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THE MODELLING OF THE STRUCTURE OF LIQUID AND AMORPHOUS SELENIUM USING THE MONTE-CARLO METHOD

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The paper describes a model for the structure of amorphous and liquid selenium. The model calculations give a radial distribution function (RDF) which is compared with the experimental RDF determined by X-ray and neutron measurements. The assumed initial structures, deformed by the Monte-Carlo calculations, were: monoclinic structures of α-Se and β-Se composed of 52 eight atom rings and a model of trigonal selenium composed of 49 nineteen atom chains. The potential of interatomic interactions was calculated taking into account pair intramolecular interactions in rings or chains and pair intermolecular interactions between atoms from neighbour rings or chains. Interatomic interactions were described by the sum of two Lennard-Jones potentials and Morse's potential. The models were tested for the temperatures: $T = 293$ K (amorphous Se) and for $T = 523$ K and 623 K (liquid Se). Energetic equilibrium was achieved after calculating at least 166 thousand atomic configurations, while RDF was calculated on the basis of at least 124 thousand configurations. Better agreement between the calculated and experimental RDF was achieved by starting from the models of α-Se and β-Se — which suggests the existence of the Se-8 phase in amorphous and liquid selenium.

1. *Introduction*

The structure of liquid and amorphous selenium is not quite clearly explained although it was a subject of many investigations in which X-ray measurements [5, 8, 13, 17, 18, 19] and neutron diffraction [4, 5, 13, 15] most often were used. It is difficult to distinguish the structural forms of crystalline Se which exist (in deformed form) in liquid and amorphous selenium from the shape of the experimental radial distribution functions (RDF). These difficulties come from the fact that eight atom rings and long chains have two nearest neighbours and two further neighbours at almost the same distances [1, 2, 3, 10, 20] and, in addition, both these forms give quite the same first peaks of RDF. The analysis of RDF for the greater distances is difficult because different configurations of atoms have the same

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values of functions and because the experimental errors are in diffraction data. The aim of this work was to construct, using the Monte-Carlo method, a model for the structure of liquid and amorphous selenium which could make possible a discussion of the experimental RDF achieved from neutron measurements for liquid selenium at the temperatures $T = 523$ K, 623 K [13] and from X-ray diffraction measurements for amorphous Se at the temperature 293 K [13].

The algorithm of Monte-Carlo method used contained the following parts:

(a) The calculation of initially assumed model structure (of trigonal Se or monoclinic α-Se and β-Se).

(b) The disordering of initially assumed structure by the Monte-Carlo method (Metropolis' algorithm) [12], until reaching the state of energy equilibrium.

(c) The RDF calculation for the state of energy equilibrium was performed on the number of configurations, suitable to obtain results of modelling provided confidence level equal 0.955.

These interatomic potential parameters were taken as optimal for which the minimum of the function $\sum_{r_i}(\mathrm{RDF}_{\mathrm{exp}}(r_i)-\mathrm{RDF}_{\mathrm{theor}}(r_i))^2$ was found for $2.0\ \text{Å} \leqslant r_i \leqslant 6.5\ \text{Å}$, in steps of $r = 0.05$ Å.

The interpretation of different shapes of the RDF for liquid and amorphous Se determined by various authors are often in contradiction. Richter [18] firmly excludes the existence of Se-8 rings in amorphous phase, suggesting the existence of chains and showing the possibility of the occurrence of three forms of amorphous selenium depending on the technique of sample preparation.

Long and coworkers [9], Malaurent and Dixmier [11] applied the model of long chains to the analysis of amorphous Se structure, but they did not achieve any good agreement of the theoretical and experimental RDF. The method of molecular dynamics was applied for simulations of the Se-8 molecule in [14]. The results show the existence of the ring-phase in amorphous selenium. Satow and coworkers [19], comparing the RDF determined from X-ray diffraction and from the microcrystalline model, suggest that the contribution of the phase of the deformed Se-8 molecules in amorphous Se is 75%–85%. The analytical solution of the density distribution for a model of the system of atoms conserving short range order (assuming a gaussian function for the mass distribution) was given and applied to amorphous selenium by Unger [21]. He achieved much better agreement with the experimental RDF for models of the deformed monoclinic α-Se and β-Se than for the model of deformed trigonal selenium. Averbach and coworkers [8, 16] applied the Monte-Carlo calculations taking into account only these changes of atom positions which make the theoretical RDF closest to the measurement. In effect they elaborated a geometric model of the structure of amorphous selenium for which the RDF was in good agreemnet with the experimental diffraction data. Based on these calculations they suggest that amorphous Se consists of 60% deformed rings and 40% deformed chains [16].

In the paper [6] the Metropolis algorithm of the Monte-Carlo method [12] was completed with the condition of accepting only such changes of atomic positions which make the theoretical and experimental RDF closer [16]. That allowed the achievement of good agreement with the experiment for the three initial maxima of RDF for the deformed ring model.

It is worth noticing that — in contrast to Averbach et al. [8, 16] and Unger [21] — the calculations in this work are not limited only to the pure geometrical treatment of the mutual arrangement of atoms in the model, but in calculations the potentials of interatomic interactions were also included similarly to [6, 9, 14]. The calculations were performed according to the Metropilis' algorithm of the Monte-Carlo method [12].

2. *Models of structure of liquid and amorphous selenium*

The RDF was calculated for the models of initial structures [7] deformed with the Monte-Carlo method [12, 22, 23]:

(a) model of α-Se structure composed of 52 eight atom rings,
(b) model of β-Se structure composed of 52 eight atom rings,
(c) model of trigonal Se structure composed of 49 nineteen atom chains.

The lattice parameters of the above mentioned models were taken from the literature [1, 2, 3, 10, 20].

In the models of α-Se and β-Se composed of 8 elementary cells completed with Se-8 molecules on the side walls of the model, no boundary conditions were introduced. In the model of trigonal selenium which is a cuboid with a rhomb in the base, the boundary conditions were determined by an outer layer of chains whose atoms did not change their positions during the calculations.

After performing many tests, the interactions between atoms in models were assumed in the form of the pair potentials:

(a) the interaction between two nearest neighbours from a chain or a ring connected with the covalent bonding described by the Lennard-Jones potential:

$$V(r) = E_{\mathrm{LJ}}\left[\left(\frac{r_0}{r}\right)^{12} - 2\cdot\left(\frac{r_0}{r}\right)^{6}\right], \tag{2.1}$$

where E_{LJ} is the dissociation energy of the bonding; r_0 — the potential parameter,

(b) the interaction between two second neighbours from a ring or a chain connected with the covalent bonding, described by the Morse's potential:

$$V(r) = E_{\mathrm{M}}[\exp(-2a(r-r_r)) - 2\cdot\exp(-a(r-r_r))], \tag{2.2}$$

where E_{M} is the dissociation energy of the bonding; a, r_r — the potential parameters,

(c) the interaction between neighbours from different rings or chains connected with the Van der Waals interaction described by the Lennard-Jones potential with E_{LJM} and r_{OM} as parameters.

In models with the initial structures α-Se and β-Se the intermolecular interactions were calculated for the atoms from neighbour rings when the distance between atoms was less than 6 Å. In the model with trigonal Se as the initial structure the intermolecular interactions were calculated for five neighbours from each of the six nearest chains. The calculation of the average potential energy during the sampling of the positions of atoms allows the estimation of whether the model reaches the state of thermodynamic equilibrium and whether it is possible to start the calculation of the RDF. The thermodynamic equilibrium of the system was reached for the initial models α-Se and β-Se after calculating 166400 configurations while for the model of trigonal selenium after the generation of 216000 configurations. The average potential energy for one atom of the model in the state of thermodynamic equilibrium is a bit less for structures obtained from initial α-Se and β-Se models than for the structure based on trigonal Se.

This is due to not including all of the intermolecular interactions for Se-8 molecules situated on the outer walls of the model.

The RDF was calculated on the basis of:

(a) 124800 configurations from eight atoms letting the Se-8 molecule be situated in the centre of the model — for initial models α-Se and β-Se

(b) 162000 configurations from 45 atoms situated in the centre of the model for the trigonal Se as the initial structure.

3. *Discussion of the results and conclusions*

The final result of a computer simulation of liquid and amorphous Se structure was the determination of the optimal parameters of interatomic potentials for the investigated models. They are shown in Table I. The comparison of the modelled and the experimental radial distribution function is shown in figures 1–3. Fig. 1 represents the modelling results for amorphous Se ($T = 293$ K). Fig. 2 and Fig. 3 represent the modelling results for liquid Se ($T = 523$ K and $T = 623$ K). The structure of amorphous Se ($T = 293$ K) is quite well simulated by the model with β-Se as an initial structure (Fig. 1b). It reconstructs the first ($r = 2.35$ Å) and the second ($r = 3.70$ Å) maximum of RDF and shows qualitative agreement in the region of three small maxima ($r = 4.4$ 4.75, 5.15 Å). The obtained maximum for $r = 5.4$ Å comes from a deformed ring and is a bit shifted from the experimental maximum. The model with α-Se (Fig. 1a) as the initial structure gave somewhat worse results.

TABLE I

Optimal parameters of the interatomic potentials for models of amorphous and liquid Se structure obtained from the crystallographic Se structure deformed by the Monte-Carlo method

T[K]	Intramolecular potential					Intermolecular potential	
	first neighbour		second neighbour			E_{LJM}[eV]	r_{OM}[Å]
	E_{LJ}[eV]	r_0[Å]	E_M[eV]	r_r[Å]	a[Å^{-1}]		
293	0.195	2.32	0.075	3.7	3.3	0.01	3.7
523	0.190	2.32	0.035	3.7	3.3	0.01	3.7
623	0.190	2.32	0.035	3.7	3.3	0.01	3.7

For liquid Se ($T = 523$ K), the model of β-Se (Fig. 2b) as the initial structure produced three first maxima of RDF ($r = 2.35$, 3.70, 4.65 Å) and also qualitatively the fourth maximum ($r = 5.65$ Å). The model of deformed α-Se (Fig. 2a) did not reproduce the third maximum of RDF and gave the shifted maximum overlapped with the fourth one.

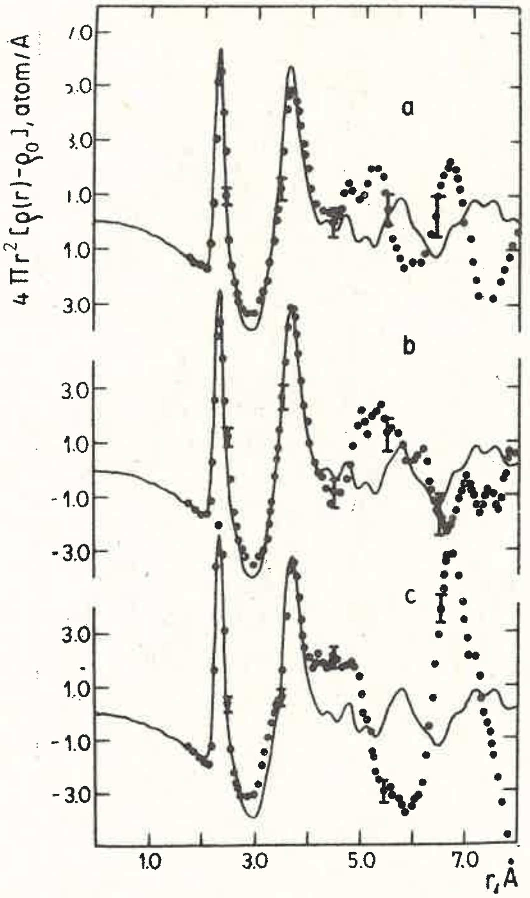

Fig. 1. The comparison of the modelled and experimental RDF for amorphous Se ($T = 293$ K) for different initial models: (a) α-Se, (b) β-Se, (c) trigonal Se. The potential parameters as in Table I

At the temperature $T = 623$ K the deformed α-Se (Fig. 3a) allowed the obtaining of the results reproducing the first and the second maximum ($r = 2.35$, 3.70 Å) and qualitatively the maxima of $r = 4.55$, 5.45, 7.55 Å). The RDF calculated for the deformed β-Se model (Fig. 3b) shows partial overlapping of the third and the fourth maximum.

The model of deformed trigonal Se (Fig. 1c, 2c, 3c) does not show good agreement with experiment in the region $4\ \text{Å} \leqslant 5\ \text{Å}$, and also gives an additional maximum ($r = 6.7$ Å at $T = 293$ K, 523 K or $r = 7.0$ Å at $T = 623$ K).

The presented calculations suggest the domination of the deformed ring phase in amorphous and liquid Se which confirmes the results of Averbach [8, 16], Unger [21], Satow [19]. The results of computer simulations show better agreement of the modelled and experimental RDF for models composed of deformed rings but the quality of the results does not allow the exclusion of the presence of chains absolutely. The folding of RDFs for the models of deformed rings Se-8 and deformed trigonal Se (Fig. 4) leads to an interesting result. The additional maximum from deformed trigonal Se does not appear distinctly if the contribution of Se-19 chains does not exceed 25% (Fig. 4a). This allows one to formulate a careful conclusion that the maximal content of chains in the amorphous phase should not exceed 25% — what is confirmed by Satow and coworkers [19].

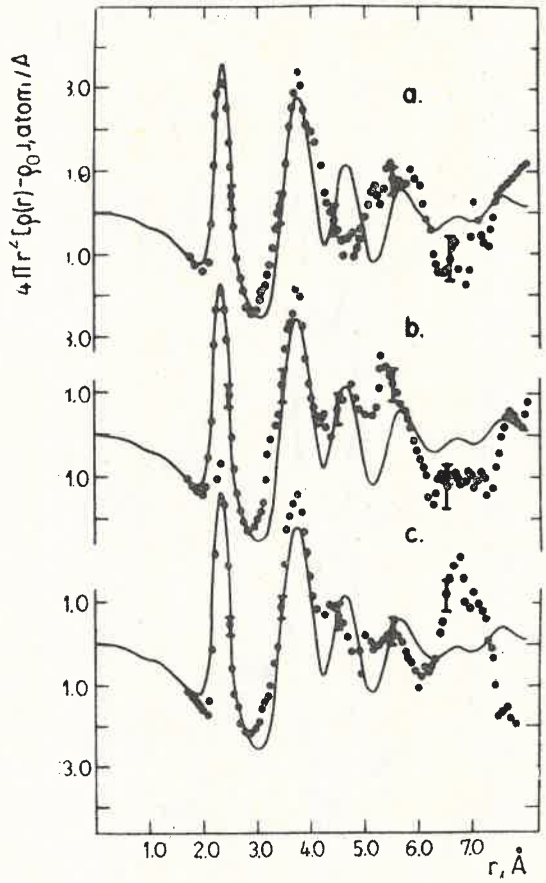

Fig. 2. The comparison of the modelled and experimental RDF for liquid Se ($T = 523$ K) for different initial models: (a) α-Se, (b) β-Se, (c) trigonal Se. The parameters of interatomic potentials are shown in Table I

The error of the modelled results is indicated in all figures, assuming the confidence level as equal to 0.955. The calculations from modellings performed by the Monte-Carlo method suggest that a more precise determination of the shape of the pair interatomic potentials does not lead to any significant improvement of the results, but requires very long work by a computer.

Based on the literature and on the results of the calculations, the following conclusions can be drawn:

(a) The modelling of structure of amorphous and liquid selenium by the Monte-Carlo method (Metropolis algorithm) [12] allowed the achievement of a good fit of the first and the second maximum of RDF. Assuming that the deformed Se-8 molecules are the only elements of structure — qualitative agreement for the third and the fourth maximum was reached (Fig. 1b, 2b, 3a). The results of modelling do not exclude the possibility of existence of small amounts of long chains Se-n, but the maximum for $r = 6.7$ Å ($T = 293$ K., 523 K) or for $r = 7.0$ Å ($T = 623$ K) — appear only in modelling — excluding the possibility of their great percentage.

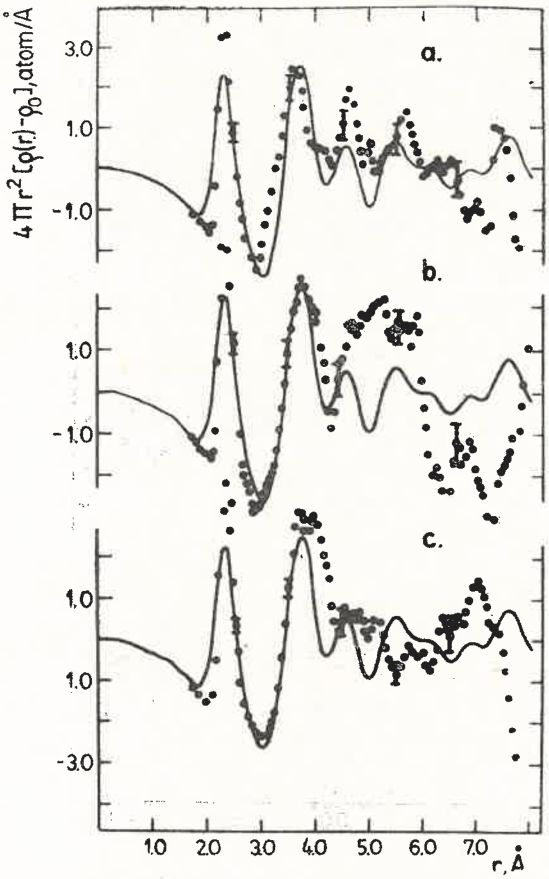

Fig. 3. The comparison of the modelled and experimental RDF for liquid Se ($T = 623$ K) for different initial models: (a) α-Se, (b) β-Se, (c) trigonal Se. The parameters of interatomic potentials are shown in in Table I

(b) The results of folding of RDFs for deformed rings and deformed chains suggest, after taking the errors into account: an experimental error (of the order of 10–15%) and estimation of RDF by the Monte-Carlo method, that their maximal contribution can be about 25%.

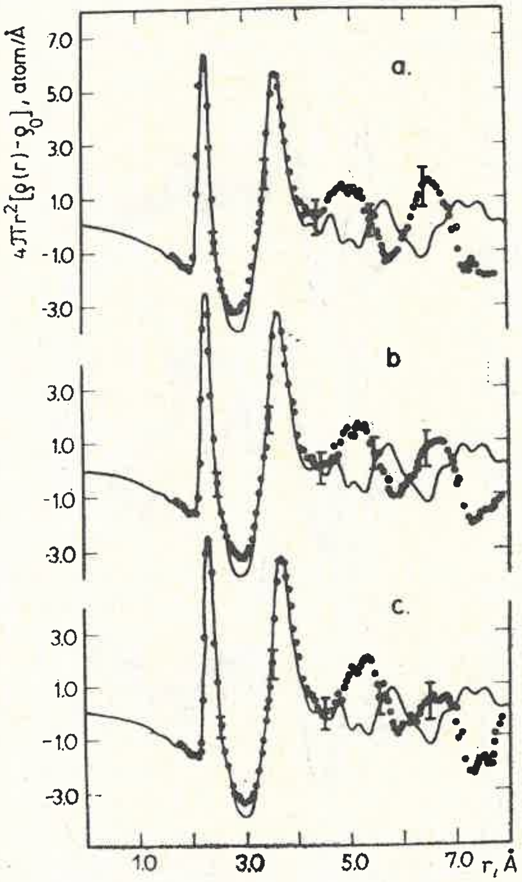

Fig. 4. The models of amorphous Se structure ($T = 293$ K) obtained from the folding of RDFs for Se-8 rings and Se-19 chains. The model includes: (a) 25% chains, (b) 15% chains, (c) 5% chains. If the contribution of chains in RDF folding exceeds 25% — the maximum for $r = 6.7$ Å appears. This maximum is not observed in the measurement. It suggests the maximal contribution of the chain phase in amorphous Se

(c) In the works of Averbach et al. [8, 10] a very good fit of the modelled and experimental RDF was achieved but only as a result of the spatial packing of atoms. But this method does not give any information on the interatomic potentials.

(d) The two basic causes result in the imperfection of the presented results of the simulation by the Monte-Carlo method:

— the structural cause — a results of the conditions assumed for models. For example: in the model of deformed trigonal Se, the Se-19 chains cannot burst in the process of modelling. The deformed rings also cannot burst and change into short chains. Also the boundary conditions can afflict the shape of RDF. The presented results of calculations show that the model of deformed rings fit the experiment better than the model of deformed chains.

— the dynamic cause — connected with the interatomic potentials. It seems very unlikely that by changing the parameters in the potential formulas assumed above one could improve the results of simulation. This is a conclusion from many test calculations of the investigated models assuming 7 potential parameters.

The obtained results of modelling suggest a replacement of the pair potential approximation by the interaction of three or more atoms.

(e) Worth noticing is a good repeatability of the experimental RDF determined in different laboratories [4, 5, 8, 13, 15, 18, 19].

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