A modelling study on liquid arsenic tritelluride: reverse Monte Carlo modelling

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The Reverse Monte Carlo (RMC) technique was performed to obtain a model for Arsenic Tritelluride, As_2Te_3, which is at liquid phase, fitting to neutron diffraction total static structure factor. The understanding of structure of this kind of materials is increasingly having importance and the atomic structures need to create a realistic model whereas the model is not unique. In order to analysis of the structure we have only investigated to describe the trend in structural terms. Thus, we have shown and have analyzed the modelling results of both the partial pair distribution functions and the partial static structure factors. Also the correctness of model was determined by what we have calculated the distribution of the number within first co-ordination shell for each pair and the bond angel distributions for each triplet. During the construction of model we have used plausible constraints which are include chemical properties such as minimum and maximum bond lengths and average coordination numbers. Finally, the modelled liquid chalcogenide structure was visualized to produce a three-dimensional atomic image. The calculated results of all these properties using RMC modelling are in good agreement with both experimental data and other theoretical calculations.

1. Introduction

In the 1980s the idea of carrying out a computer refinement of atomistic three-dimensional structural models of liquids, glasses and other disordered materials was established. This idea developed in part from original work using inverse Monte Carlo methods to glasses and to disordered substitutional alloys [1,2]. During current time there are two principle methods that are in common use; The Reverse Monte Carlo (RMC) method [3], and the empirical potential structure refinement (EPSR) method [4,5].

The liquid As-based chalcogenides mixtures such as As_2Te_3 and As_2Se_3, have a three-dimensional network structure. The As and chalcogen atoms have basically three-fold and two-fold coordination, respectively. The electronic structure of these liquid mixtures is semiconducting in character near triple point [6]. They exhibit metallic properties with increasing temperature and pressure. The electrical conductivity measurements [7,8] showed that in the liquid As_2Te_3 the semiconductor-metal (SC-M) transition occurs just above the melting point.

Many theoretical and experimental measurements are reported on this As_2Te_3. Experimentally Endo *et. al.* measured the extended X-ray absorption fine structure (EXAFS) spectra [9,10] for liquid As_2Te_3 and they investigated the bond length between atoms and the coordination number for each atom as a function of temperature. On the other hand, the structure of As_2Te_3 glass has been reported to be different from that of crystal, i.e. shorter nearest-neighbour distance and a small coordination number than the respective value in the crystal [11]. Recently, Shimojo *et.al.* have studied the

atomic and electronic structures in l-As_2Te_3 by *ab-inito* molecular dynamics simulations [12]. They suggested that the local structure of this material does not change qualitatively with increasing temperature. To our knowledge there is theoretical work on the atomic structure, static structural properties, the distribution of the number within first co-ordination shell and bond angle distributions in these liquid chalcogenides all within one realistic model. The Reverse Monte Carlo (RMC) method has been developed by McGreevy and Pusztai [3] and may be used to produce of three-dimensional model of a disordered structure that agrees with the measured diffraction data within experimental error. RMC has been to analyse NDIS data for a number of systems, including superionic conductors [13], molten salts [14, 15], ionically conducting glasses [16,17] mixtures of binary molten salts [18], metallic glasses [19] and magnetic materials [20] among other examples.

An advantage of the RMC method is that it is comparatively easy to use and data sets from different techniques, for example diffraction, EXAFS, NMR, etc. can be fitted 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.

In this study, we report the results of RMC simulation and discuss the atomic configurations of liquid As$_2$Te$_3$.

2. Theory

Detailed review of RMC modelling can be consulted for the methodology and examples [21-24]. Now we will just give a briefly description on theory. RMC is a method which is used to produce three-dimensional models of disordered materials that agrees quantitatively with data sets from different techniques, for example neutron diffraction, X-ray and EXAFS, can be fitted simultaneously within their different experimental errors. The technique is similar to Metropolis Monte Carlo scheme [25] together with one difference that the atoms are moved to minimize the difference between the measured structure factor and the calculated structure factor instead of to minimize the potential energy of the system. The atoms which are placed in a box with periodic boundary conditions are randomly moved in order to minimize standard chi-square distribution,

$$\chi^2 = \sum_{i=1}^{k} \left(S^C(k_i) - S^E(k_i) \right) / \sigma^2(k_i)$$

where $S^C(k_i)$ and $S^E(k_i)$ are the calculated and the experimental structure factors respectively and $\sigma^2(k_i)$ is an estimation of experimental errors. The random moves are accepted if χ^2 is reduced and are accepted with probability $\exp(-\Delta\chi^2)$ if χ^2 is increased. All other moves are rejected. The moving of atoms are continued until χ^2 converge to an equilibrium value that it oscillates. Eventually, χ^2 will reach a stable value, and the structures obtained after additional successive moves are averaged to produce final refined structure.

In this study, we have used RMCA_v3.14 [26] as a tool for refining a model using experimental observes than the usual use of constructing a model whereas the model is not unique. It was performed step by step in order to get a realistic model for liquid As$_2$Te$_3$ at 700K fitting to neutron diffraction total static structure factor [27]. At the beginning of the simulation procedure some questions rise about configuration will be initially constructed that they need some answers: How many atoms we should use in order to make realistic system? Should initial configuration be crystalline or already relaxed structure? The answers may change depend on under investigating system. 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. RMC method is essentially a statistical mechanics method and it is automatically maximize the entropy. Actually our experience [28] and previous works [29, 30] shown that the results of RMC simulations are independent from initial configurations and number of

atoms whereas larger configurations give less noise on distribution functions. Due to these facts we chose a randomly positioned initial configuration has 20000 atoms including 8000 As atoms and 12000 chalcogen atoms in a cubic box. The box length is adjusted as 43.58A by the measured density, 0.0302 Atoms/A^3 [31]. Also, it is necessary to give the minimum closing distances between the particles for the realization of this method but it is not obvious how to determine these minimum values. Therefore we tested the minimum hard-sphere pairwise distances between 2.2A and 2.6A, and found about 2.3A, 2.4A and 2.5A for As-As, As-Te and Te-Te pairs, respectively. After adjusting initial parameters, as a first step, we run hard-sphere RMC with cut-off constraints of pairs, no diffraction data fitting, in order to eliminate the overlap positions of atom pairs. Using this step it is provided that the atoms are better distributed in the cubic box without overlap. Then fitting procedure to diffraction data was applied on first configuration. During this stage, σ was step by step changed 0.01 to 0.0001 when it begun to oscillating around an equilibrium value. Data of one diffraction experiment is not enough for adequate model construction or refining of a model. It is relatively easy to build extra constraints into the refined model by adding coordination number constraints or requiring the model to have agreement with local atomic arrangements. So, we preferred to use some other plausible constraints which include chemical properties such as coordination of atoms and average coordination numbers under first coordination shell. These constraints balance the short range order and they arrange simultaneously information about both long-range and short-range order. After a series of RMC simulations, the configuration was become ready to visualizing of three-dimensional molecular image. At the end of the refinement procedure, the intension is that the computer model is a good representation of the actual atomic structure in the liquid ally. Fig.1 represents a snapshot which shows an atomic structure of As$_2$Te$_3$ obtained by RMC modelling with 20000 atoms in supercell at 700K that it is in liquid phase.
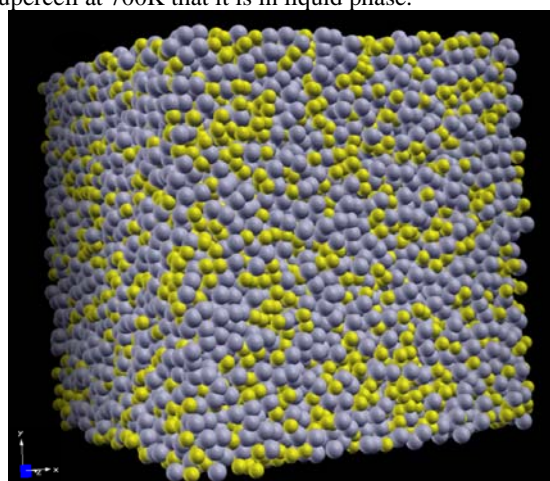

Fig. 1. Atomic structure of liquid As2Te3 obtained from RMC modelling. As and Te atoms defined with yellow and grey balls, respectively.

3. Results and discussion

The computer model is refined until the data agree sufficiently well with experimental one. From resulting configuration we have calculated the total structure factor, $S(k)$, and radial distribution function (RDF) based on RMC modelling technique for liquid As_2Te_3 alloy at 700K. RDF is equivalent to $4\pi\rho r^2 G(r)$, where ρ and $G(r)$ indicate measured density and total pair distribution function, respectively. Figs. 2(a) and 2(b) show a comparison between our RMC results and experimental data for total structure factor and RDF [27]. In Fig. 2(b), the RMC modelling based curve is in good consistency whereas height of first peak is little bit higher than experimental one. Besides, the peak positions and the intermediate range trends have been well constructed. It has been happened by applying the successive constraints.
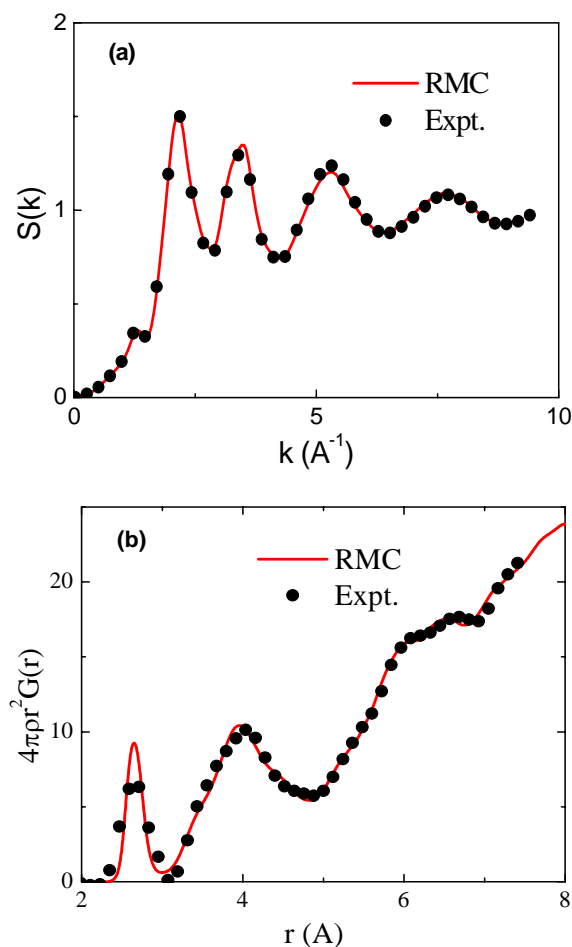
belong to final configuration are presented in Fig. 3(a) for As-As, As-Te and Te-Te pairs. Fourier transforms of $g_{ij}(r)$ yield the partial static structure factors, $S_{ij}(k)$ which are shown in Fig. 3(b) at same pairwise order. It should also be noted that neutron scattering lengths of As and Te atoms are close to each other, $b_{As}=6.58fm$, $b_{Te}=5.80fm$ [32]. Therefore, $g_{ij}(r)$s are essentially giving almost same information. Some experimentally techniques used to obtain information at level of partial pair distribution function are either preventively expensive or yield limited spatial resolution. Due to these facts, the modelling tools are increasingly having importance. Our RMC results with respect to partial pair distribution functions have sharp first peaks. The total pair distribution function is a combination of partial pair distribution functions. So, this consequence corresponds to an answer that why the calculated first peak of RDF is higher than experimental one. It is remarkable that no smoothing has been applied onto the curves obtained by post-processing calculations.
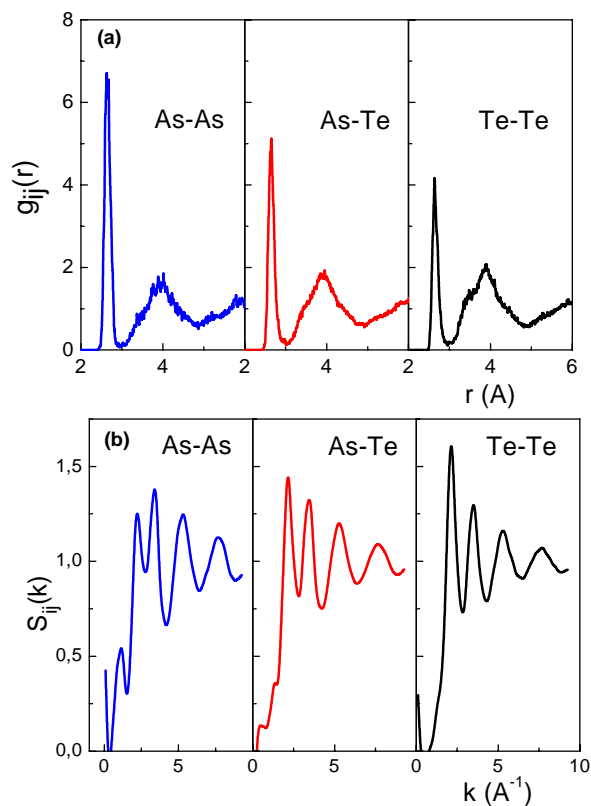

Fig. 2(a) Total structure factor and, 2(b) radial distribution function for liquid As_2Te_3.

Fig.3(a) Partial pair distribution functions and 3(b) partial static structure factors.

In order to learn deeply information on disordered system it is necessary to know the three partial pair distribution functions and partial structure factors. Both of them are calculated from the resulting computer model. The calculated partial pair distribution functions, $g_{ij}(r)$,

It is interesting to investigate the angular distribution of the bonds between first-neighbour atoms. Fig.4 shows the six partial bond angle distributions. All of the system have a first peak about 60 degree and a second peak around 90-100 degree.
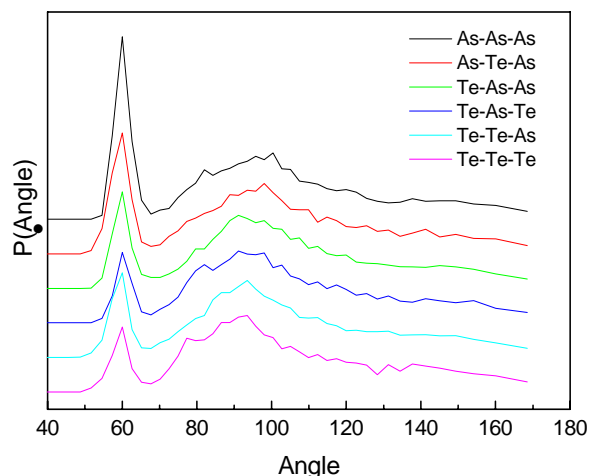
Fig. 4. Bond angle distributions obtained from RMC model configuration.

In Fig. 5, we also have calculated the distribution of the neighbours under first coordination shell for different atomic pairs in liquid As_2Te_3 obtained from RMC simulations.
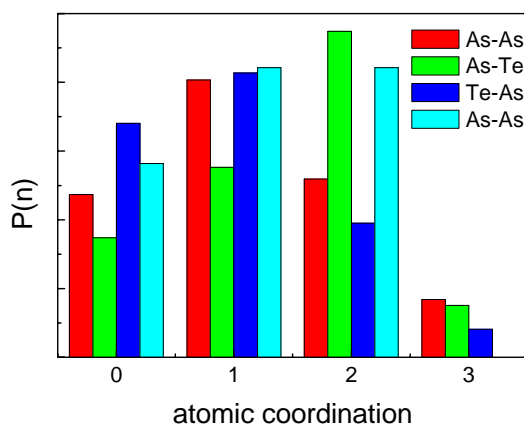

Fig. 5. The distribution of number of neighbours within the first coordination obtained from RMC model configuration.

From the pair distribution functions, number of nearest neighbours for liquid As_2Te_3 alloy was calculated. In Table, we present average coordination numbers which are compared those mentioned in Ref. [12]. Our presented results are about 15% lower than Shimojo *et. al*. results for As-As and As-Te pairs.

Table. Average coordination numbers

	As-As	As-Te	Te-Te
Present work	1.29	1.52	1.10
Ref.[12]	1.44	1.77	1.14

4. Conclusions

This study has been focused on the structural aspects of liquid As_2Te_3 alloy. The understanding of structure of this kind of materials is increasingly having importance and the atomic structures need to create a realistic model. From the RMC configurations it is possible to calculate any distribution functions without time-dependent one because of it does not work within time domain. Our simulation shows a disorder structure, not a chain-like structure which was reported. Based on our structural results, we have suggested possible explanations for some peculiar features of the microscopic properties of this liquid.

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