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2005 J. Phys.: Condens. Matter 17 S3317

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J. Phys.: Condens. Matter **17** (2005) S3317–S3324 doi:10.1088/0953-8984/17/45/017

Local structure of liquid Rb–Se mixtures: chain- and interstitial void-structure near the miscibility gap

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Received 15 September 2005
Published 28 October 2005
Online at stacks.iop.org/JPhysCM/17/S3317

Abstract

Neutron diffraction measurements, and structural modelling by reverse Monte Carlo simulation, have been performed for liquid Rb–Se mixtures in the Se-rich concentration range. In the liquid mixtures some of the Se chains are strongly bent to form ring-like Se chains with Rb atoms at the chain ends, creating a large amount of voids. The shortened Se chains link up to form a large cluster, and Rb atoms sit around it near the boundary of the miscibility gap at low temperature. The structure factor $S(Q)$ exhibits a small pre-peak at ~ 1.3 Å^{-1}. From the void analysis it has been revealed that the observed pre-peak corresponds to a pre-peak in the concentration–concentration structure factor due to the chemically ordered packing of the interstitial voids and Se chains in the structure.

1. Introduction

The phase diagram of the Rb–Se binary mixture [1] exhibits the existence of a liquid–liquid phase separation region (miscibility gap) in the concentration range between 0 and 20 at.% Rb. The upper critical solution point exists at 10 at.% Rb and 254 °C. In 1990 Hoshino and Endo [2] found that the electrical conductivity of liquid (l-) Se increases upon the addition of Rb by three or four orders of magnitude, and that the miscibility gap disappears by application of pressure of over 1060 bar. One can expect the strong effects on the short- and intermediate-range structure in alkali–chalcogen mixtures owing to the charge transfer as a consequence of the large electronegativity difference between alkali and chalcogen atoms. From the neutron diffraction (ND) measurements for l-K–Te mixtures Fortner *et al* [3] found that there appears a narrow pre-peak in the structure factor $S(Q)$ of l-$K_{50}Te_{50}$ indicative of a formation of chain-like polyanions. *Ab initio* molecular dynamics (MD) studies [4, 5] confirmed the existence of polyanionic chains of a few Te atoms within a K^+ matrix. A recent work by Kawakita *et al* [6] on l-Rb–Te mixtures has demonstrated that upon the addition of Rb the conductivity of l-Te decreases substantially, in contrast to that of l-Rb–Se mixtures, and the interaction between the

0953-8984/05/453317+08$30.00 © 2005 IOP Publishing Ltd Printed in the UK

neighbouring Te chains weakens. Since the packing density in chalcogen material is rather low, interstitial voids are an inherent feature of the structure. Recently Caprion and Schober [7], using MD simulation, investigated the origin of a shoulder in the low-Q side of the first peak of $S(Q)$ observed for liquid and amorphous Se. They proposed that the appearance of the shoulder is associated with the correlation between voids in the structure.

In the present paper we report the results of ND and reverse Monte Carlo (RMC) simulation for l-Rb–Se mixtures in the Se-rich concentration range. We also discuss how the local geometry of covalently bonded Se chains and the spatial distribution of voids are influenced by a tendency of segregation near the miscibility gap.

2. Experimental details

The samples of liquid Rb–Se mixtures were prepared as described elsewhere [6]. The elastic ND measurements for the l-$Rb_{20}Se_{80}$ mixture in a wide temperature range were carried out using the HIT-II spectrometer in KEK, Japan. The sample was sealed in a cylindrical fused silica cell [8]. Before the measurements each sample was heated up to 500 °C in order to achieve a uniform phase. Then the scattering intensity was accumulated for about 8 h so that sufficient statistical quality was achieved.

The standard RMC technique developed by McGreevy [9] is used here to produce models for the l-mixtures. A brief summary of the procedure is as follows. The number of Rb and Se atoms is 8000 in total and the size of a cell was about $60 \times 60 \times 60$ Å^3. The closest distances that two atoms were allowed to approach each other are set to be 2.0, 3.2 and 2.7 Å for Se–Se, Rb–Rb and Rb–Se atom pairs, respectively. The fittings were performed to minimize the residual error of $S(Q)$ times Q. After hundreds of accepted motions for each atom, an excellent agreement between experimental data and RMC calculation was obtained.

3. Results

Figure 1 shows the temperature variation of $S(Q)$ for the l-$Rb_{20}Se_{80}$ mixture obtained from ND measurements. The amplitude of oscillation in $S(Q)$ becomes large with decreasing temperature. There exists a small pre-peak located at about 1.3 Å^{-1}, which is a signature of intermediate-range order [10]. The $S(Q)$ for l-Se at 300 °C plotted together in this figure has a shoulder around 1.3 Å^{-1}. The evidence that the pre-peak in the l-$Rb_{20}Se_{80}$ mixture is more distinctly separated from the first peak of $S(Q)$ compared to that for l-Se suggests that the addition of Rb causes an increase in the degree of intermediate-range order. Only the pre-peak exhibits a decrease in intensity with decreasing temperature, while the intensities of all peaks in $S(Q)$ other than the pre-peak increase with decreasing temperature in the normal manner expected of the Debye–Waller (DW) factor.

RMC simulation is useful for aiding our understanding of the atomic arrangements in the liquid mixture. The curves in figure 2 show the experimental structure factor $S(Q)$ (circles) and the corresponding fit (solid line) produced from the RMC configurations for the l-$Rb_{20}Se_{80}$ mixture at 500 °C. Excellent agreement is found between the produced RMC structure and the experimental ND results. The neutron weighted partial structure factors $S_{\mathrm{Se-Se}}(Q)$, $S_{\mathrm{Rb-Se}}(Q)$ and $S_{\mathrm{Rb-Rb}}(Q)$ are also shown in this figure. Of particular interest, the pre-peak at 1.3 Å^{-1} in the experimental $S(Q)$ is caused by the pre-peak of $S_{\mathrm{Se-Se}}(Q)$ at the same Q. The curve at the upper panel of figure 2 shows the concentration–concentration structure factor $S_{\mathrm{cc}}(Q)$ (in the Bhatia–Thornton formalism) divided by $c_{\mathrm{Rb}}c_{\mathrm{Se}}$ (c_{Rb} and c_{Se} denote Rb and Se concentration in mole fraction). A rise of $S_{\mathrm{cc}}(Q)$ in the lower Q region is observed.

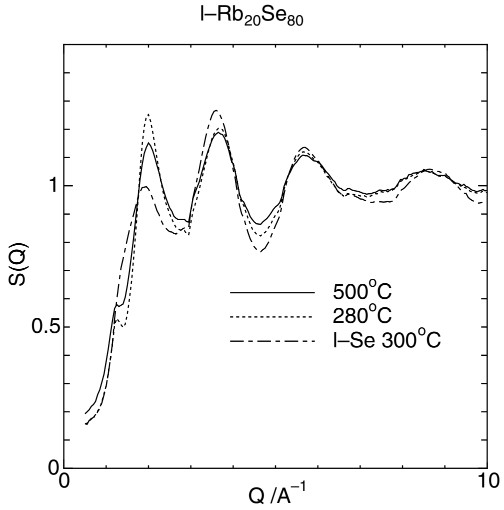

Figure 1. Temperature variation of the structure factor $S(Q)$ for the l-$Rb_{20}Se_{80}$ mixture at 500 and 280 °C together with $S(Q)$ for l-Se at 300 °C.

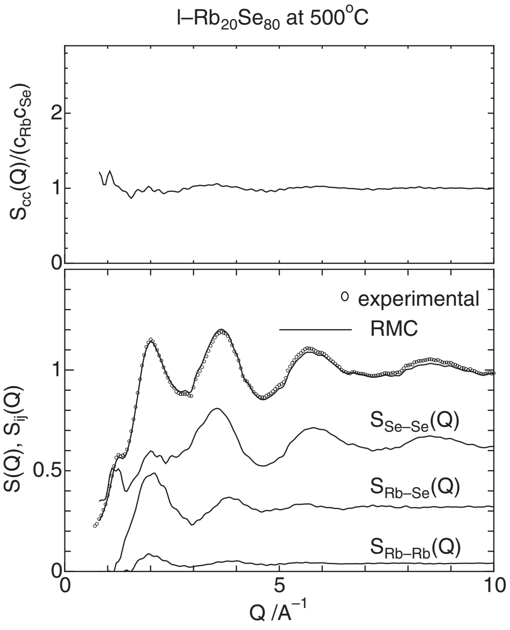

Figure 2. Experimental $S(Q)$ (circles) for the l-$Rb_{20}Se_{80}$ mixture at 500 °C, and the corresponding RMC fit (solid line) together with the neutron weighted partial structure factors $S_{ij}(Q)$ produced from RMC configurations. The upper panel shows the concentration–concentration structure factor $S_{cc}(Q)/c_{Rb}c_{Se}$.

Figure 3 show the computed $g(r)$ for the RMC model (full line) and the neutron weighted partial pair distribution functions $g_{Se-Se}(r)$, $g_{Rb-Se}(r)$ and $g_{Rb-Rb}(r)$ at 500 °C. The estimated coordination number of Se–Se from the RMC $g(r)$ indicates that Se chain molecules are formed by fewer than 10 Se atoms on average. There exists the first peak of $g_{Rb-Se}(r)$ at 3.6 Å near

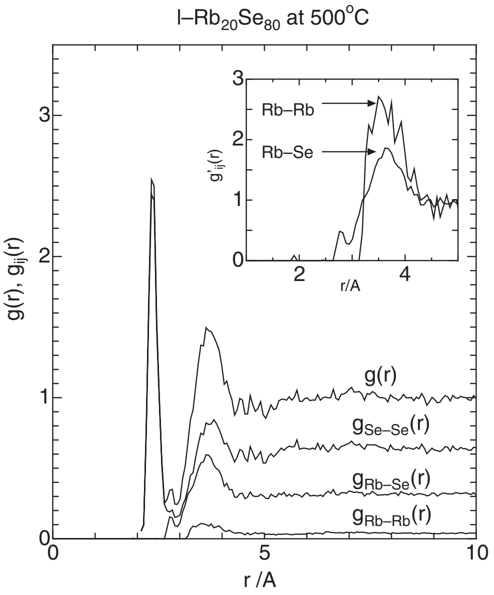

Figure 3. The computed pair distribution function $g'(r)$ from the RMC model of the l-$Rb_{20}Se_{80}$ mixture (full line) at 500 °C together with the neutron weighted partial pair distribution functions $g_{ij}(r)$ (full line) obtained by RMC simulation. In the inset of the figure $g'_{\mathrm{Rb-Rb}}(r)$ and $g'_{\mathrm{Rb-Se}}(r)$ curves near the first peak without any weighting for concentration or cross section are compared.

the second peak of $g_{\mathrm{Se-Se}}(r)$. The $g_{\mathrm{Rb-Rb}}(r)$ curve contains a large statistical noise due to low Rb concentration. The partial pair distribution functions for Rb–Rb and Rb–Se without any weighting for concentration or cross section, $g'_{\mathrm{Rb-Rb}}(r)$ and $g'_{\mathrm{Rb-Se}}(r)$ are compared in the inset of figure 3. From the data for $g'_{\mathrm{Rb-Rb}}(r)$ the nearest-neighbour distance between Rb atoms is estimated to be 3.5–3.9 Å, which is shorter than that in l-Rb–Te mixtures. This implies that two Rb atoms come close together.

4. Discussion

Snapshots of the characteristic RMC configurations of Rb and Se atoms in the l-$Rb_{20}Se_{80}$ mixture at 500 and 280 °C are shown in figures 4(a) and (b). The figures present a 10 Å thick slice of a part of the RMC configuration. The grey and black circles represent Se and Rb atoms, respectively. The neighbouring Se atoms whose distance apart is smaller than 3.1 Å are connected by grey bonds. At high temperature Rb atoms are distributed uniformly in space and are mainly located near the ends of Se chains. It is clearly recognizable that the two Rb atoms are located very close together, which is consistent with the results of $g'_{\mathrm{Rb-Rb}}(r)$ shown in the inset of figure 3. It is noticed that there exist a large number of voids surrounded by the ring-like Se segments composed of a few Se atoms at high temperature. The recent EXAFS analysis supports the characteristic structural features, as mentioned above. When one approaches the boundary of the miscibility gap by lowering the temperature down to 280 °C, the shortened Se chains link up and aggregate to form a large cluster, and Rb atoms sit around the large clusters. The shaded area in figure 4 represents growing clusters of Se segments linked by more than 60 Se atoms.

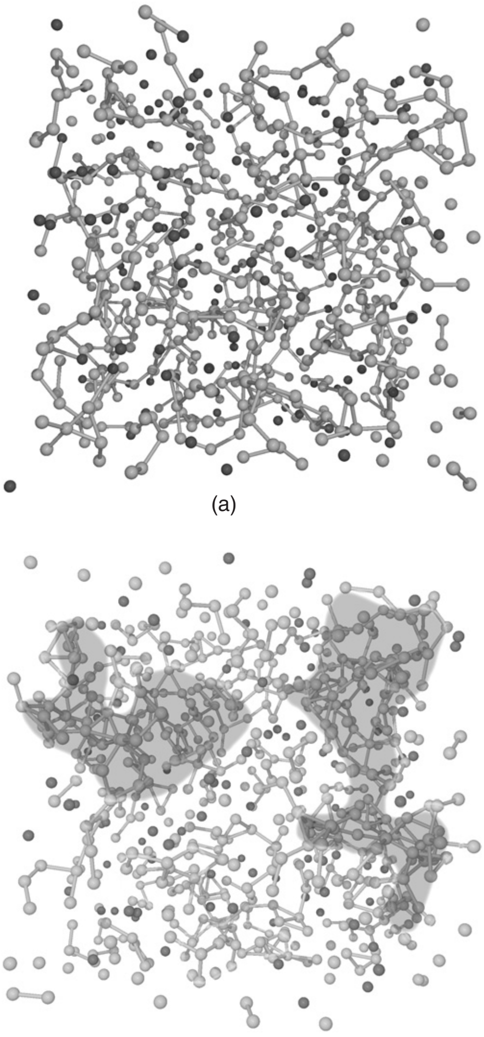

Figure 4. Snapshot produced from RMC configurations around Se (grey) and Rb (black) for the l-$Rb_{20}Se_{80}$ mixture at 500 °C (a) and 280 °C (b). The shaded area represents growing clusters of Se segments linked by more than 60 Se atoms.

Herwig *et al* [11] have studied the structure of isolated Se nanoclusters doped with Na atoms, Na_2Se_N with $N = 4$–8. It has been proposed that the Na_2Se_N clusters contain horseshoe-like shaped polyanionic chains and the overall bonding situation is well described as something between the border cases $(Na_2)^+(Se_N)^-$ and $(Na^+)_2(Se_N)^{2-}$. The local structure and charge transfer of l-Rb–Te mixtures have been studied by Shimojo *et al* [5] using *ab initio* MD simulation. The partial pair distribution functions which they obtained indicate that the Rb–Rb distance in the l-$Rb_{20}Te_{80}$ mixture is ∼4.5 Å, much larger than that in the l-$Rb_{20}Se_{80}$ mixture, suggesting strong suppression of Rb and its nearest Rb neighbours. The differences in the Rb distribution between l-Rb–Te and Rb–Se mixtures can be interpreted in terms of geometry of chalcogen chains and alkali atom configurations. That is, Te chains in l-Rb–Te

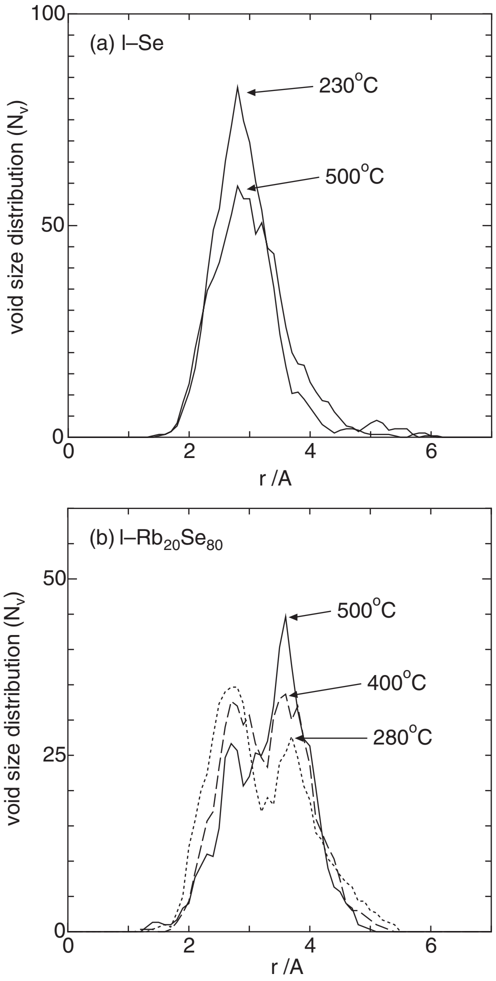

Figure 5. The interstitial void size distribution in the RMC model of the l-$Rb_{20}Se_{80}$ mixture at 500, 400 and 280 °C.

mixtures are stretched and two single Rb atoms are located at the ends of a Te chain, while Se chains in l-Rb–Se mixtures are strongly bent to form a ring-like (horseshoe-like) shape and two Rb atoms come close together through an attractive interaction, which reduces the charge transfer from Rb atoms to Se atoms. The bonding interactions between Rb and Rb atoms and between Rb and Se atoms may be crucial for understanding of the stability of void structures, which is reflected in the intensity of the pre-peak in $S(Q)$ (see figure 1). These findings suggest that a tendency for segregation may make the polyanion complexes unstable.

The existence of the pre-peak in $S(Q)$ is indicative of the existence of intermediate-range order in the liquid mixture. Caprion and Schober [7], using MD simulation, investigated the origin of a shoulder in liquid and amorphous Se specimens with high and low densities, changing the temperature and pressure. They found a pre-peak for the Se specimen at lower density while not at higher density, which led them to the conclusion that the shoulder is a signature of correlation between voids in the structure. As seen in figure 4, there exist a large number of voids in the l-Rb–Se mixture. A method of Delaunay tessellation [12–15] which

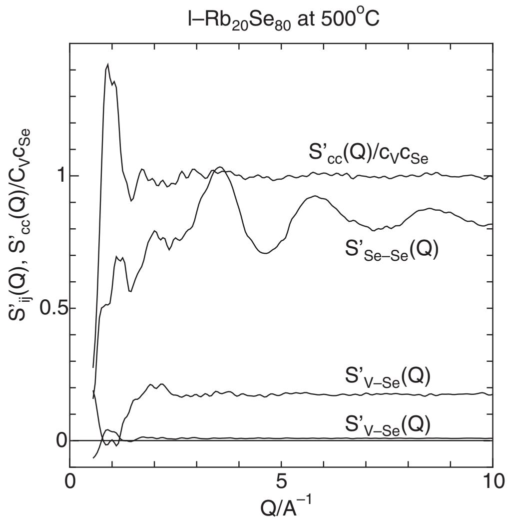

Figure 6. Concentration–concentration structure factor $S'_{\mathrm{cc}}(Q)/c_{\mathrm{V}}c_{\mathrm{Se}}$ involving Se-atom and interstitial-void positions in the RMC model for the l-Rb$_{20}$Se$_{80}$ mixture at 500 °C and also the calculated partial structure factors $S'_{\mathrm{Se-Se}}(Q)$, $S'_{\mathrm{V-Se}}(Q)$ and $S'_{\mathrm{V-V}}(Q)$ with the concentration weight.

packs a given configuration space with tetrahedra formed by bonding contiguous pairs of atoms was applied to investigate the size distribution of interstices or voids. All interstices or voids were sorted according to their sizes, and interstitial spheres were inserted sequentially, starting from the largest interstices or voids. Since each compartment should correspond to a void, the subset of nonoverlapping voids (500 voids) was identified. Figure 5 shows the size distribution N_{V} of the nonoverlapping spherical voids as a function of the circumscribed sphere radius r of a tetrahedron in the l-Rb$_{20}$Se$_{80}$ mixture at 500, 400 and 280 °C. The distribution N_{V} for the l-Rb$_{20}$Se$_{80}$ mixture has two well-defined peaks around $r = 2.7$ and 3.6 Å and the peak intensity around 3.6 Å increases with increasing temperature, while the peak intensity around 2.7 Å decreases. The geometrical configuration of Se chains and voids is that the space filled by the small voids of $r \sim 2.7$ Å corresponds to the interstices between adjacent Se chains and the large voids of $r \sim 3.6$ Å create the ring-like Se chains composed of 6–8 Se atoms. The fraction of nonoverlapping voids to total Se atoms is about 7%.

A number of models [10, 16, 17] based on different structural assumptions have been proposed with the aim of explaining the structural origin of the pre-peak. Elliott [10] has interpreted the pre-peak in $S(Q)$ of chalcogenide glasses as a chemical order pre-peak reflecting the ordered packing of atoms and voids. Knowing the positions of the interstitial voids and Se atoms, one can calculate the partial structure factor $S'_{ij}(Q)$ involving Se atoms and interstitial void centres. Figure 6 shows $S'_{\mathrm{V-Se}}(Q)$, $S'_{\mathrm{Se-Se}}(Q)$ and $S'_{\mathrm{V-V}}(Q)$ together with concentration–concentration structure factor in the void–Se system $S'_{\mathrm{cc}}(Q)$ divided by $c_{\mathrm{V}}c_{\mathrm{Se}}$ (c_{V} and c_{Se} denote void and Se concentration) for the l-Rb$_{20}$Se$_{80}$ mixture at 500 °C. Interestingly, $S'_{\mathrm{cc}}(Q)$ has a well-defined pre-peak around 1 Å^{-1}, and $S'_{\mathrm{V-Se}}(Q)$ has the corresponding minimum around 1 Å^{-1}, and $S'_{\mathrm{Se-Se}}(Q)$ has the corresponding maximum around 1.1 Å^{-1}, though this value for the position of the peak is somewhat smaller than that observed experimentally. In conclusion the observed pre-peak for $S(Q)$ in l-Rb–Se mixtures corresponds to the pre-peak of $S'_{\mathrm{cc}}(Q)$ due to the chemically ordered packing of interstitial voids and Se atoms in the structure.

5. Conclusion

The results for ND measurements and structural analysis using RMC modelling give some new insights into the short- and intermediate-range order in l-Rb–Se mixtures in the Se-rich concentration range. The Se chains in the l-mixtures are strongly bent to form ring-like Se chains with Rb atoms at the chain ends, creating a large amount of voids. The interaction between Rb and Se atoms is weak and two Rb atoms come close together. When one approaches the boundary of the miscibility gap by lowering the temperature the short Se chains link up to form a large cluster, and Rb atoms sit around it. It is worth mentioning that the bonding interactions between Rb atoms significantly influence the stability of the void structure and a tendency for segregation may make the polyanionic complexes unstable.

The $S(Q)$ of l-Rb–Se mixtures has a small pre-peak at ~ 1.3 Å^{-1}. From the analysis on the size and position of voids using the Delaunay tessellation method it has been found that the small voids of ~ 2.7 Å radius occupy the space corresponding to the interstices (~ 3.6 Å) between adjacent Se chains and the large voids of ~ 3.6 Å radius are surrounded by the ring-like Se chains composed of 6–8 Se atoms. The observed pre-peak in $S(Q)$ is interpreted as a chemical order pre-peak reflecting the relative arrangements of Se atoms and voids.

Acknowledgment

The authors are grateful to Professor A Ueda of Kyoto University for helpful discussions.

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