$ | $\begin{gathered} \hline-120,94,181, \\ -120,- \\ 57,179,182,180 \\ \hline \end{gathered}$ | $\begin{gathered} \hline-89,-56,180, \\ 180 \end{gathered}$ |
| 12 | $\begin{gathered} \hline-80,- \\ 58,180, \\ -58 \end{gathered}$ | $\begin{gathered} \hline-113,-58,178, \\ 183,183,179,180 \end{gathered}$ | $\begin{gathered} \hline-104,- \\ 74,190, \\ -57,-71,173 \end{gathered}$ | $\begin{gathered} \hline-128,-68,193, \\ -60,180,180,180,180 \end{gathered}$ | $\begin{gathered} \hline-89,-51,189, \\ -51 \end{gathered}$ |

*Note: The values of dihedral angles are given in consistency: $\varphi, \psi, \omega$ (main chain, upper line), $\chi_{1}, \chi_{2}, \chi_{3}, \chi_{4}, \chi_{5}$ (side chain, low line).

The low-energy conformation are stabilized by hydrogen bonds in formation of which the side chains of residuals with opposite charged functional groups Arg2 and Glu3 (table 2) take part. The hydrogen atoms of peptide groups (NH) of main chain Cys1, carboxyl group of side chain of glutaminic acid (Glu3) and atoms of peptide group in main chains of Glu3 and Ala5 residuals also take part in formation of hydrogen bonds.
According to calculation results, glutaminic acid plays the essential role in formation of stabilizing contacts as takes part in both non-valent interactions and electrostatic contacts with neighboring residuals in chains. The values of dihedral angles of 12 low-energy conformational states of CREKA molecule, which can be used for study of its structure analogs and conformational dynamics.

## CALCULATION OF ELECTRON STRUCTURE OF CREKA MOLECULE

The electron structure of CREKA molecule is investigated with the help of semi-empirical quantumchemical methods CNDO/2 and MNDO with use of
parameterized calculation schemes AM1 and PM3 widely developed and well enough approved at investigations of electron-conformational properties of biological molecules. The wide choice of quantum-chemical methods based on different approximations is caused by necessity of objective analysis of obtained results. The revealing of general elements of spatial and electron structures of CREKA molecule supposedly responsible for unique pharmacological effects of investigated compound is the aim of such investigations.

At calculation of parameters defining the electron structure of peptide molecule the atom coordinates belong to equilibrium nuclear configurations in twelve lowenergy conformational states of molecule calculated by method of conformational analysis (tables 1 and 3) are used. In all methods only the atom orbitals with principal quantum number corresponding to highest orbitals of isolated atoms populated by electrons and valent electrons are taken into consideration. The equation solution of self-consistent field with convergence parameter $10^{-8}$ can be obtained at maximum number of cycles, which is not more than 500 .




(6)
(4)

(5)

(7)


(11)

(12)

Fig. 2. Low-energy conformation states of CREKA molecule on data of theoretic conformational analysis.

The difference of total energy on previous and following iteration step is the main parameter of convergence criterion.

The least activation energy value of nuclear repulsion is realized in structure 1 , table 1 . Such clear correspondence isn't observed for electron energy. As it is seen from table 4 the state with energy global minimum (conformation 1, table 1) dominates in comparison with total electron energy values. The lowest value of total electron energy is caused by well energy balance of electron cloud stabilization and repulsion of atom residuals. In spite of the fact that electron energy value of this structure is less than other configuration ones. The faborable localization of atom nuclears compensates this fact. Finally, conformation 1 has the biggest bond energy value, which is the main criterion of stability. The following four conformations with relative energy
$0.3-0.9 \mathrm{kcal} / \mathrm{mol}$ on bond energy value are lower than conformation 1 as inter-frame repulsions increase more essentially than stabilizing electron contributions. The most value of electron energy is observed in conformation 7 , which is also characterized by more strong repulsion of atom frames. The opposite picture is revealed for conformation 9 , in which the minimum value of nuclear repulsion energy is compensated by most value of molecule electron energy. Thus, one can conclude that between conformations being in the relative energy interval $0-5 \mathrm{kcal} / \mathrm{mol}$ the essential divergence of differentiation character of low-energy states isn't observed at calculations of molecular mechanics and CNDO/2 method. In spite of the difference in absolute value of calculated parameters of electron structure, the analogous picture is observed for other quantum-chemical calculation methods.
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