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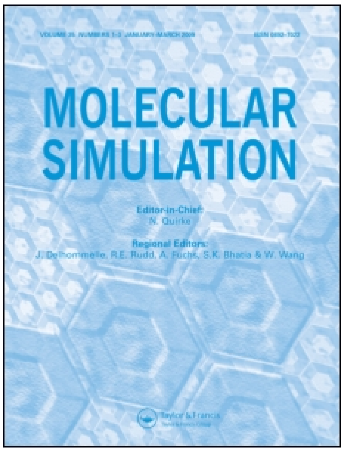

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Competing Topological and Chemical Orders in Liquid Selenium Tellurium Alloys

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COMPETING TOPOLOGICAL AND CHEMICAL ORDERS IN LIQUID SELENIUM TELLURIUM ALLOYS

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The structure of liquid selenium tellurium alloys has been investigated by a tight binding Monte Carlo simulation. The semi empirical tight binding approximation allows to deal with the directional covalent bonding characteristic of this system in a simple and efficient way. The interplay of the chemical ordering tendency and of the size effect that favors a phase separation between unlike atoms is shown to be responsible for the complex thermodynamic and structural behaviour of this system. The results are in agreement with the conclusions drawn from a previous study based on a statistical mechanical modelling of this system.

Keywords: Alloys; selenium-tellurium; tight binding Monte Carlo

I. INTRODUCTION

Liquid binary alloys of selenium and tellurium exhibit a particularly interesting thermodynamic behaviour, related to the structural changes in the melt. At normal pressure liquid selenium is a semi conductor, whereas tellurium undergoes a semiconductor to metal transition around the melting temperature. This transition in liquid tellurium is driven by the gradual increase of the number of first neighbours, from 2 in the solid or supercooled liquid state, to 3 in the liquid at high temperature (about 1000 K). The consequences of this structural change are clearly reflected in the thermodynamic properties of mixing in the liquid state: the enthalpy of mixing is weakly negative (about -2.4 kJ/mole) at temperatures just above the melting point of tellurium (450°C), and becomes positive in the tellurium rich side at higher temperatures [1]. This complex structural and thermodynamic behaviour can be understood in a simple way, if one assumes that tellurium changes from a 2-fold coordinated semi-conducting state (Te^{II}) at low temperature to a 3-fold co-ordinated metallic state (Te^{III}) at higher temperatures. A simple statistical thermodynamics model can be derived [2] with the following basic assumptions:

- as in a regular solution model, the total energy is a sum of first neighbour pair interactions, constant with concentration,
- the binary Se Te system is treated as a ternary system (Se, Te^{II} and Te^{III})
- the connectivity of each atom is explicitly taken into account to derive the Gibbs energy of mixing.

This simple model is correct as far as a thermodynamic modelling is concerned, but the real system is in fact more complex, as can be seen from Figure 1, that presents a detailed analysis of the contributions of the six first neighbours to the pair correlation function $g(r)$ of pure liquid tellurium. This quantity has been calculated [3] in a simulation box containing 1152 atoms, with the model described below and the parameters indicated in Table I. The two well defined first peaks indicate that the chain structure of

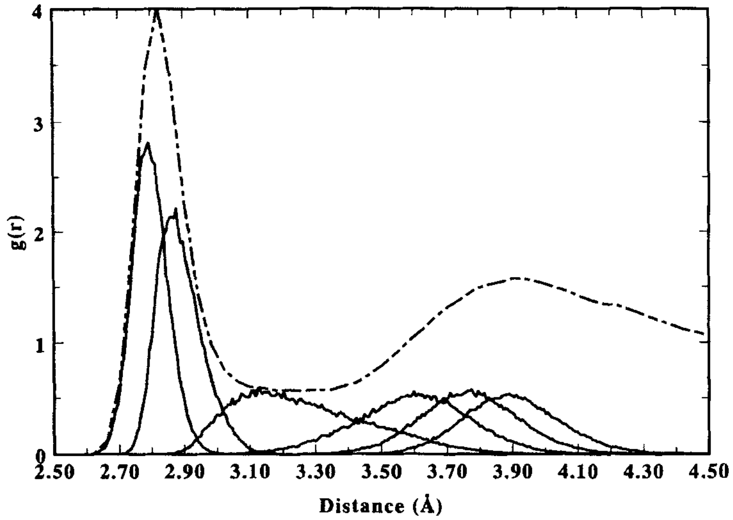

FIGURE 1 Detailed contributions of the 6 first neighbours (full curves) to the pair correlation function $g(r)$ (dash dotted curve) of liquid tellurium. The first two peaks (around 2.85 Å) correspond to the bonds within the chains. The four others are interchain bonds. One of them (widely spread around 3.15 Å) is clearly shorter than the others. The corresponding distances in the solid are 2.86 Å (within the chains) and 3.46 Å (between the chains).

TABLE I Parameters of the tight binding model used in the simulations

	Se-Se	*Se-Te*	*Te-Te*
q_λ	2.73	2.36	2.00
$\beta^{ij}_{0pp\sigma}$(eV)	4.98	4.18	3.39
p_{ij}	6.29	6.50	6.75
V_0^{ij}(eV)	9.98	9.14	11.54
α(Å)	2.40	2.78	3.16
δ(Å)	0.22	0.22	0.22

tellurium is preserved in the liquid state, and the broad third neighbour contribution (around 3.15 Å) corresponds to an interchain bond, more loosely defined as the 2 strong covalent bonds within the chain, but significantly shorter than the interchain bonds in the solid (3.46 Å).

In the simple model mentioned above, the addition of selenium to pure tellurium stabilises 2-fold co-ordinated tellurium, the species with the same co-ordination number (Te^{II} and Se) exhibit a weak ordering tendency (in agreement with the fact that the solid state phase diagram displays a continuous solid solution), and species with different co-ordination numbers (Te^{III} and Se) and (Te^{II} and Te^{III}) have a tendency to segregate. As the entropy of mixing is strong enough, the alloy remains macroscopically homogenous in the experimentally accessible temperature range, but the observed clustering tendency could give rise to inhomogeneities at the microscopic scale. Small Angle Neutron Scattering experiments have been attempted without significant results [4], probably because either no microdomains of significant size exist or, if such microdomains exist, the contrast between them is too weak.

The aim of this paper is to present a first approach to the study of the structure of this complex liquid alloy and to analyse the relative weight of the two competing effects that, according to the simple statistical thermodynamic model mentioned above, govern the behaviour of this system, namely: a weak chemical ordering tendency between selenium and tellurium, and a clustering tendency due to the topological changes in the liquid structure.

II. TIGHT BINDING MODEL AND COMPUTER SIMULATION

A. The Model

Liquid selenium has been studied by various approaches including *ab-initio* Molecular Dynamics [5, 6] and Tight Binding Monte Carlo simulation [7].

To our knowledge, no *ab-initio* molecular dynamics study of liquid tellurium has been reported. This can be related to the difficulties encountered within the LDA approximation to stabilise the crystal structure of selenium or tellurium [8, 9]. In order to study binary Se Te melts we rely on our previous work on the pure elements. The total energy is the sum of an attractive electronic term, calculated in a tight binding approximation, and an empirical repulsive term. The attractive energy (E_a) is due to the broadening of the electronic levels into a band of partially filled states. It writes:

$$E_a = \int_{-\infty}^{E_f} E\, n(E)\, dE \tag{1}$$

where $n(E)$ is the electronic density of states, and E_f the Fermi level. The electronic density of states is approximated at the fourth moment level. The p electron resonance plays the major role in the stabilisation of the structure. Contrary to our previous work on selenium [7], the s electrons are also included and, consequently, a new set of parameters has been used for selenium. In this model, the only interactions between the chains are the electronic interactions leading to a covalent bond. Other contributions to the total energy, among which the long range dispersion forces, are not included. The tight-binding hopping integrals between two atoms (i and j) are assumed to vary with the distance following:

$$\beta_\lambda^{ij} = \beta_{0\lambda}^{ij} \left(\frac{r}{r_0}\right)^{-q_\lambda^{ij}} F_a\left(\frac{r}{r_0}\right) \tag{2}$$

where the symbol λ denotes the ssσ, spσ, ppσ and ppπ interactions and $r_0 = 2.32$ Å is a distance unit. The damping term F ensures a smooth variation at the cut off distance (4.2 Å). It also enables one to treat the stronger first neighbour interactions at distances around 2.32 Å (selenium) and 2.86 Å (tellurium), and the weaker long bond interactions (around 3.45 Å) within the same formalism. It writes:

$$F\left(\frac{r}{r_0}\right) = \left(1 + \exp\left(\frac{(r/r_0) - \alpha}{\delta}\right)\right)^{-1} \tag{3}$$

An empirical repulsive term (E_r) is added to prevent the atoms from collapsing. It is given by:

$$E_r = \frac{1}{2} \sum_{\text{pairs}} V_0^{ij} \left(\frac{r}{r_0}\right)^{-p_{ij}} F_r\left(\frac{r}{r_0}\right) \tag{4}$$

This empirical repulsive term plays a key role for the stability of the structure. Therefore it seems pointless, in order to study a liquid structure, to develop the electronic density of states beyond the fourth moment level as long as the basic trends (directional bonding, ability to stabilise, at least qualitatively, the various high pressure phases) of the chemical bonding are well reproduced. The values of the parameters used are given in Table I. The hopping integrals and repulsive term for Se-Te coupling are calculated by:

$$\beta_\lambda^{\mathrm{SeTe}} = (\beta_\lambda^{\mathrm{SeTe}} \beta_\lambda^{\mathrm{TeTe}})^{1/2} \qquad q_\lambda^{\mathrm{SeTe}} = (q_\lambda^{\mathrm{SeSe}} q_\lambda^{\mathrm{TeTe}})/2$$

$$p_{\mathrm{SeTe}} = (p_{\mathrm{SeSe}} + p_{\mathrm{TeTe}})/2 \tag{5}$$

The prefactor V_0^{SeTe} is adjusted so as to obtain a correct order of magnitude for the enthalpy of mixing.

B. Computer Simulation

A constant pressure Monte Carlo algorithm would be best suited to facilitate the sampling of the chemical order in the liquid. In such a case, the fluctuations of the volume of the box could favour the exchange of particles of different sizes, which is the major problem encountered here. However, the simple model used here neglects the longer range dispersion forces. In order to compensate this missing contribution to the total energy, a non-zero constant pressure would have to be applied to maintain the simulation box at a realistic density. This is not a simple task in a binary system, and, consequently, these preliminary calculations have been performed with a canonical algorithm (fixed number of atoms, volume and temperature) on a relatively small box containing 144 atoms with an average density ($d = 0.0265$ atoms/Å^3). The changes of the atomic density with the concentration are not taken into account: they are indeed rather weak and their effect is negligible on the quantities that have been calculated here.

The Monte Carlo procedure consists of randomly alternating two kinds of moves: atomic displacement moves, and attempts to exchange the positions of two atoms of different kinds. These trial moves are accepted or rejected according to the classical Metropolis algorithm. If one considers the covalent bond lengths in pure crystalline Se(2.32 Å) or Te(2.86 Å) as indicative of their atomic sizes, it is clear that very few exchanges of 2 randomly selected Se and Te atoms will be accepted for physically reasonable temperatures, even with the relatively soft repulsive potentials used (p_{ij}

are in the range 6–7). The reason why the crystals can accommodate such large atomic size differences is that the crystalline structures, which are made by stacking helical chains, are open and not very dense. In order to lower the rejection rate of the atomic exchanges during the Monto Carlo run, a more elaborate exchange procedure has been devised. First, taking advantage of the chain structure of the liquid, the two atoms to be exchanged are chosen as neighbours along a chain. Second, their positions after the swap are chosen so as to minimise the overlap with neighbouring atoms, by treating the atoms as hard spheres. The efficiency of the process is still very low (rejection rate of the order of 99% at $T = 460°C$), but, as the MC runs are very long (at least 20000 attempted displacement steps/atom, and 2000 attempted exchanged steps/atom), the equilibrium of the system is generally reached. In addition, different starting configurations (liquid alloy at the current concentration, heated at 2500 K and gradually cooled down) have been used at each composition to check the convergence of the simulations.

III. RESULTS

Figure 2 shows the energy of mixing at $T = 460°C$, compared to the experimental enthalpies of mixing [1]. As the prefactor of the repulsive heteroatomic term V_0^{SeTe} has been adjusted for this purpose, the sign and the order of magnitude of the enthalpies of mixing are correct. The fluctuations of the energies are rather large (standard deviation $\approx 10^{-2}$) due to the small size of the box, and the energy differences between the alloy and the pure elements are small (e.g.: at 50% Te, $\langle U_{\mathrm{SeTe}} \rangle = -2.174$ eV/atom, $\langle U_{\mathrm{Se}} \rangle = -2.119$ eV/atom, $\langle U_{\mathrm{te}} \rangle = -2.196$ eV/atom, so that $\Delta H_{\mathrm{mix}} = -.016$ eV/atom). Consequently, the error bars on the enthalpies of mixing are large, and the positive value of the energy of mixing at $x_{\mathrm{Te}} = 0.15$, is to be taken with cautions. Although particularly long MC runs have been performed (50000 attempted displacements steps/atoms, 10000 attempted atomic exchanges), starting from different high temperature configurations, the very high ($\approx 99.5\%$) rejection rate of the attempted exchanges makes it possible that the system does not reach its equilibrium. A physical reason for this very slow convergence is that it is clearly more difficult to insert large tellurium atoms in a matrix of smaller selenium than the contrary. Indeed,. with the parameters used, the partial energy of mixing at low concentrations is nearly zero on the selenium rich side, and negative on the tellurium side. The calculations on the selenium rich side definitely require a better algorithm for the exchange of atoms with large size difference. The interest-

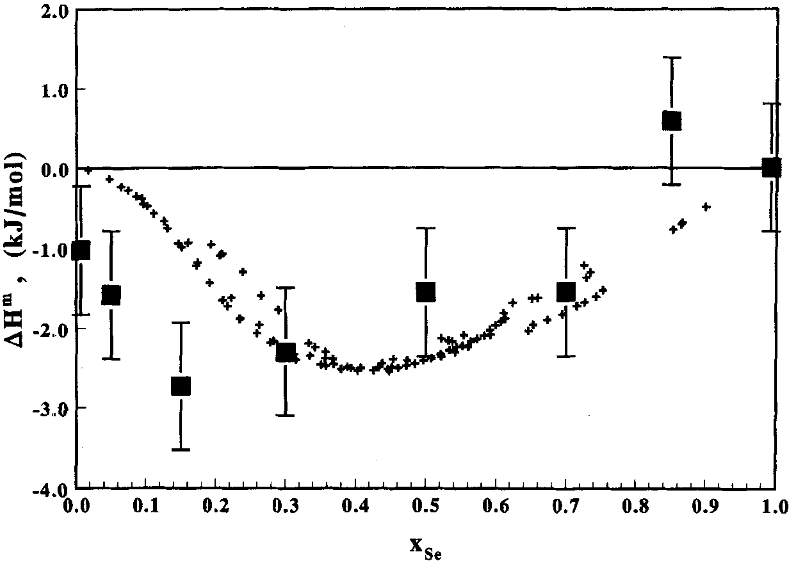

FIGURE 2 Energy of mixing at $T = 460°C$ (full squares, with error bars), compared to the experimental enthalpies of mixing (+) quoted in [1].

ing point to notice is that, in agreement with the experimental data, the minimum is clearly shifted to the tellurium rich side.

This asymmetric behaviour with respect to the concentration is also visible on the total structure factors $S(q)$ calculated from the pair correlation functions that are directly measured during the course of the run. They are plotted on Figure 3, and can be compared with the experimental structure factors obtained by Bellissent [10], plotted on Figure 4. The continuous change of the structure factors when the concentration is varied is rather well reproduced as far as the peak positions and heights are concerned. The same effect as that observed on the enthalpies of mixing is found: the transition to a 'tellurium-like' structure takes place at too high tellurium concentrations. This is due to the choice of the Se-Te crossed parameters defined by equations (5). We did not try to improve the choice of these parameters, as it requires to perform a full set of calculations, which are necessarily very long due to the poor efficiency of the exchange algorithm used.

The state of chemical order in the liquid can be analysed by considering the partial pair correlation functions and structure factors. Table II presents the partial coordination numbers ($N_{\mathrm{TeTe}}, N_{\mathrm{SeTe}}, N_{\mathrm{SeSe}}$) calculated by integrating the partial radial distribution functions from zero to their first minimum, and the average total coordination number (N_{total}) compared with the

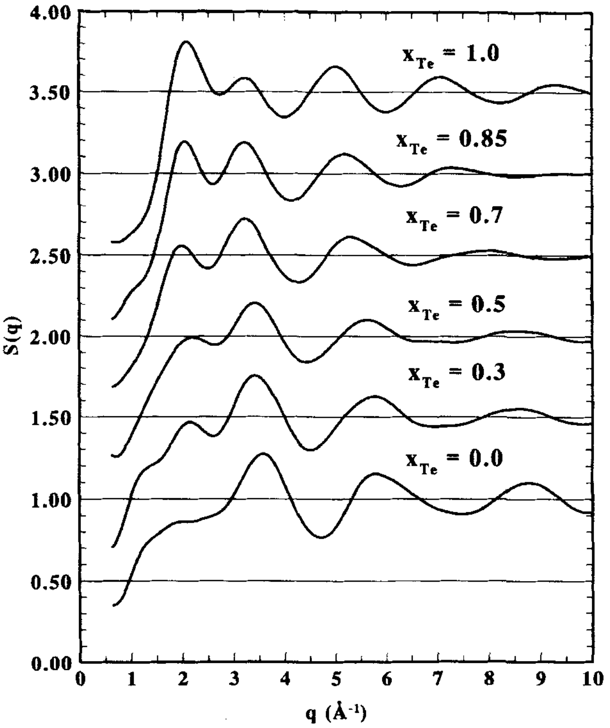

FIGURE 3 Structure factors calculated at various tellurium concentrations, at $T = 460°C$. The different curves have been shifted to preserve legibility.

experimental result from [10]. The total co-ordination number, directly calculated on the total radial distribution function, is not exactly the sum of the partial co-ordination numbers, due to the different integration limits that have been used. Considering the large errors on the experimental values, they agree fairly well: – i.e. – there is a gradual decrease of the number of first neighbours, as the tellurium concentration decreases. On the tellurium rich side, N_{SeTe} is not significantly different from the value that can be expected for a "random" alloy:

$$N_{SeTe} = 2x_{Te}(1 - x_{Te})N_{total}$$

On the contrary, for $X_{Te} \leqslant 0.5$, N_{SeTe} is lower, indicating a tendency for phase separation. This is consistent with the fact that the calculated enthalpy of mixing is found weakly positive at $X_{Te} = 0.15$.

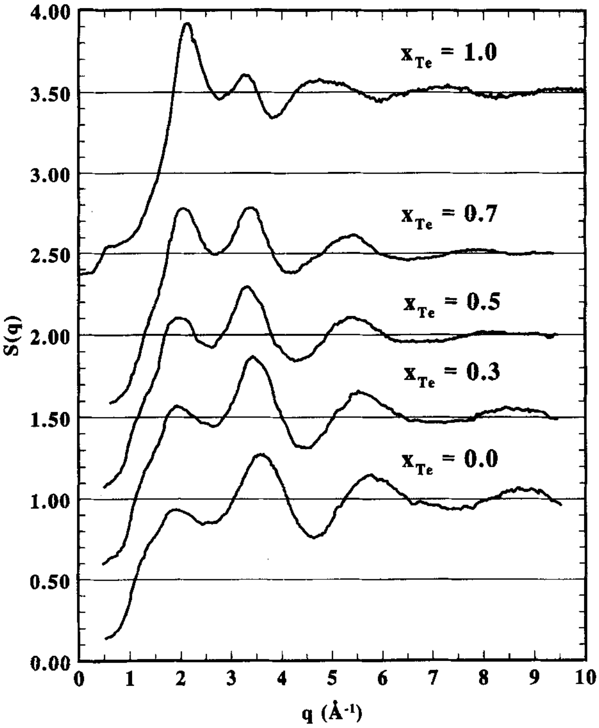

FIGURE 4 Experimental structure factors at various tellurium concentrations obtained by Bellissent [10]. The different curves have been shifted to preserve legibility.

TABLE II Partial co-ordination numbers, total co-ordination numbers, and comparison with the experimental (neutron scattering [10]) data.

X_{Te}	N_{teTe}	N_{SeTe}	N_{SeSe}	N_{total}	N_{exp}
1	–	–	–	2.40	2.6
0.95	2.27	0.27	0.00	2.40	2.6
0.85	1.65	0.70	0.08	2.38	2.5
0.70	1.08	1.04	0.27	2.38	2.2
0.50	0.78	0.61	0.81	2.20	2.1
0.30	0.20	0.84	1.12	2.21	2.1
0.15	0.11	0.41	1.70	2.10	2.1
0	–	–	–	2.10	2.1

This analysis is confirmed when considering the Bhatia Thornton partial structure factors ($S_{NN}(q), S_{Nc}(q)$ and $S_{cc}(q)$) that are defined (for a binary AB liquid) by:

$$S_{NN}(k) = c_A^2 a_{AA} + c_B^2 a_{BB}(k) + 2c_A c_B a_{AB}(k)$$

$$S_{Nc}(k) = c(c[a_{AA}(k) - a_{AB}(k)] - (1-c)[a_{BB}(k) - a_{AB}(k)])c = c_A$$

$$S_{cc}(k) = 1 + c_A c_B(a_{AA}(k) + a_{BB}(k) - 2a_{AB}(k))$$

where $a_{AA}(k), a_{AB}(k), a_{BB}(k)$ are the Fourier transforms of the partial pair correlation functions that are directly averaged during the MC run. Figure 5 presents $S_{cc}(q)$ calculated at various concentrations. Due to the small size of the simulation box (144 atoms, 16.0 × 18.4 × 18.4 Å), the calculated structure factors are not significant for q values lower than 1 Å^{-1}. Thus, the small scattering vector behaviour of $S_{cc}(q)$, indicating a clustering tendency at low tellurium concentrations, should be confirmed by simulations on a larger box.

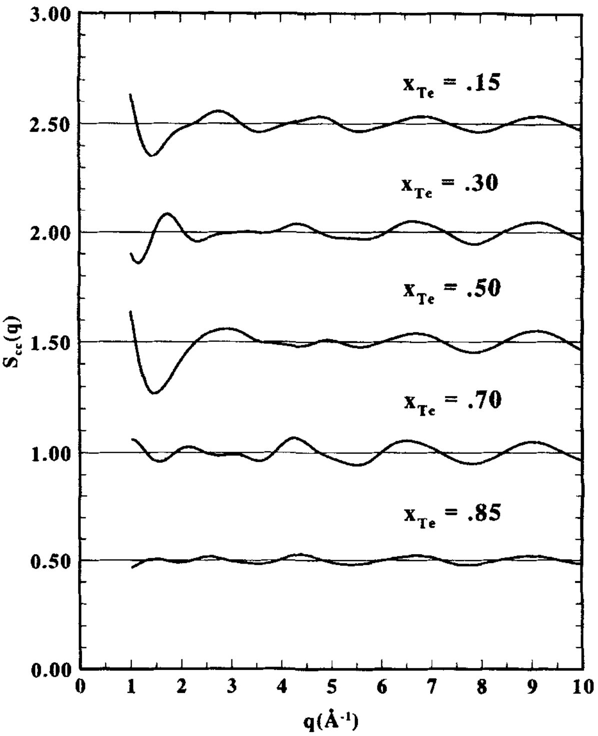

FIGURE 5 Partial Bhatia Thornton concentration-concentration structure factor ($S_{cc}(q)$ – indicative of the chemical order in the liquid) at various tellurium concentrations.

IV. CONCLUSIONS

The tight binding Monte Carlo simulations presented here yield a model liquid alloy in good agreement with the available structural and thermodynamic data, although the quantitative concentration dependence is not fully reproduced. The task of obtaining both structural and thermodynamic properties by computer simulation is clearly a difficult one, specially in such a complex case. This first approach supports the existence of structural inhomogeneities in the melt. A visual analysis of the configurations indicates that two-fold co-ordinated domains and three-fold co-ordinated domains tend to segregate, in agreement with the conclusions drawn from our previous thermodynamic analysis of this system [2]. The size of the domains is typically of the order of 5 to 15 atoms. These calculations clearly show the competing roles of the chemical ordering tendency between Se and Te, and the size effect that favours a phase separation. The effect of the temperature has not yet been investigated. One should expect rapid changes on the tellurium rich side, due to the structural changes undergone by tellurium. In order to obtain more reliable results, the efficiency of the exchange steps in Monte Carlo algorithm has to be improved. This can be achieved by using ⟨⟨softer⟩⟩ potentials – the problem is then to keep a correct succession of the higher pressures phases of the elements –, and by working out a better exchange algorithm, possibly using a biased Monte Carlo method.

References

[1] Ghosh, G., Sharma, R. C., Li, D. T. and Chang, Y. A. (1994). The selenium tellurium system, *J. Phase Equilibria*, **15**(2), 213–24.

[2] Amzil, A., Gilbert, M., Bichara, C. and Mathieu, J.-C. (1996). Thermodynamic and structural analysis of selenium – tellurium melts, *J. Phys.: Cond. Matter*, **8**, 5281–93.

[3] Bichara, C., Raty, J.-Y. and Gaspard, J.-P. (1996). Structure and bonding in liquid tellurium, *Phys. Rev. B* **53**(1), 206–11.

[4] Bellissent, R. (1991). private communication.

[5] Hohl, D. and Jones, R. (1991). First principles Molecular Dynamics simulation of liquid and amorphous selenium, *Phys. Rev. B* **42**, 3856.

[6] Kirchhoff, F., Gillan, M. J., Holender, J. M., Kresse, G. and Hafner, J. (1996). Structure and bonding in liquid selenium, *J. Non-Cryst. Solids*, **8**, 9353–7.

[7] Bichara, C., Pellegatti, A. and Gaspard, J.-P. (1994). Chain structure of liquid selenium investigated by a tight binding Monte Carlo simulation, *Phys. Rev. B* **49**, 10, 6581–6.

[8] Kresse, G., Furthmuller, J. and Hafner, J. (1994). Theory of the crystal structure of selenium and tellurium: the effect of the generalized gradient corrections to the local density approximation, *Phys. Rev. B* **50**, 13181.

[9] Kirchhoff, F., Binggeli, N., Galli, G. and Massida, S. (1994). Structural and bonding properties of solid tellurium from first-principles calculations, *Phys. Rev. B* **50, 9063.**

[10] Bellissent, R. (1982). Short range order in the disordered states of selenium tellurium mixtures, *Nuclear Instruments and Methods*, **199**, 289–94.