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Equilibrium structure of germanium selenide Ge_nSe_m clusters

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A refined model for the interionic interactions in Ge_nSe_m clusters by an analysis of data on their molecular structures has been studied. The adopted potential energy function is based on the interionic force model proposed by Akdeniz and Tosi. The microscopic model used for Ge_nSe_m clusters incorporates the Born Model of cohesion and shell model for vibrational motions, bond length and crystal defects. Busing overlap repulsive energy form have been used with electron shell deformability described through the effective valences, the electric and overlap polarizabilities of the ions. The equilibrium molecular structures have also been predicted by the molecular dynamics calculations based on proposed model. 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 GeSe is obtained by Variational Hypernetted Chain (VMHNC) approximation and molecular dynamics (MD) simulation using the effective potential derived from the interionic force model within the polarizable ion potential.

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1. Introduction

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, a refined model of polymeric structures which can be studied on the computations of large clusters containing chalcogenide glasses. Among the chalcogenide glassy systems, Ge-Se compounds are most extensively studied for many years through experimental measurements like neutron diffraction experiments, [2-5].

In the last decade, the GeSe compounds have attracted the interest of many workers because of high glass-forming ability of materials, e.g. most experimental, as well as theoretical, studies dealt with $GeSe_2$, for which the glass formation is easiest [6, 7]. The GeSe system was the first in which formation of an intermediate phase was demonstrated experimentally by Boolchand *et al* [8] and further developed theoretically by Thorpe *et al* [9]. Upon melting, GeSe remains semiconductor, which distinguishes it from all III-V and some II-VI semiconductor compounds. Ge and Se have close atomic numbers and sizes and for natural isotropic abundances their coherent neutron scattering lenghts are similar It is not therefore possible to resolve the local coordination environments of Ge and Se by using conventional neutron or x-ray diffraction methods to measure total structure factors. In recent study, van Roon et. al. [10] performed Generalized-Gradient-Approximation ab initio molecular dynamics on Ge-Se system and analyzed the structure of l-GeSe. Raty *et al* [11] have analyzed distance correlations and dynamics of liquid GeSe, confirming the local order of the liquid to be close to that of low-temperature crystalline phase. They have also presented the evidence of Peierls distortion which is directly responsible for the semiconductor behaviour of the melt [11].]

However there are a few number studies of the equilibrium geometries of GeSe. The scope of the present work is to further describe the equilibrium structure. In this work our attention have majored on the ground state structure of GeSe and to determine the equilibrium and static structure of Ge_nSe_m clusters using the Interionic Force Model which for the static and dynamic structure and energetic of neutral and charged molecular clusters [12-17]. 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 [15].We have also obtained the equilibrium geometries of TaO_n [17], Ge_nS_m [18] and PSe_n [19] clusters.

To our knowledge, this model has not been applied to the case of Germanium Selenide clusters before. This important is issue to obtain a reliable description of interactions for Ge_nSe_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_nSe_m. We show that the evaluated model and molecular dynamic studies for Ge_nSe_m is in a reasonably good agreement with experimental data, except first diffraction peak. 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 with the (VMHNC) and molecular dynamics simulation for chalcogenide clusters. To what extent is it accurate to assume that the model parameters describing the chalcogen ions can be transferred to different alloys. For these purposes we focus on the Ge_nSe_m chalcogenides.

2. Theory

2.1 Interionic Force Model

Following the earlier studies [12-19], we use the interionic force model for germanium selenide 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 selenides. The handled function by a computer programme [12] can be given in the form of $U(\{r_{ij}\},\{p_i\})$ is

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

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 selenides and by the shell deformation energy of U_{shell}. In the above equation, the overlap repulsive potential in the form proposed by Busing can be given as [20],

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

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,

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

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

$$U_{pol}^{cl}(\{\mathbf{r}_{ij}\},\{\mathbf{p}_i\})=\sum_{i\neq j}\left[-z_i e\frac{\mathbf{p}_j\cdot\mathbf{r}_{ij}}{r_{ij}^3}+\frac{1}{2}\frac{\mathbf{p}_i\cdot\mathbf{p}_j}{r_{ij}^3}-\frac{3}{2}\frac{(\mathbf{p}_i\cdot\mathbf{r}_{ij})(\mathbf{p}_j\cdot\mathbf{r}_{ij})}{r_{ij}^5}+\frac{1}{2\alpha_c}\sum_j p_j^2\right] \tag{4}$$

and the shell deformation energy can be written as

$$U_{shell}(\{\mathbf{r}_{ij}\},\{\mathbf{p}_i\})=\frac{\alpha_s}{\alpha_c}\sum_{i_j,j}\mathbf{p}_j\cdot\hat{\mathbf{r}}_{ij}\left|\frac{d\,\Phi_{ij}(r_{ij})}{d\,r_{ij}}\right| \tag{5}$$

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

$$\mathbf{p}_c=\alpha_c\,\mathbf{E}_c(\{\mathbf{r}_{ij}\},\{\mathbf{p}_i\})+\alpha_s\sum_{i_j}\hat{\mathbf{r}}_{ic}\left|\frac{d\,\Phi_{ic}(r_{ic})}{d\,r_{ic}}\right| \tag{6}$$

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

2.1.1 Computational method

We handle the potential function given in Eq.(1) by a computer programme [12] 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.

2.1.2 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 [22-23]. 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)

$$h_{ij}(r) = c_{ij}(r) + \sum_{l=1}^{2} \rho_l h_{il}(r) * c_{lj}(r) \qquad (7)$$

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

$$c_{ij}(r) = h_{ij}(r) - \ln\left\lfloor g_{ij}(r) e^{\beta v_{ij}(r) + B_{ij}(r)} \right\rfloor \qquad (8)$$

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.* [22], 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. [22-23].

2.1.3 Molecular dynamic simulation procedure

Using the model potential molecular dynamic calculations were performed in the microcanonical ensemble (N V E) with a time step of 3 fs with DL_POLY code [24]. The initial configuration of the system containing 1728 (864 Ge and 864 Se) particles placed on a rhombic cell. This gave our model the correct stoichiometry and by construction a number density closes to the experimental one of 0.0377 A^{-3} [10]. The configuration was then melted at 3000K over approximately 2ps and then we cooled the liquid to the final temperature of 1000K. The cooling process took 2 ps. During termalization to the final temperature, we have saved the results every 20 steps. Also the long-range nature of the Coulomb interaction is taken into account by Ewald's summation and the Newtonian equations of motion are integrated using the Leapfrog Verlet method

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 GeSe. The equilibrium of Ge_nSe_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_nSe_m clusters obtained from the interionic force model. The model parameters used in our calculations reported in Table 1. Other parameters are taken from our previous studies on Ge_nS_m [18] and PSe [19]. The ionic radius of Ge, R_M is 0.98Å and its stiffness parameter ρ_M= 0.0527 Å has been determined as by fitting the bond length in germanium sulfur molecule [18]. The proportionality holds between R_M and ρ_M for the metal ions (R_M / ρ_M = 18.6), except Ge_2Se_6. For Ge_2Se_6.the hardness parameter ρ_M has been determined from a fitting of the bond length in germanium selenide molecule. For determining the potential parameters for Se, we assume that fluorine close to oxygen in periodic table so from this point of view Br close to Se. The value of ionic radius of selenium R_x is chosen to close the value of Bromide's. R_x and the stiffness parameter ρ_X of the selenides are 1.77Å, and 0.248Å, respectively [19]. The van der Waals coefficent of the selenides C_X is 6.35 ($eÅ^{5/2}$) [19]. The electrical polarizability of selenides α_X is the value of 2.46 $Å^3$ taken from Ref.[19].

In our calculations, we choose the effective valance value which gives the agreeable results with the overall charge neutrality conditions in Germanium based Selenide clusters.

Table 1. Interionic force model parameters (M=Ge and X: Se).

	Z_M	Z_X	α_X ($Å^3$)	α_S ($Å^3$/e)
GeSe	0.1064	-0.1064	2.46 [a]	0.61 [c]
$GeSe_2$	1.0600	-0.5300	2.46	0.61
$GeSe_3$	2.2680	-0.7560	2.46	0.61
$GeSe_4$	3.9960	-0.9990	2.26 [b]	0.61
Ge_2Se_4	1.7000	-0.8500	2.46	0.61
Ge_2Se_6	2.5500	-0.8500	2.46	0.61
Ge_4Se_8	2.0000	-1.0000	2.46	0.61

[a]Ref.[25], [b] present work , [c] Ref. [19].

We have also calculated bond lengths r, vibrational frequencies W and bond angles of Ge_nSe_m in equilibrium and compared by those obtained by other works [10, 26, 27, 28].

Table 2. Geometrical parameters of Ge_nSe_m. Distances are in Å and angles in degrees

	Parameters	Present work	*ab initio*		Parameters	Present work	*ab initio*
GeSe	r (Ge-Se)	2.52	$2.52^{a,b}$	$GeSe_4$	r (Ge-Se)	2.41	-
	W (cm^{-1})	25.08	-		W (cm^{-1})	407.15	-
					$\angle Se_3\text{-}Ge_1\text{-}Se_5$	113.66^0	-
$GeSe_2$	r (Ge-Se)	2.38	2.38^a	Ge_2Se_6	r (Ge_1-Se_5)	2.34	-
	W (cm^{-1})	273.88	-		r (Ge_1-Ge_2)	3.27	-
	$\angle Se_2\text{-}Ge_1\text{-}Se_3$	166.26^0			W (cm^{-1})	381.34	-
$GeSe_3$	r (Ge-Se)	2.37	2.37^c		$\angle Se_3\text{-}Ge_1\text{-}Se_5$	110.29^0	$103.42^{0\ e}$
	W (cm^{-1})	375.68	-	Ge_4Se_8	r (Ge_1-Se_7)	2.17	-
	$\angle Se_2\text{-}Ge_1\text{-}Se_3$	115.72^0	-		r (Ge_1-Ge_2)	2.95	-
Ge_2Se_4	r (Ge_1-Se_4)	2.25	-		r (Ge_2-Ge_3)	3.01	-
	r (Ge_1-Ge_2)	3.11	-		W (cm^{-1})	400	$401\text{-}399^d$
	W (cm^{-1})	491.28	-		$\angle Se_5\text{-}Ge_1\text{-}Se_7$	127.85^0	-
	$\angle Se_3\text{-}Ge_1\text{-}Se_4$	133.50^0	-				

[a][26], [b][10], [c][27], [d][28] [e][29].

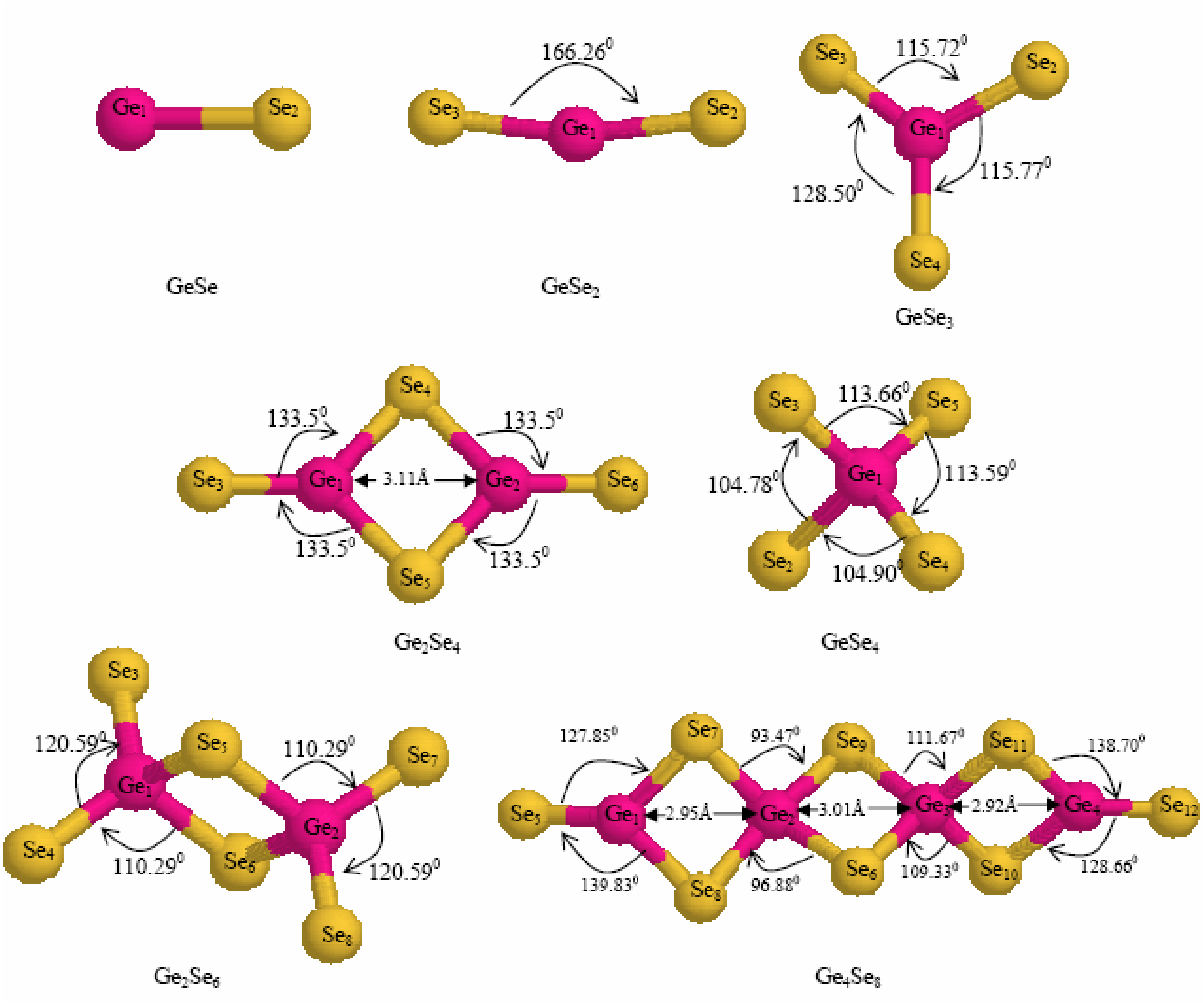

Fig 1. The structural geometries of Ge_nSe_m clusters obtained by the interionic force model.

Firstly, we now present the results for the molecular structure of Ge_nSe_m obtained from the interionic force model in Fig.1.

It appears in Fig. 1 that the calculated bond lengths of Ge-Se and Ge-Ge are excellent agreement with ab initio data [10, 26, 27]. We determine these quantities for $GeSe_3$ (Monomeric of Ge_2Se_6), the bond length of Ge-Se (2.37 Å) as calculated by ab initio [27].

The bond length values of Ge-Se in GeSe, $GeSe_2$, $GeSe_3$ are fitted the same value taken from ab initio calculations [10, 26, 27]. We determine the quantities for $GeSe_4$ from the measured vibrational frequency value to its topmost stretching mode frequency (W=407.15 cm^{-1}) in our calculations. Ge_2Se_4 is the dimeric of $GeSe_2$ and the bond length values of Ge-Se, Ge-Ge in Ge_2Se_4 are 2.25 Å, 3.11 Å respectively.

For Ge_4Se_8 (Dimeric of Ge_2Se_4) there are no ab initio calculations in literature yet to compare with our results. The vibrational frequency value of Ge_4Se_8 is fitted the same value taken from quantum chemical methods calculation of Fejes [28].

3. 2. Interatomic interactions and liquid structure

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

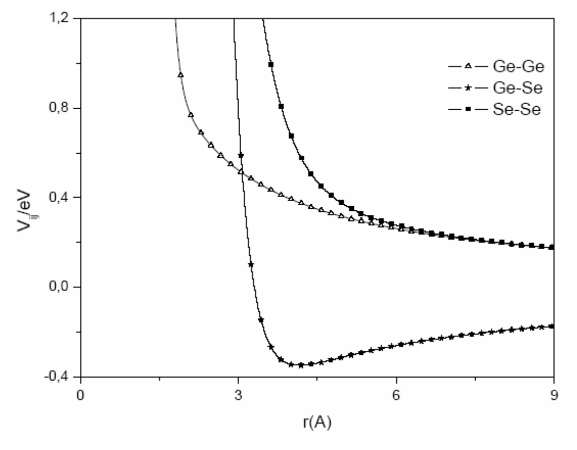

Fig 2. Effective pair potentials for GeSe at T = 1000K,

In Fig. 2 that the depth of the primary potential well for different species V_{GeSe} 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-Se.

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 and MD partial pair distribution functions of liquid GeSe are illustrated by comparing with experimental results of Petry and Salmon [7] in Figs 3-5 . The calculations are carried out at the thermodynamic state for the number density of GeSe ρ = 0.0362 A^{-3} at T=1000K.

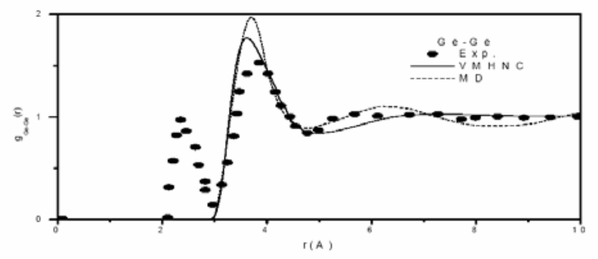

Fig 3. Partial pair distribution functions of liquid Ge-Ge, in GeSe

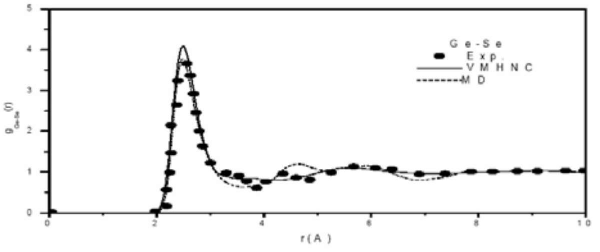

Fig 4. Partial pair distribution functions of liquid Ge-Se, in GeSe.

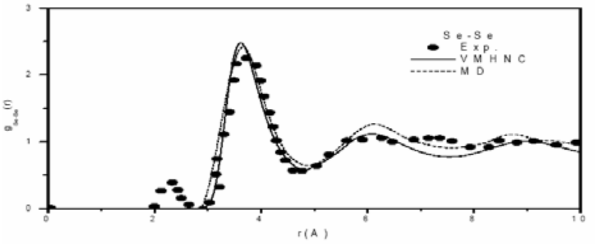

Fig. 5. Partial pair distribution functions of liquid Se-Se, in GeSe

It is seen in Figs. 3-5 that The VMHNC theoretical results agree well with the experimental values and observed that therotical and simulated results of g(r) show same behaviour. The oscillations of the g(r) appears to be discrepancies. The origin of such discrepancies as exist between VMHNC calculation and MD are due to the temperature dependence of partial distribution functions. In our result the main peaks are higher than the experimental values. This might be the sign of homocoordination tendency. Also it is seen in figs 3-5 the minima of the VMHNC results are much agreeable than the MD results. However long-range interactions are different except Ge-Se interaction

4. Conclusions

The equilibrium and structural properties of molten Ge_nSe_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_nSe_m systems using the interionic force model. The liquid structure of GeSe 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 selenide. We have found general agreement with the proposals and the quantative structural results of Petry and Salmon [7] . At a given value of the ionic radius the main factors governing the relative stability of different local configurations are the metal-selenide Coulomb attractions and screening by counterions.

Finally, we have propsed a model for the ionic interactions in the germanium selenide 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 selenide atoms. We have displayed some simple and reasonable trends of selenide 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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