

Modelling study of liquid chalcogenide of $\text{Se}_{20}\text{Te}_{80}$ alloy depending on temperature

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The structural properties of the liquid chalcogenide of $\text{Se}_{20}\text{Te}_{80}$ alloy have been calculated using Reverse Monte Carlo (RMC) modelling technique at three thermodynamic states which are at 420°C, 530°C and 650°C. The quality of models has been improved using fitting procedure to neutron diffraction data. The atomic configurations and bond angle distributions of these systems have been calculated. The static structural functions of the liquid chalcogenide alloy belong to the resulting model where used plausible constraints have been compared with available experimental values. Finally, the obtained results correspond to related thermodynamic states show that the RMC modelling technique can be used to product three-dimensional atomic configurations.

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1. Introduction

The chalcogenide elements such as Se, Te and their alloys have very interesting properties in the liquid state. In the solid state, both Se and Te are semiconductors composed of helical chains in which each atom is bonded to two adjacent atoms by covalent bonds. In the liquid state, however, they exhibit very different properties from each other. Liquid Te exhibits metallic properties in contrast to liquid Se in which the helical chain structure is more or less preserved [1]. The liquid chalcogenide of Se-Te alloys has been extensively studied because of various physical properties on metal-nonmetal transition in liquid state. The two elements display close similarities. They have the same number of valence electrons, their p band is two-thirds filled with four electrons, and their stable crystalline phases are trigonal arrangements of helical chains. Their crystal structure derives from a Peierls distortion of a simple cubic structure. It is clear that the various electronic properties [2] and thermodynamic properties [3] show the anomalous temperature dependence. This temperature dependence of calculated structural functions of liquid Se-Te alloys can be explained by a gradual transition from two- fold coordination to the three-fold one.

The liquid chalcogenide of Se-Te system has properties between these two extremes and undergoes a non-metal-metal transition with increasing temperature and pressure. A generally accepted structural model is the following. Te atoms are either two-fold or three fold coordinated in a continuous random network and the latter bonding is responsible for its nearly metallic properties. The strong temperature and pressure dependence of its properties comes from an increase of three coordinated bonding. Addition of Se causes the twofold coordination

to become more stable and the transition on the metallic state shifts towards higher temperature and pressure [4].

The structure of non-crystalline $\text{Se}_x\text{Te}_{(1-x)}$ system has been of the most extensively studied in liquid, amorphous and glasses states using a variety of structure and spectroscopic methods: x-ray and neutron scattering [5-7], x-ray absorption fine-structure (XAFS) techniques [8-10], Mössbauer spectroscopy [11], vibrational spectroscopy [12-15], inelastic neutron scattering [16,17] and molecular-dynamics simulations [18-20]. These studies, which have also included variations of temperature as well as pressure and composition, indicate a progression from a nonmetallic to metallic-like as temperature or pressure increase or x decreases. This electronic transition has generally been viewed as a consequence of a simultaneous change in local structure or coordination. Evidence for this is based in part upon radial distribution function studies in semi-metallic liquid Te which suggest a nearest – neighbor coordination that is approximately three near the melting point [6,21]. This contrasts with the twofold coordination of insulating, chainlike liquid Se which suggest that a concentration in the Te-rich alloys exists for which the structure changes.

The Reverse Monte Carlo (RMC) method has been developed by McGreevy and Pusztai [22] and may be used to produce of three-dimensional model of mainly disordered and crystalline structures that agrees with the measured diffraction data. One of the most advantages of the RMC method is that it is comparatively easy to use and data sets from different experimental techniques, e.g. neutron, X-ray, EXAFS and NMR, can be fitted separately or can be combined all data simultaneously while respecting quantitatively their different experimental errors. Furthermore it is relatively easy to build extra constraints into refined model by, for example, adding coordination number constraints obtained from, e.g. NMR

methods, or requiring the model to have agreement with local atomic arrangements know from, e.g. EXAFS measurements. A disadvantage is that it is difficult to build in molecular structure to the model apart from using rather crude constraints that risk trapping the simulation in local minima. The RMC is widely used on material science [23-30].

In this paper, we report temperature dependence of the results of RMC simulations and discuss atomic configurations of the liquid chalcogenide $\text{Se}_{20}\text{Te}_{80}$ system.

2. Theory

The most widely used program which implants the algorithm is now as RMCA [31]. The detailed information and reviews on the algorithm of the standard RMC method are described in Ref. [32]. Here we will just give a summary about RMC algorithm.

1. N atoms are placed in a cubic cell with periodic boundary conditions. The cell is surrounded by images of itself. The atomic number density should be the same as experimental value. The positions of the atoms are chosen randomly.

2. The partial pair distribution functions are calculated from the initial configuration using by

$$g_{ij}^{Co}(r) = \frac{n_{ij}^{Co}(r)}{4\pi r^2 dr \rho c_i} \quad (1)$$

where superscripts C and o mean “calculate” and “old”, respectively. ρ is the atomic number density, c_i is the concentration of atoms type i , and $n_{ij}^{Co}(r)$ is the atom type j at a distance between r and $r+dr$ from a central atom of type i , averaged over all atoms as centres.

3. $g_{ij}^{Co}(r)$ transforms to reciprocal space in order to obtain the partial static structure factors

$$S_{ij}^{Co}(k) = \rho \int_0^\infty 4\pi r^2 (g_{ij}^{Co}(r) - 1) \frac{\sin kr}{kr} dr \quad (2)$$

where k shows the momentum transfer.

4. The total structure factor is calculated using by

$$S^{Co}(k) = \sum c_i c_j b_i b_j (S_{ij}^{Co}(k) - 1) \quad (3)$$

where b_i is the coherent neutron scattering length for atom type i .

5. The difference between the measured total structure factor, $S^E(k)$, and determined from the configuration one is calculated by

$$\chi_o^2 = \sum_{i=1}^k (S^{Co}(k_i) - S^E(k_i))^2 / \sigma^2(k_i) \quad (4)$$

where the sum is over the k experimental points and σ represent the experimental error.

6. One atom moves at random if any two atoms approach closer than cut-off distance, the move is rejected. One new atom is chosen and a new random move is made.

7. The new partial pair distribution functions, the new partial structure factors, the new total structure factor, and the difference are calculated by

$$\chi_n^2 = \sum_{i=1}^k (S^{Cn}(q_i) - S^E(q_i))^2 / \sigma^2(q_i). \quad (5)$$

where n means “new”.

8. If $\chi_n^2 < \chi_o^2$, the move is accepted and the new configuration becomes the old one. If $\chi_n^2 > \chi_o^2$, it is accepted with probability $\exp(-(\chi_n^2 - \chi_o^2)/2)$.

Otherwise it is rejected.

9. It returns to step 6 and process is repeat again.

This cycle repeat that χ^2 decrease upto converge an equilibrium value. Thus, the atomic configuration corresponding to equilibrium should be consistent with the experimental total structure factor within the experimental error.

3. Results and discussion

In order to investigate the possible effects of the starting configurations, the following model was constructed. First the initial configuration was generated by a random distribution of 10000 atoms including 2000 Se atoms and 8000 Te atoms in a cubic cell. The structure parameters, (temperature, number densities and size of cells) are listed in Table 1. Alloy densities are taken from Thurn and Ruska [3]. In this table It has been observed that the densities are increasing with temperature.

Table 1. The structure parameters.

T(°C)	$\rho(\text{Å}^{-3})$	Number of Atom	L(Å)
420	0.02627	10000 (2000 Se+8000 Te)	36.23681
530	0.02672	10000 (2000 Se+8000 Te)	36.02998
650	0.02688	10000 (2000 Se+8000 Te)	35.96059

Figs. 1(a), 1(b) and 1(c) show typical atomic configurations of the liquid chalcogenide of $\text{Se}_{20}\text{Te}_{80}$ obtained by simulations at 420°C, 530°C and 650°C, respectively. In these figures, many chain-like structures are closely observed as expected by diffraction

experiments. In addition, the temperature variation for the configuration is not clear.

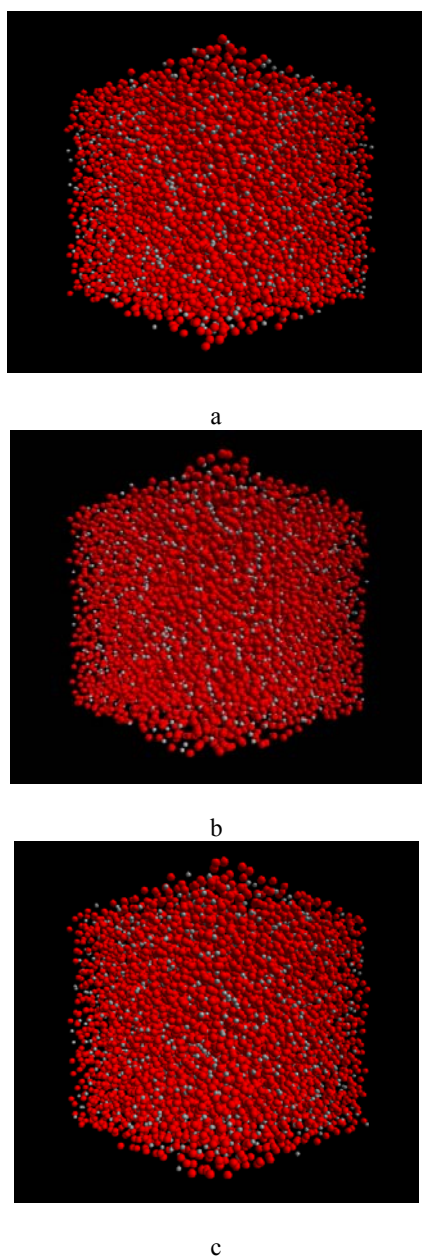


Fig. 1. Typical atomic configurations obtained by RMC simulations for the liquid chalcogenide of $\text{Se}_{20}\text{Te}_{80}$ at (a) 420°C, (b) 530°C and (c) 650°C. Se and Te atoms defined with grey and red balls respectively.

We have calculated the total structure factors based on RMC method for the liquid chalcogenide of $\text{Se}_{20}\text{Te}_{80}$ alloy at several temperatures. In Fig. 2, a comparison of our RMC fitted to total structure factors with neutron diffraction data [33] are made. For the liquid chalcogenide of $\text{Se}_{20}\text{Te}_{80}$, there is a good agreement between RMC method an experiment at 420°C, 530°C and 650°C.

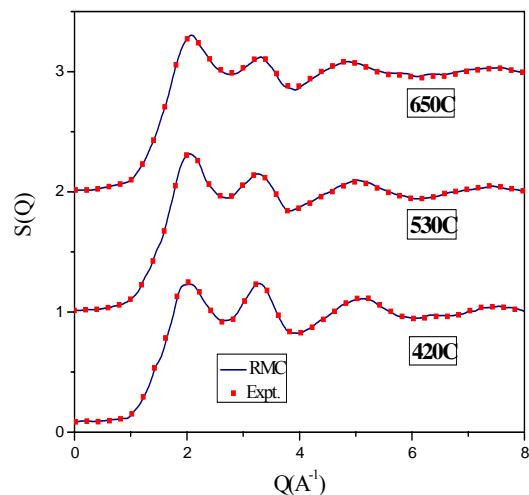


Fig. 2. Total structure factors of the liquid chalcogenide of $\text{Se}_{20}\text{Te}_{80}$ at several temperatures.

The total pair distribution functions were derived from total structure factors by usual Fourier transformation (Fig. 3). Studies of the total radial distribution functions in liquid chalcogenide of $\text{Se}_{20}\text{Te}_{80}$ have suggested that the transition from three-fold to two-fold bonding is relatively smooth [6]. This is based on variations of the area of the first total radial distribution function peak with composition.

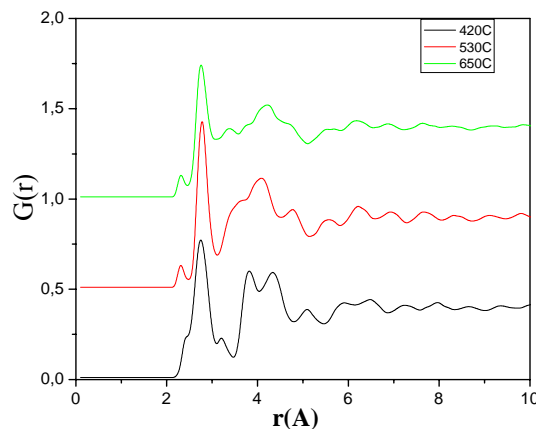


Fig. 3. Total pair distribution functions of the liquid chalcogenide of $\text{Se}_{20}\text{Te}_{80}$ at several temperatures.

In order to obtain some information about short-range order of the structure of liquid chalcogenide of $\text{Se}_{20}\text{Te}_{80}$, it is necessary to know the three partial pair distribution functions. The calculated functions belong to final configuration are presented in Fig. 4 for Se-Se, Se-Te and Te-Te pairs at several temperatures. As shown in figures the temperature variation of the main peak position of pair distribution functions is not significant in the present temperature range. The width of main peak becomes narrower with increasing temperature whereas the first coordination number is increasing. It is observed that the second peak positions shift with increasing temperature

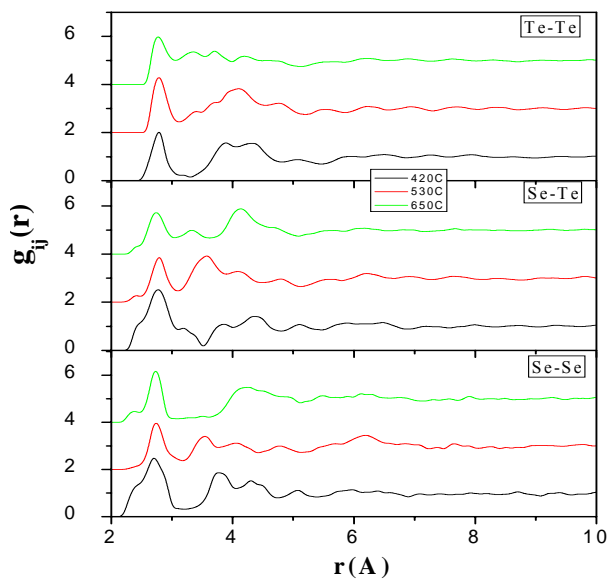


Fig. 4. Partial pair distribution functions of the liquid chalcogenide of $\text{Se}_{20}\text{Te}_{80}$ at several temperatures.

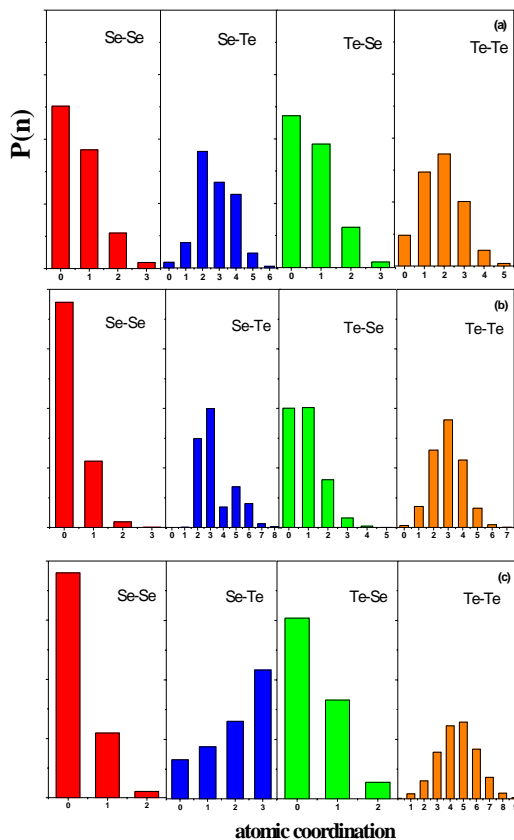


Fig. 5. The distribution of number of neighbours within the first coordination shell obtained from RMC resulting configuration at (a) 420°C, (b) 530°C and (c) 650°C. Se and Te atoms defined with grey and red balls respectively.

As shown in Fig. 5, we have calculated the distribution of the neighbors under first coordination shell for different atomic pairs in liquid chalcogenide of $\text{Se}_{20}\text{Te}_{80}$ obtained from RMC simulations at several temperatures. In each histogram, the number of coordination becomes larger at higher temperature. This change may indicate the temperature dependence of coordination number. There is an agreement between this result and the calculated partial pair distribution functions.

4. Conclusions

RMC study of liquid chalcogenide of $\text{Se}_{20}\text{Te}_{80}$ alloy has been carried out to reveal the origin of the characteristic temperature dependence of various properties related to structure order in atomic scale. Using this modeling technique, local information on $\text{Se}_{20}\text{Te}_{80}$ has easily obtained rather than hardly and costly experiments. Beside the distributions of the neighbor atom pairs under first coordination shell has been derived from refined model. Finally, the obtained results correspond to related thermodynamic states show that the RMC modelling technique can be used to product three-dimensional atomic configurations.

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