

## QUANTUM-CHEMICAL MODELING OF CHLORINE-DOPED AND HYPERVALENT DEFECTS PARTICIPATION IN RECONSTRUCTION OF THE a-Se STRUCTURE\*

O. A. Kondakova, A. S. Zyubin, S. A. Dembovsky, N. S. Kurnakov

Institute of General and Inorganic Chemistry of RAS Leninsky pr.31,  
119991 - Moscow, Russia

The quantum-chemical modeling of the defects emerging at the implantation of chlorine molecules in a-Se network and their interactions with the basic structural elements as well as with the hypervalent configurations (HVC), which were found out earlier was carried out at the ab initio level with account of the electron correlation. The most typical position of chlorine atoms in amorphous selenium network was picked out. It has been shown that fragments with Se-Cl terminal bond are able to interact both with chains and with HVC creating new defects. Such complexes can change the bond directions in a local area and also they create additional levels in the band gap.

(Received June 25, 2001; accepted November 29, 2001)

*Keywords:* Quantum-chemical modeling, Amorphous semiconductor, Defects

### 1. Introduction

The drastic change of the electrical characteristics of a-Se is observed at the introducing of chlorine impurity on the order of 1% or less [1-3], in spite of the preceding proposal about a negligible influence such small additions at the properties of non-crystalline semiconductors. The acute drop of resistivity up to  $10^9 \Omega\text{cm}$  in a chlorine doped selenium is accompanied by lowering of conductivity activation energy by 0.26 eV in comparison with non-doped a-Se. The same results were obtained in the investigation of chlorine-doped liquid selenium [4-6]. The conductivity of the melt increases by 6 times with the increase of temperature [5,6].

Such changes can be explained both by formation of impurity defects and interaction of chlorine atoms with already existence ones. The main previous hypothesis is the model of charged centers  $D^+$ ,  $D^-$  [7-9]. It can be described as follows for the case of Se:Cl. Impurity atoms terminate already existing dangling bonds (D) or insert into Se-Se bonds destroying them. The another variant is Cl atom occupies the interstitial position attracting one electron from the lone pair of Se atom and forming a  $C_2^+$  center. If chlorine is located near the middle of chain appears a volume charge. Since the neutral Cl atom at the end of chain cannot produce free charge carriers then interstitial atoms become the main donor centers [3,7,8].

Two additional bands absent in the IR spectra of non-doped a-Se are observed in the spectra of Cl-doped selenium [10]. The  $335 \text{ cm}^{-1}$  band is interpreted, enough reliable, as a vibration of Se-Cl terminal bond. The origin of  $960 \text{ cm}^{-1}$  band is still unclear.

The aim of this work is to investigate the properties of possible configurations arising at the interaction of Cl atoms with elements of a-Se network, to consider the results of interaction of chain terminated by chlorine with such defects as VAP-d and  $C_4^0$  described in the previous papers [11,12] and also to estimate the participation of Cl atoms in the process of network reconstruction.

### 2. Calculation method

The calculations of the model clusters were carried out at the ab initio level with account of the electronic correlation both in the frame of density functional method (B3LYP) [13] and with the help of second order of perturbation theory at the Moller-Plesset scheme (the standard variant MP2). The B3LYP approach was used for the optimization of clusters geometrical parameters and MP2 was used for refinement of their energy characteristics. The influence of core electrons was modeled by

---

\* presented at the First International Workshop on Amorphous and Nanostructured Chalcogenides, Bucharest, June 25-28, 2001

pseudopotential LANL2 [14] with the appropriate valence-split basis set with the addition of polarizing d-AO. The more detailed describing of cluster approach and basis set choice are presented in [12].

### 3. Results

The modeling of chlorine imbedding into the a-Se network shows that the most stable configurations forming at the interaction of  $\text{Cl}_2$  molecule with the network elements are chains with dangling bonds terminated by halogen atoms.

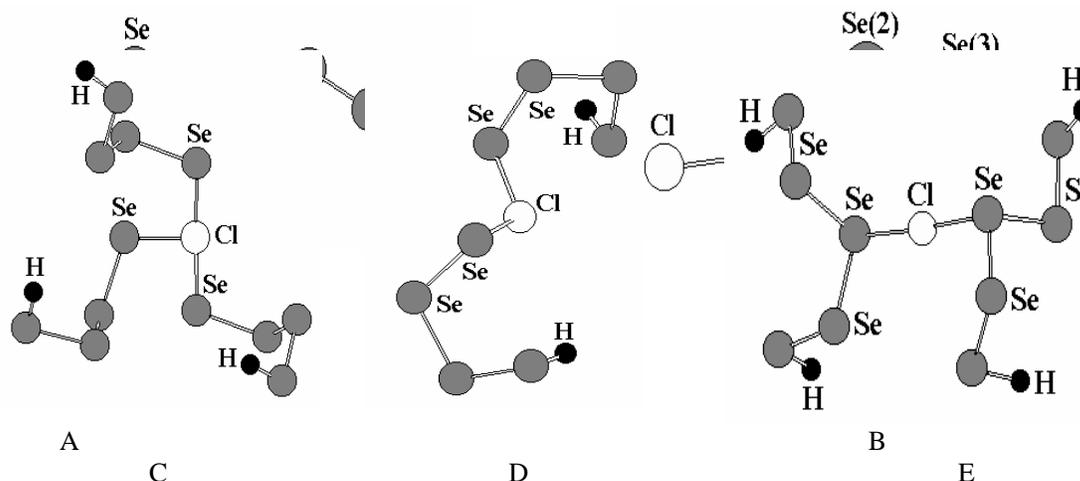


Fig. 1. The configurations arising as a result of interactions between Se chains and Cl atoms.

The total energy of two neutral half-chains  $\text{HSe}_4\text{Cl}$  (Fig.1B) is with 19 kcal/mole lower than the one of initial components:  $\text{Se}_8\text{H}_2$  chain (Fig.1A) and  $\text{Cl}_2$  molecule. The formation of terminal Cl-Se- fragment creates a well defined alternation of Se-Se bonds, whose characteristics are presented in Table 1. The charge transfer to Cl atom is not very essential.

Table1. The bond lengths, (in Å) and atomic charges, (in e) for the neutral  $\text{HSe}_4\text{Cl}$  half-chain (Fig.1B).

Bond	Se(1)-Cl	Se(1)-Se(2)	Se(2)-Se(3)	Se(3)-Se(4)	Se(4)-H	
Bond length	2.24	2.33	2.41	2.37	1.49	
Atom	Cl	Se(1)	Se(2)	Se(3)	Se(4)	H
Atomic charge	-0.17	0.12	0	0	-0.13	0.16

The neutral defect represented at the Fig.1C is unstable and breaks down on the  $\text{HSe}_4\text{Cl}$  and  $\text{Se}_8\text{H}_2$  fragments. The positively charged defects simulating  $\text{Cl}^+$  incorporation into Se chain (Fig. 1D) or  $\text{Cl}^+$  interaction with two chains (Fig. 1E) were calculated as well. The values of relative energies of such defects with negatively charged  $\text{HSe}_5^*(\text{Se}_5\text{H}_2)_2$  fragment as counterpart are above than the one for the neutral  $\text{ClSe}_n\text{H}$  and  $\text{HSe}_m\text{H}$  structures on 148 and 132 kcal/mole correspondingly. Thus one can conclude that the formation of charged defects at the interaction of  $\text{Cl}_2$  molecule with the structural units of a-Se is unfavorable and the probability of their existence is very low.

In order to estimate the role of the terminal Cl-Se- fragments in the process of network modification the interaction of  $\text{HSe}_2\text{Cl}$  half-chain both with the basic element of network ( $\text{HSe}_4\text{H}$  chain) and with defects VAP-d and  $\text{C}_4^0$  has been computed. The scheme of the bonds switching due to transition from one configuration to the other with the participation of the chain terminated by Cl is represented at the Fig.2. To estimate the potential barrier on the way of such transformation, the scanning of the part of potential surface along R and r coordinates (table 2) was accomplished. The R value corresponds a distance between the centers of Se(1)-Se(2) and Se(3)-Cl bonds, r - is Se(1)-Se(2) bond length. The appropriate relative energies are presented in Table 2. In accordance with these data the value of potential barrier for  $2\text{A} \rightarrow 2\text{C}$  transition does not exceeded 18 kcal/mole. The hypervalent complex 2B with  $r = 2.8$  and  $R = 2.7$  Å corresponds to the vicinity of the barrier. The bond lengths and atomic charges for this configuration are presented in Table 3. The transformation of hypervalent

defect 2B into configuration 2C leads to the bonds switching as a result of possible deformation of the surrounding network (Se(1)-Se(2) bond stretching).

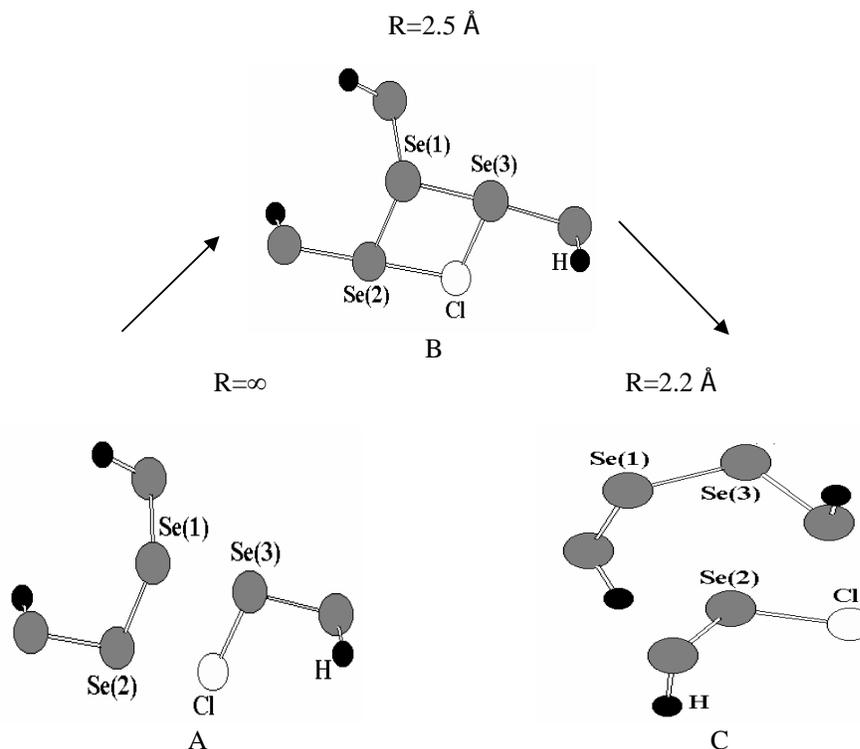


Fig. 2. Schematic representation of the bond switching at the interaction of Cl-Se<sub>2</sub>H fragment with Se-Se bond.

Table 2. The potential surface of a structure transformation at the interaction of a chain Se<sub>4</sub>H<sub>2</sub> with a chain Cl-Se<sub>2</sub>H. R, Å – distance between the centers of Se(1)-Se(2) and Se(3)-Cl bonds, r, Å – the length of Se(1)-Se(2) bond.

Δ E, kcal/mole							
r \ R	2.4	2.5	2.6	2.7	2.8	~	4.48
2.8	0	-	-	-	-		-
2.7	7.2	8.4	11	14.2	17.7		-
2.6	16.3	17.8	20.2	23.2	16.5		-
2.5	29.2	30	32.2	34.4	9.2		-
2.4	10.6	11.5	3.3	0.3	-2		-
2.3	11.3	-	-	-	-		-
2.2	-	-	-	-	-		-15.7

Table 3. The distances (Å) and charges (in e) of the received configurations at the interaction of Se<sub>4</sub>H<sub>2</sub> with a chain Cl-Se<sub>2</sub>H (Fig.2). Charges of H atoms aren't indicated.

Distance, Å	R=∞	R=2.5	R=2.2
Se(1)-Se(3)	2.83	2.51	2.39
Se(2)-Cl	2.76	2.48	2.26
Se(1)-Se(2)	2.41	2.43	4.48
Se(3)-Cl	2.29	2.33	5.89
Charge			
Q Se(1)	0	0	0
Q Se(2)	0	0	0.1
Q Se(3)	0.1	0.13	0
Q Cl(4)	-0.17	-0.14	-0.19

The VAP-d and  $C_4^0$  defects are local minimums of potential surface with more higher relative energy as compared with usual structure units [11,12]. Their interaction with terminal Se-Cl fragment can form new Cl-doped HVC as well. The scheme of Se-Cl bond interaction with VAP-d is drawn in the Fig. 3.

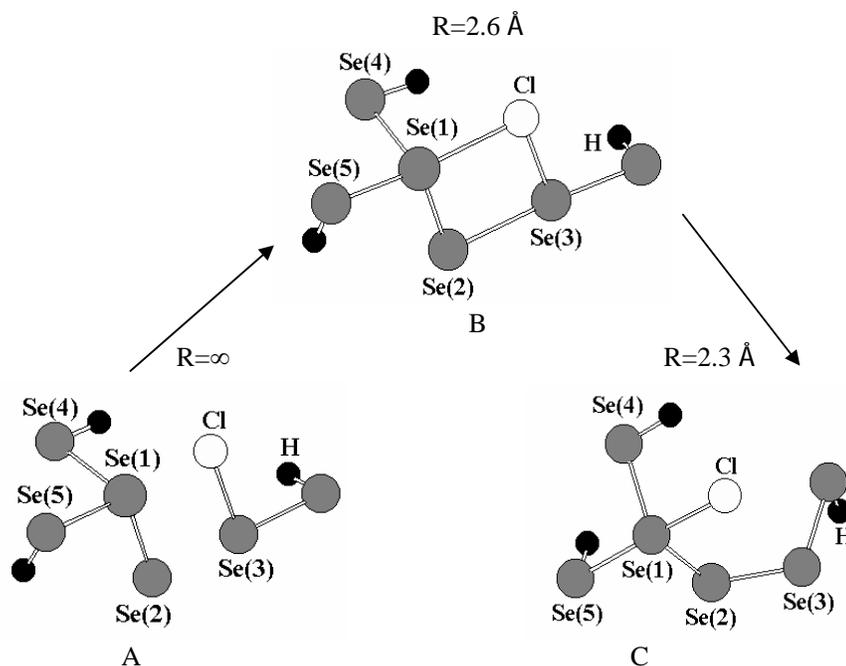


Fig. 3. Schematic representation of the Cl-Se fragment interaction with VAP-d defect.

The hypervalent 3B structure corresponds to the top of barrier as well as in the previous case. However in this case the final configuration (3C) differs from the initial one (3A). The Cl-doped defect with the four-coordinated Se atom is created as a result of overcoming of barrier  $\sim 23$  kcal/mole (table 4). The bonds inside the complex are nonequivalent (the variations up to  $0.2 \text{ \AA}$ ) as we can see from the data of table 5, and due to reorganization of these bonds it is possible to expect the formation of several configurations with close energies. Obviously the presented cluster is too small for investigation of non-rigidity, and will be made at more extended system.

The  $C_4^0$  defect represents a  $C_{2v}$ -like structure with two long bonds ( $2.72 \text{ \AA}$ ) and two short ones ( $2.4 \text{ \AA}$ ). So far as the interaction of Se-Cl fragment with the long Se-Se bond must occur much easier than with more short and strong one, the closing of Se(1)-Se(8) and Se(6)-Cl bonds (Fig. 4) was considered in the calculations. In the transitional configuration (Fig.4B) an additional Cl-Se(1) bond is formed. This interaction starts at more long distances  $R$  than in previous cases. The barrier of the transition to configuration 4C is slightly higher than for the other structures  $\sim 28$  kcal/mole (table 6). The final defect is of the same type as in the previous case (Cl-Se $\equiv$ ), but with more close values of Se-Se bond lengths and with more large Se-Cl distance (Table 7). Obviously it will be need to investigate the properties of this HVC at more large model cluster.

Table 4. The fragment of potential surface for structure transformation at the interaction of VAP - d defect ( $\text{Se}_3\text{Se}_3\text{H}_2$ ) with Cl-SeSeH chain. R, (Å) – distance between the centers of Se(1)-Se(2) and Se(3)-Cl(4) bonds, r, (Å) – the length of Se(1)-Se(2) bond.

$\Delta E$ , kcal/mole						
R \ r	2.3	2.4	2.5	2.6	2.7	2.8
2.8	0	-	-	-	-	-
2.7	6.4	10.2	14.2	19	24.3	29.8
2.6	14.8	18.7	23	25.6	30.9	35
2.5	34.9	29.8	-16.2	-15.7	-14.1	-12.3
2.4	32.4	27.5	-19.7	-	-	-
2.3	31.6	27.2	-20.4	-	-	-

Table 5. The distances (Å) and charges (in e) of the received configurations at the interaction of VAP-d of  $\text{Se}_n$  chain with the chain Cl- $\text{Se}_n$  (Fig.3). Charges of H atoms aren't indicated.

Distance, Å	R= $\infty$	R=2.6	R=2.4
Se(1)-Se(2)	2.28	2.3	2.51
Se(2)-Se(3)	2.81	2.61	2.35
Se(1)-Cl	2.79	2.58	2.54
Se(1)-Se(4)	2.49	2.5	2.6
Se(1)-Se(5)	2.49	2.48	2.4
Se(3)-Cl	2.32	2.36	3.46
Charge			
Q Se(1)	0.27	0.27	0.35
Q Se(2)	-0.2	-0.16	0.1
Q Se(3)	0.14	0.14	0
Q Se(4)	-0.15	-0.17	-0.34
Q Se(5)	-0.11	-0.1	0
Q Cl	-0.19	-0.18	-0.4

Table 6. The potential surface of structure transformation at the interaction of the  $\text{C}_4^0$  defect ( $\text{Se}_4(\text{SeH})_4$ ) with Cl-SeSeH chain (the interaction with the “long” bond of defect  $\text{C}_4^0$ ). R, Å – distance between the centers of Se(1)-Se(2) and Se(6)-Cl bonds, r, Å – the length of Se(1)-Se(2) bond.

$\Delta E$ , kcal/mole							
R \ r	2.75	2.8	2.85	2.9	3.0	~	4.38
4.0	0	-	-	-	-		-
3.1	8.4	-	-	-	-		-
3.0	13	13.3	13.9	14.6	16.6		-
2.9	19.3	19.6	20.1	20.9	22.8		-
2.8	28.1	28.3	28.9	29.7	31.8		-
2.7	6.1	4	2.7	1.2	-1.2		-19.9

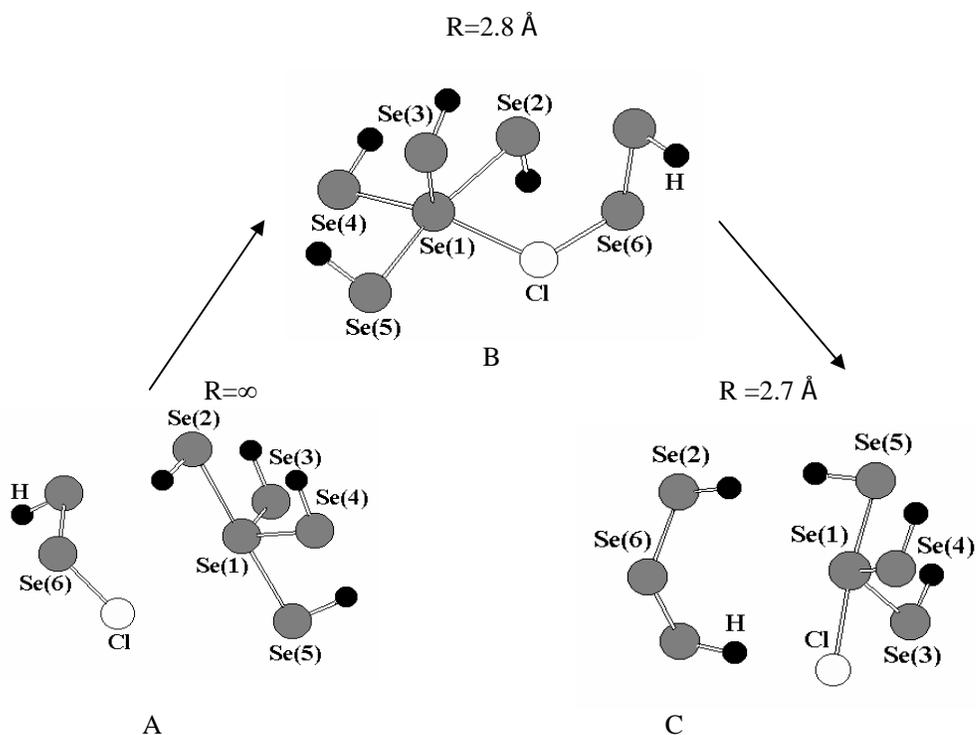


Fig. 4. Schematic representation of the Cl-Se fragment interaction with  $C_4^0$  HVC.

Table 7. The distances ( $\text{\AA}$ ) and charges (in e) of the received configurations at the interaction of defect  $C_4^0$  with the chain  $\text{Cl-Se}_n$  (Fig.4). Charges of H atoms aren't indicated.

Distance, $\text{\AA}$	$R=\infty$	$R=2.8$	$R=2.7$
Se(1)-Se(2)	2.73	2.78	4.36
Se(1)-Se(5)	2.72	2.69	2.41
Se(1)-Se(3)	2.4	2.47	2.5
Se(1)-Se(4)	2.4	2.42	2.41
Se(1)-Cl	3.67	2.61	2.9
Se(2)-Se(6)	4.34	3.01	2.52
Se(6)-Cl	2.26	2.29	4.86
Charge			
Q Se(1)	0.29	0.29	0.31
Q Se(2)	-0.42	-0.42	-0.22
Q Se(3)	0	-0.2	-0.22
Q Se(4)	0	0	0
Q Se(5)	-0.35	-0.33	0
Q Se(6)	0	0.14	0
Q Cl	-0.18	-0.15	-0.48

The behavior of energy levels of highest occupied and lowest unoccupied MO (HOMO and LUMO) represents on qualitative level the possible changing of band gap. In considered cases only

3C and 4C defects form an additional level of acceptor type in the band gap. All other Cl-related levels are formed in valence or in conductivity bands and do not emerge in the band gap (Fig. 5).

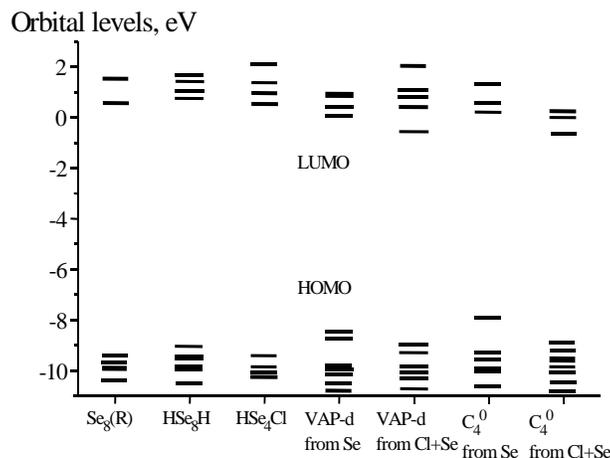


Fig. 5. The electronic levels (eV) of highest occupied and lowest unoccupied MO for network fragments of a-Se and a-Se:Cl.

#### 4. Conclusions

According to the obtained results the most energetically favorable positions of chlorine atoms in the a-Se network are at the end of chains. In this situation chlorine terminates the existence of dangling Se-Se bonds. The others neutral and charged defects which have been considered in this work are less stable. The interaction of terminal Se-Cl fragment with selenium chain can lead to switching of bonds in the local area of the network. The similar character of rearrangement is observed for interaction of Cl-Se with the VAP-d and  $C_4^0$  HVC. In this case it is possible the creation of new configurations which are able to form the additional acceptor levels in the band gap of a-Se.

#### Acknowledgement

This work was supported by Russian Foundation of Basic Research, Grant No 00-03-32646.

#### References

- [1] G. B. Abdullaev, S. I. Mekhtieva, D. Sh. Abdinov, G. M. Aliev, *phys. status solidi*, **11**, 891 (1965).
- [2] V. A. Twaddell, W. C. Lacourse, J. D. Mackenzie, *J. Non-Cryst. Sol.*, **8-10**, 831 (1972).
- [3] M. C. Assuncao, *J. Non-Cryst. Sol.*, **136**, 81 (1991).
- [4] M. Yao, S. Hosokawa, H. Endo, *J. Non-Cryst. Sol.*, **59&60**, 1083 (1983).
- [5] S. Hosokawa, M. Yao, T. Yoshimura, H. Endo, *J. Phys. Soc. Japan*, **54**, 4717 (1985).
- [6] K. Maruyama, Y. Kawakita, M. Yao, H. Endo, M. Misawa, *J. Phys. Soc. Japan*, **60**, 3032 (1991).
- [7] R. S. Street, N. F. Mott, *Phys. Rev. Lett.*, **35**, 1293 (1975).
- [8] N. F. Mott, E. A. Davis, *Electronic Processes in Non-Crystalline Materials*, Clarendon Press, Oxford (1979).
- [9] B. L. Gelmont, B. T. Kolomiets, K. D. Tsendin, *phys. status solidi A*, **91**, 319 (1985).
- [10] M. C. Assuncao, *Infrared Physics*, **31**, 587 (1991).
- [11] S. A. Dembovsky, A. S. Zyubin, F. V. Grigor'ev, *Gl. Phys. Chem.*, **26**, 333 (2000).
- [12] A. S. Zyubin, F. V. Grigor'ev, S. A. Dembovsky, *Russ. Journal of Neorg. Chem.*, **8**, (2001) unpublished.
- [13] A. D. Becke, *J. Chem. Phys.*, **98**, 5648 (1993).
- [14] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, et al., *J. Comput. Chem.*, **14**, 1347 (1993).