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Equilibrium structure of germanium sulfur Ge_nS_m clusters

S. SENTURK DALGIC*, M. CALISKAN
Department of Physics, Trakya University, 22030, Edirne, Turkey

We determine a refined model for the interionic interactions in **Ge_nS_m** clusters by an analysis of data on their molecular structures. The adopted potential energy function is based on the interionic force model proposed by Akdeniz and Tosi. The microscopic model used for **Ge_nS_m** clusters incorporates the Born Model of cohesion and shell model for vibrational motions, bond length and crystal defects. Electron shell deformability is described through the effective valences, the electric and overlap polarizabilities of the sulfurs. The two different overlap repulsive energy form have been tested. The equilibrium molecular structure has also been predicted with molecular dynamics simulation. It has been shown that the calculated bond lengths and bond angles are in good agreement with experimental data and those obtained by chemical structure calculations. In addition, the liquid structure of GeS_2 is obtained by Variational Hypernetted Chain (VMHNC) approximation using the effective potential derived from the interionic force model within the polarizable ion potential.

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1. Introduction

Understanding the nature of the chemical bond in mixed clusters between transition metal and chalcogenides is of great interest in many areas of science because of their technological importance. Clusters containing chalcogenides are theoretically one of the most investigated systems due to their foreseen practical usage possibilities in different electronic, laser technology and photonic devices [1]. In cluster studies, the starting point is the geometrical structure. It is known that there is no experimental technique that can provide direct information on cluster geometry for larger systems. Therefore, theoretical study is the only method to obtain geometrical information on larger clusters at present. The accuracy of the computed geometries depends on the level of the theory used. The better theory can handle the small size of the cluster. On this aspect, we propose a refined model of polymeric structures which can be studied on the computations of large clusters containing chalcogenide glasses. Among the chalcogenide glassy systems, germanium binary chalcogenide glasses are most extensively studied for many years through experimental measurements [2,3].

However, theoretical calculations can be an alternative tool in order to understand the physical mechanisms occurring at the atomic scale and explaining the results observed in experiments, [4]. On this line, the structure and physical properties of g-GeS_2 have been investigated using different theoretical approaches and molecular dynamics (MD) simulations [5-11]. Holomb and co-workers have proposed the localized states model of GeS_2 glasses based on electronic states of Ge_nS_m clusters calculated by using time dependent – density functional theory (TD-DFT) [9]. They have calculated the band gaps and molecular orbital energies of Ge_nS_m clusters using TD-DFT and DFT/BLYP methods, respectively.

Also Holomb and co-workers used resonant Raman and absorption edge spectroscopy with first-principle calculations in order to study the structure of GeS_2 glasses (g-GeS_2). They were prepared these glasses under different melt temperatures and cooling rates [5]. The computational part occurs of first-principal calculations on small atomic Ge_nS_m ($1<n<3$, $1<m<9$) clusters using the Gaussian-03 quantum chemical program package based on Hartree-Fock (HF) method [5,12].

In addition, Drabold and co-workers study the structural, dynamical and electronic properties of glassy g-GeS_2 with the use of ab initio MD simulations at room temperature [4]. In their calculations they used "FIREBALL 96" molecular dynamic code which based on the Sankey-Niklewski Scheme [13].

Although cluster modeling simulations were performed on GeS_2, [5,9-11] it appears that GeS_2 compounds have not been the topic of extensive MD investigations yet, contrary to other Ge-chalcogenides [4]. In order to perform such investigations one has to decide what kind of description is adequate for GeS_2. Researchers have noticed that taking mostly covalent bonding into account in GeS_2 a first-principles approach seems appropriate [4].

The purpose of the present study was to determine the equilibrium and static structure of Ge_nS_m clusters with the interionic Force Model which for the static and dynamic structure and energetic of neutral and charged molecular clusters [14-19]. In a recent series of our previous works, we have applied this theory to CuO and CuS systems inorder to determine their equilibrium and static structures [18]. We have also obtained the equilibrium geometries of TaO_n clusters [19].

To our knowledge, this model has not been applied to the case of Germanium chalcogenides. This important is issue to obtain a reliable description of interactions for Ge_nS_m would allow the investigation of the liquid structural properties. In the present paper, we evaluate an ionic force model for the potential energy function of Ge_nS_m. We show that the evaluated model for Ge_nS_m is in a reasonably good agreement with observation and abinito MD studies. The calculated structural trends for these systems are compared with each other and discussed with the choice of parameters for the systems of present interest and the approximate theory used.

In this work we test the accuracy of the interionic force model for chalcogenide clusters. To what extent is it accurate to assume that the model parameters describing the chalcogen ions can be transferred between different chalcogenide alloys. For these purposes we focus on the Ge_nS_m calgogenides.

2. Theory

2.1 Interionic Force Model

Following the earlier studies [14-19], we use the interionic force model for germanium sulphide clusters incorporates the Born model of cohesion and the shell model for vibrational motions and crystal defects.

The potential energy $U(\{r_{ij}\},\{p_i\})$ of a cluster is taken to be a function of the inter-ionic bond vectors r_{ij} and of the dipole moments p_i carried by the sulfurs. The handled function by a computer programme [14] can be given in the form of $U(\{r_{ij}\},\{p_i\})$ is

$$U=\sum_{i<j}\left[\frac{z_i z_j e^2}{r_{ij}}+\Phi_{ij}(r_{ij})-\frac{C_i C_j}{r_{ij}^6}\right]+U_{pol}^{cl}(\{r_{ij}\},\{p_i\})+U_{shell}(\{r_{ij}\},\{p_i\}) \quad (1)$$

The sum over ion pairs on the RHS of (1) includes *(i)* the Coulomb interaction of ionic point charges with effective valances z_i subject to exact charge compensation $(\sum_i z_i = 0)$, *(ii)* the overlap repulsive interaction described by a central pair potential $\Phi_{ij}(r_{ij})$, and *(iii)* the van der Waals interaction with an interaction strength C_i being attributed to each ion. These rigid-ion terms are supplemented by the classical polarization energy U_{pol}^{cl} of the induced dipoles on the sulfur and by the shell deformation energy U_{shell}. In the above equation, the overlap repulsive potentials are written in the form proposed by Busing [20],

$$\Phi_{ij}(r)=f(\rho_i+\rho_j)\exp\left[\frac{R_i+R_j-r}{\rho_i+\rho_j}\right] \quad (2)$$

where R_i and ρ_i are characteristic radii and hardness parameters of the individual ions and f is chosen to have the standard value $f=0.05\ e^2/A^2$. Proportionality between R_i and ρ_i can be used for metal ions. Based on the interionic force model we define the rigid ion potential form which is similar the TAPT potential [21] as called as the modified TAPT potential (MTAPT) in this work,

$$V_{ij}(r_{ij})=\frac{Z_i Z_j e^2}{r_{ij}}+\phi_{ij}(r_{ij})+\frac{C_i C_j e^2}{r_{ij}^6} \quad (3)$$

In order to test the accuracy of the effective potentials used in our liquid structure calculations, another overlap repulsive energy form called as Born-Mayer potential [22] has been applied.

$$\phi_{ij}^{BM}(r_{ij})=A\exp\left[-\frac{r_{ij}}{\rho_{ij}}\right] \quad (4)$$

The classical polarization energy in Eq. (1) is defined as,

$$U_{pol}^{cl}(\{\mathbf{r}_{ij}\},\{\mathbf{p}_i\})=\sum_{i\neq j}\left[-z_i e\frac{\mathbf{p}_j\cdot\mathbf{r}_{ij}}{r_{ij}^3}+\frac{1}{2}\frac{\mathbf{p}_i\cdot\mathbf{p}_j}{r_{ij}^3}-\frac{3}{2}\frac{(\mathbf{p}_i\cdot\mathbf{r}_{ij})(\mathbf{p}_j\cdot\mathbf{r}_{ij})}{r_{ij}^5}+\frac{1}{2\alpha_c}\sum_j p_j^2\right] \quad (5)$$

and the shell deformation energy can be written as

$$U_{shell}(\{\mathbf{r}_{ij}\},\{\mathbf{p}_i\})=\frac{\alpha_s}{\alpha_c}\sum_{i\,j,j}\mathbf{p}_j\cdot\hat{\mathbf{r}}_{ij}\left|\frac{d\,\Phi_{ij}(r_{ij})}{d\,r_{ij}}\right| \quad (6)$$

where α_c is the electrical polarizability of the chalcogen and α_S is a short-range polarizability. The sum is in restricted to run over i_j = metal ions which are first neighbours of the *j*-th chalcogen. Minimization of the potential energy given in Eq.(1) with respect to the dipoles yields the dipole p_c on a chalcogen as

$$\mathbf{p}_c=\alpha_c\,\mathbf{E}_c(\{\mathbf{r}_{ij}\},\{\mathbf{p}_i\})+\alpha_s\sum_{i_j}\hat{\mathbf{r}}_{ic}\left|\frac{d\,\Phi_{ic}(r_{ic})}{d\,r_{ic}}\right| \quad (7)$$

where E_c is the self-consistent electric field on the chalcogen .

Computational Method:

We handle the potential function given in Eq.(1) by a computer programme [14] which performs two basic task: *(i)* from a given starting configuration the structure of a cluster is first optimized by searching for zero-force configurations corresponding to extreme in the total energy, and *(ii)* deformations of each zero-force structure are then studied for an assessment of its mechanical stability and for the evaluation of its vibrational frequencies.

In order to perform the static calculations in this work, the programme follows the dynamic evaluation of the cluster by means of molecular dynamics using the simple Verlet algorithm. After an equilibration period of 5000 time steps, we have computed the properties during a run of 5000 configurations. The time step was 0.01ps.

Liquid State Theory (VMHNC):

In our structural calculations, one of the integral equation theories which has shown to be very reliable theory of liquids VMHNC has been carried out [23-26]. However in the present work we use the HNC solution for our structural calculations. Like the most liquid state theories the VMHNC solves the Ornstein–Zernike (OZ) equation, which for a homogeneous, isotropic, binary system reads (i, j =1, 2)

$$h_{ij}(r) = c_{ij}(r) + \sum_{l=1}^{2} \rho_l h_{il}(r) * c_{lj}(r) \qquad (8)$$

which defines the partial direct correlation functions, $c_{ij}(r)$, in terms of the total correlation functions $h_{ij}(r) = g_{ij}(r) - 1$, where $g_{ij}(r)$ denote the partial pair distribution functions and ρ_l denote the partial ionic number densities. Now, Eq.(8) is supplemented by the exact closure relation

$$c_{ij}(r) = h_{ij}(r) - \ln\left[g_{ij}(r) e^{\beta v_{ij}(r) + B_{ij}(r)}\right] \qquad (9)$$

where $V_{ij}(r)$ are the interatomic pair potentials and the $B_{ij}(r)$ assumed to be zero for the HNC solutions. Formally the generalization of liquid state from monatomic to binary fluids, we have now a set of three coupled integral equations relating the partial pair distribution functions $g_{ij}(r)$ to the pair potentials $V_{ij}(r)$. The partial pair distribution functions are related to Ashcroft-Langreth (AL) partial structure factors $S_{ij}(q)$. For the binary liquid alloys we have carried out the VMHNC integral equation theory in which was extended by Gonzalez *et al*. [23], so as to minimize the configurational Helmholtz free energy functional $f^{VMHNC}(\beta, \rho, x_l)$ by the variational condition taking into account $B_{ij}(r) = 0$. For useful details about the VMHNC calculations of the partial structure factors, the reader is referred to Ref. [23-26].

3. Results and discussion

The presentation of the results is divided into two parts. The first one concerns with molecular structure for which the ab initio MD data are available. The second one deals with interionic pair interactions in GeS_2. The equilibrium of Ge_nS_m molecules are described as follows: (a) This is for the optimization of the configuration of the cluster by minimization of its energy towards states of static (stable and unstable) equilibrium. (b) This is for the evaluation of its vibrational frequencies and of its static and dynamic evaluation constant energy.

.3.1. Molecular Structure

Firstly, we now present the results for the equilibrium structure of Ge_nS_m clusters obtained from the interionic force model. The model parameters used in our calculations reported in Table 1. For full assessment of the model parameters describing the germanium based sulphure clusters, we have assumed transferability of a number of parameters between different systems as in our earlier studies [18,19]. Nevertheless, we could not minimize the system using the alternative repulsive potential as Born-Mayer form. The transferred parameters for Sulphure are (i) the short range polarizability α_S and the van der Waals coefficient $C_{X,}$ the stiffness parameter ρ_x describing the contribution of the sulfur in the Busing form of the Ge-S overlap repulsions taken from [18]. As already indicated in our earlier work [18], we use an approximation for S, we though that fluorine close to oxygen in periodic table so from this point of view Cl close to S. (ii) The value of ionic radius of sulphure R_x is chosen to close the value of Chloride's which was studied in Ga based chloride clusters [17]. (iii) α_X is taken from Gupta et al. [27].

The transferred parameters for Germanium are follows: the value of ionic radius R_M are chosen to close the value of Ga given in Ref. [17]. The proportionality holds between R_M and ρ_M for the metal ions (R_M / ρ_M = 18.6), except Ge_2S_6. For Ge_2S_6.the hardness parameter ρ_M has been determined from a fit of the bond length in germanium sulfur molecule.

In our calculations, we choose the effective valance value which gives the agreeable results with the overall charge neutrality conditions in Germanium based sulfur clusters. The extension of these model parameters to the Ge based sulphure clusters as follows:

Table 1. Interionic force parameters in MX , MX_2 , MX_3 , MX_4 , M_2X_6 and M_2X_7 (M: Ge and X: S).

	Z_M	Z_X	R_M(Å)	ρ_M(Å)	R_X(Å)	ρ_X(Å)	C_X (eÅ$^{5/2}$)	α_X (Å^3)	α_S (Å^3/e)
GeS	0.862	-0.862	0.98 [a]	0.0527	1.68 [b]	0.222 [b]	4.63 [b]	2.95 [c]	0.88 [b]
GeS_2	1.724	-0.862	0.98	0.0527	1.68	0.222	4.63	2.95	0.88
GeS_3	2.586	-0.862	0.98	0.0527	1.68	0.222	4.63	2.95	0.88
GeS_4	3.856	-0.964	0.98	0.0527	1.68	0.222	4.63	1.48 [b]	0.88
Ge_2S_6	2.091	-0.697	0.98	0.0430	1.68	0.222	4.63	2.95	0.88
Ge_2S_7	3.388	-0.968	0.98	0.0527	1.68	0.211	4.63	2.65	0.99
Ge_3S_{10}	3.333	-1.000	0.98	0.0527	1.68	0.211	4.63	2.95	0.99

[a][17]. [b][18], [c][27],

We have also studied bond lengths, bond angles and frequencies. We report the calculated bond lengths in Table 2 for Ge_nS_m and Ge_nS_{3n+1} at equilibrium and compare them with data those obtained by ab initio and quantum chemical calculations with B3LYP3 methods taken from Ref. [4,5, 28]. The geometrical parameters of Ge_nS_m and Ge_nS_{3n+1}. clusters as some angles are given in Table 3. The comparable data for angles can be found in Ref. [4].

Table 2. Geometrical parameters of Ge_nS_m and Ge_nS_{3n+1}. Distances are in Å.

	Parameters	Present work	*Ab initio*		Parameters	Present work	*ab initio*
GeS	r (Ge-S)	1.96	-	GeS_4	r (Ge-S)	2.16	-
	W (cm^{-1})	582	-		W (cm^{-1})	355	355 [c]
GeS_2	r (Ge-S)	2.03	-	Ge_2S_7	r (Ge-S)	2.03	-
	W (cm^{-1})	700	-		r (Ge-Ge)	3.41	3.41 [b]
GeS_3	r (Ge-S)	2.232	2.232 [a]		W (cm^{-1})	373-427	342-419[c]
	W (cm^{-1})	632.5	447.1-845.9 [a]	Ge_3S_{10}	r (Ge-S)	2.18	-
Ge_2S_6	r (Ge-S)	2.04	-		r (Ge_1-Ge_2)	3.19	-
	r (Ge-Ge)	2.91	2.91 [b]		r (Ge_2-Ge_3)	3.19	-
	W (cm^{-1})	431	413-441 [c]		W (cm^{-1})	386	-

[a][28], [b][4], [c][5],.

Table 3. Geometrical parameters of Ge_nS_m and Ge_nS_{3n+1}. Angles in degrees.

	Parameters	Present work	Ab initio
GeS_2	∠S-Ge-S	180.00 ^{0}	-
GeS_3	∠S-Ge-S	111.76 ^{0}	-
GeS_4	∠S-Ge-S	113.91 ^{0}	-
Ge_2S_6	∠S-Ge-S	109.68 ^{0}	109.47 [a]
Ge_2S_7	∠S-Ge-S	110.56 ^{0}	110.00 [a]
Ge_3S_{10}	∠S-Ge-S	111.31 ^{0}	-

[a][4]

It appears that the calculated bond lengths of r for both systems using the interionic force model are excellent agreement with ab initio data. Our vibrational frequencies, W, are close to the other theoretical results. We determine these quantities for GeS_3 from the Ge-S bond length (2.232 Å) as calculated by ab initio [28]. The calculated frequencies are in the range of the vibrational frequencies given in Ref. [5, 28]. The bond length value of Ge-Ge in Ge_2S_6 is fitted the same value taken from ab initio calculation of Drabold [4]. The value of vibrational frequency for GeS_4 given in Table 2 is fitted to its topmost stretching mode frequency (W=355 cm^{-1})[5]. For Ge_2S_7, the bond length value of Ge-Ge is fitted the value taken from Drabold [4] that is 3.41 Å which gives the good vibrational frequency value in the reasonable range. Inorder to compare our results for Ge_3S_{10}, , there are no ab initio calculations in literature yet.

Firstly, we now present the results for the molecular structure of Ge_nS_m obtained from the interionic force model in Fig.1. The bond angles and bond lengths for Ge_2S_6 and Ge_2S_7 clusters are shown in Figs 1b and 1c. According to our knowledge the calculated values for the bond lengths and bond angles for Ge_3S_{10} is first presented here in Fig.1d.

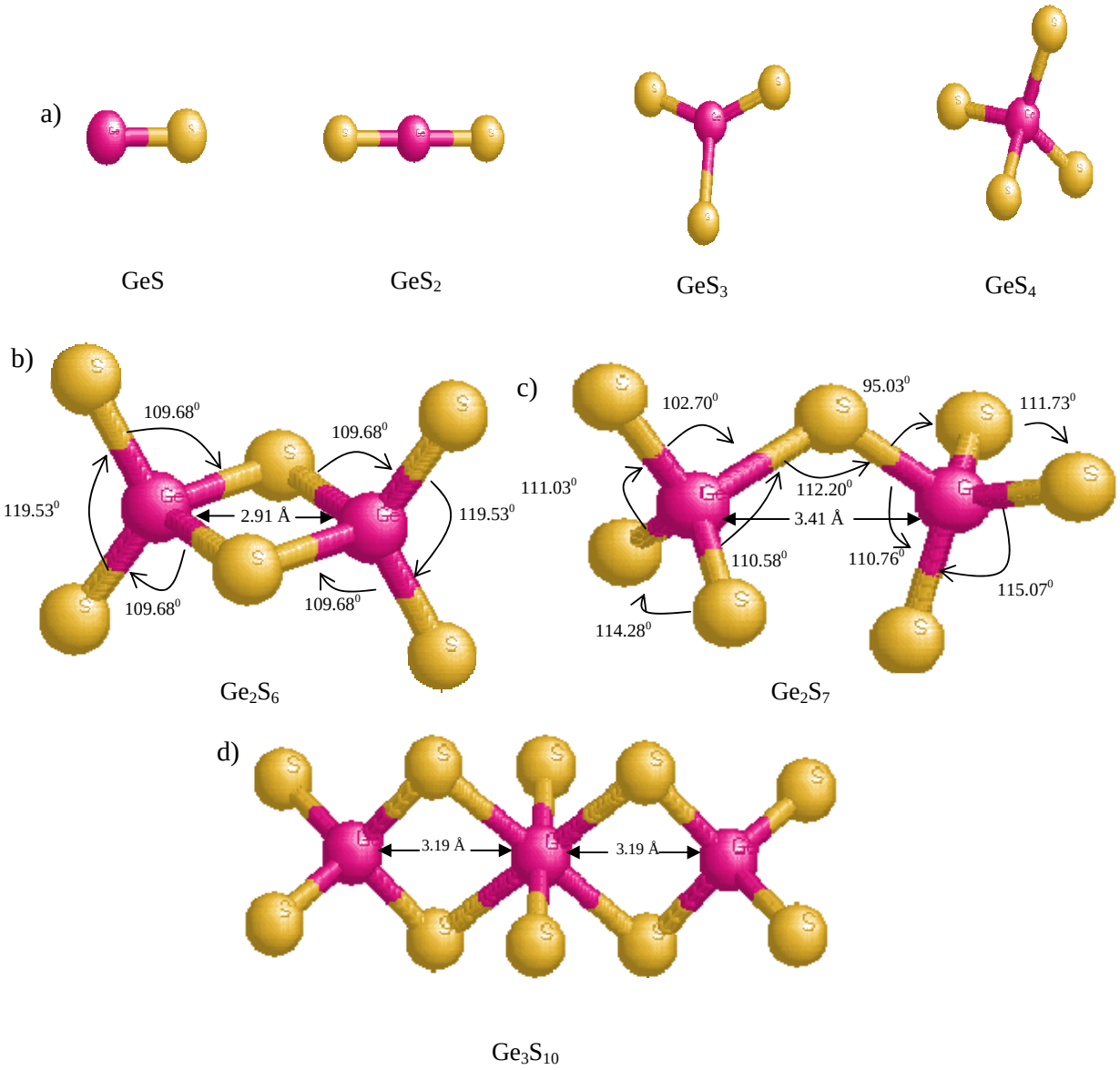

Fig 1. The structural geometries of Ge_nS_m clusters obtained by the interionic force model.

2. Interatomic interactions and liquid structure

We have also illustrated the interionic effective pair potentials for GeS in Figure 2. The rigid ion model type MTAPT potentials are computed by the parameters used in molecular structure calculations.

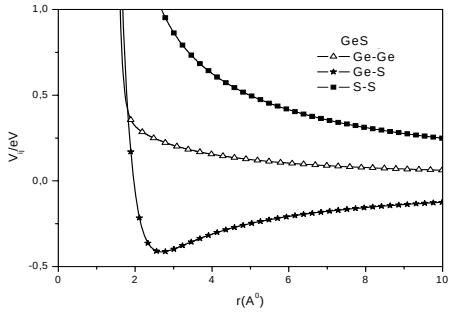

Fig. 2. Effective pair potentials for GeS_2 at T = 1113K.

In Fig. 2 that the depth of the primary potential well for different species V_{GeS} is deeper than that of others. We note that the contributions to the potentials from van der Waals interaction term are very small, however we will include them in all our calculations. The difference between the size of the positive and negative ions plays an important role at short range. Because of the different values of effective charges, the depth of minima for Ge-S.

The effective potentials given in Fig. 2 are used as input data in our liquid structure calculations within the VMHNC liquid state theory. The VMHNC partial pair distribution functions of liquid GeS_2 are illustrated by comparing with ab initio MD results of Drabold [4] in Figs 3-5. The calculations are carried out at the thermodynamic state for the number density of GeS_2 ρ = 0.0359 A^{-3} at T=1113K. [29].

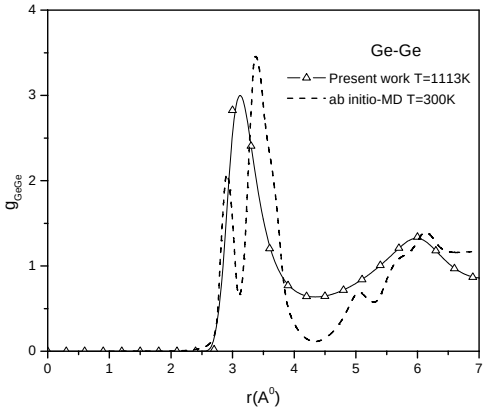

Fig. 3. Partial pair distribution functions of liquid Ge-Ge, in GeS_2.

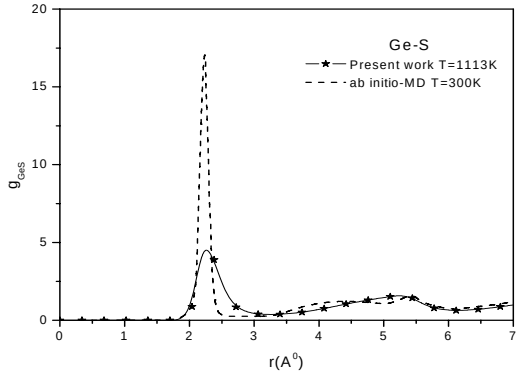

Fig 4. Partial pair distribution functions of liquid Ge-S, in GeS_2.

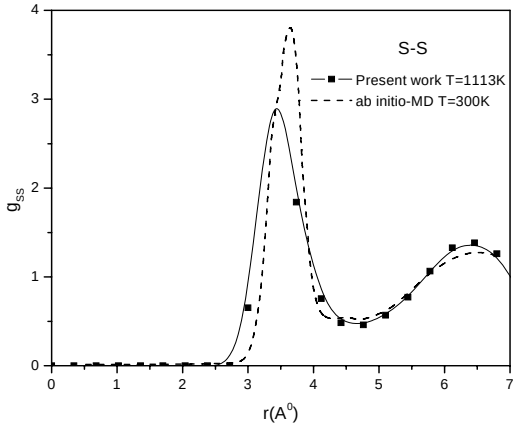

Fig. 5. Partial pair distribution functions of liquid S-S, in GeS_2

It is seen in Figs. 3-5 that The VMHNC theoretical results agree very well with the MD values. The underestimation of the heights of the main g(r) peaks appears to be discrepancies . The origin of such discrepancies as exsit between VMHNC calculation and MD are due to the temperature dependence of partial distribution functions. In Fig. 3, the first peak formed in the low temperature has lost by increasing temperature.

4. Conclusions

The equilibrium and structural properties of molten Ge_nS_m in their ground state have been studied in detail using the interionic force model. Thus, we can conclude that it is the first time that the molecular structure is shown for Ge_nS_m systems using the interionic force model. The liquid structure of GeS_2 can be obtained from the interionic force model derived potentials that take into account the effects of the effective valence and the induced polarization. We expect that our results of molecular structure, combined with the results on liquid structure should give a useful first estimate of an ionic model for germanium sulphide. We have found general agreement with the proposals and the quantative results of Mitsa and Drabold [4,5]. At a given value of the ionic radius the main factors governing the relative stability of different local configurations are the metal- sulphur Coulomb attractions and screening by counterions.

Finally, we have propsed a model for the ionic interactions in the germanium sulfur microclusters using the interonic force model.The main focus has been on the effective valence, the ionic radius and the electric and overlap polarizability of sulfur atoms. We have displayed some simple and reasonable trends of sulfur ion parameters which will be usefully extended to whole series of chalcogenide elements. It is hoped that the results should be useful in computer simulation studies of these compounds in the molten state.

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References

[1] M. A. Popescu, Physics and Applications of Disordered Materials, INOE Publishing House, Bukresh (2002).
[2] P. Armand, A. Ibanez, E. Philippot, J. of Solid State Chem. **104,** 308 (1993).
[3] K. Starbova, V. Mankov, J. Dikova, N. Starbov, Vacuum **53,** 441 (1999).
[4] S. Blaineau, P. Jund, D. A. Drabold, Phys. Rev. B **67**, 094204 (2003).
[5] R. Holomb, P. Johansson, V. Mitsa, I. Rosola, Phil. Mag. **85,** 2947 (2005).
[6] N. Mateleshko, V. Mitsa, R. Holomb, Physica B **349,** 30 (2004).
[7] X. Zhao, H. Higuchi, D. A. Drabold, Phys. Chem. Glasses **39,** 98 (1998).
[8] S. Blaineau, P. Jund, Phys. Rev. B. **69,** 064201 (2004)
[9] R. Holomb, V. Mitsa, P. Johansson, J. Optoelectron. Adv. Mater. **7,** 1881 (2005).
[10] I. Fejes, F. Billes, International J. Quantum Chem., **85,** 85 (2001).
[11] K. Jackson, A. Briley, S. Gross-man, D. V. Porezag, M. R. Pederson, Phys. Rev. B **60,** R14985 (1999).
[12] M. J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, Gaussian, Inc., Pittsburg PA, (2003).
[13] A. A Demkov, J. Ortega, O. F. Sankey, M. Grum-bach, Phys. Rev. B **52,** 1618 (1995).
[14] Z. Akdeniz, G. Pastore, M.P. Tosi Phys. Chem. Liq. **32** 191 (1996).
[15] Z. Akdeniz, M. P.Tosi, Z. Naturforschung **54a,** 180 (1999).
[16] Z. Akdeniz, Z. Çiçek, M.P. Tosi, Chem. Phys.Lett. **308**, 479 (1999).
[17] Z. Akdeniz, M. Çaliskan, Z. Çiçek,, M.P.Tosi, Z. Naturforsch. **55a,** 575 (2000).
[18] S. S. Dalgic, C. Canan, M. Caliskan, J. Optoelectron. Adv. Mater., **9,** 1719 (2007).
[19] S. S. Dalgic and M. Caliskan, 899 AIP Conference Proceedings of Sixth International Conference of Balkan Physical Union, p. 559 (2007).
[20] W. R. Busing, Trans. Amer. Crystallor. Ass. **6**, 57 (1970).
[21] H. Tatlıpınar, Z. Akdeniz, G. Pastore, M. P. Tosi, J. Phys. Condens. Matter **4**, 8933 (1992)
[22] C. R. A. Catlow, K. M. Diller, M. J. Norgett, J. Phys. C **10,** 1395 (1977).
[23] L. E. Gonzalez, A. Meyer, M. P. Iniguez, D. J. Gonzalez, M. Silbert, Phys. Rev. E**47**, 4120 (1993).
[24] L. E. Gonzalez, D. J. Gonzalez, S. Dalgic, M. Silbert, Z. Phys. **B103**, 13 (1997).
[25] S.S. Dalgic, S. Dalgic, U. Domekeli, J. Optoelectron. Adv. Mater. **5** 1263 (2003).
[26] S. Senturk Dalgıc, S. Sengul, J. Optoelectron. Adv. Mater. **9** (6)**,** 1699 (2007).
[27] D. C. Ghosh, K. Gupta, J. Theoretical and Comp. Chem. **5**, 895 (2006).
[28] V. R. Devi, M. B. Madhavi, E. L.Srihari, K. N. Shrivastava, P. Boolchand, J. Non-Crystalline Solids **351**, 489 (2005).
[29] I. Petri, P.S. Salmon, J. Non-Cryst. Solids. **293,** 169 (2001).

*Corresponding author: dserap@yahoo.com