Local structure of liquid Rb–Se mixtures near the miscibility gap

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Abstract

In the liquid Rb–Se mixture there exists a liquid–liquid phase separation (miscibility gap) in the Se-rich concentration region. In order to study how the local structure is associated with the occurrence of the miscibility gap, EXAFS and neutron diffraction measurements for liquid Se, Rb10Se90, Rb15Se85 and Rb20Se80 mixtures have been carried out. The results reveal that the interaction between Rb and Se atoms is very weak and the liquid mixtures are composed of short Se chain-molecules of which chain ends are terminated by Rb atoms. We have carried out detailed structural modeling studies using reverse Monte Carlo simulation. It is found that the chain-like or ring-like Se segments are separated by voids. The Rb atoms adsorbed to Se chain ends segregate in the void and the shortened Se chain-molecules link up with each other when one approaches the miscibility gap.

1. Introduction

The liquid–liquid phase separation (miscibility gap) in binary liquid mixture is one of the interesting problems in the field of recent ‘liquid metal’ science. The thermodynamic and electronic properties near the miscibility gap have been extensively studied [1–4], while the structural properties [5,6] have been much less investigated. The local atomic arrangements and the structural details of concentration fluctuations near the miscibility gap have not been clear. The structural studies near the miscibility gap were carried out by Ruppersberg and Knoll [5] for so-called ‘zero alloy’ liquid (l-)Li60Na40 mixed with the 7Li isotope which has a negative coherent neutron scattering length. They succeeded in deriving information on the concentration fluctuations in l-Li60Na40 near the miscibility gap from the measurements of small angle and high angle neutron diffraction (ND).

Difficulty of the structural analysis of the diffraction data for binary liquid mixture lies in the fact that the partial structure factor cannot be easily separated from the observed total structure factor. The recently developed extended X-ray absorption fine structure (EXAFS) technique [7,8] is complementary to the diffraction experiments, since it can provide selective information concerning the local structure of liquid mixtures, though less information is obtainable for the medium and long-range order. The reverse Monte Carlo (RMC) method [9,10] is also a useful technique to extract information on the atomic arrangements in real space from the structure factor data.

The structure of l-Se is characterized by covalently bonded two-fold coordination. The binary liquid mixtures
of Se with alkali elements which are easily ionized exhibit a miscibility gap in Se-rich concentration range [2,11]. It is interesting to study how the configuration of Se with orientational bonding and the spatial distribution of alkali atoms are modified as the temperature is lowered near the miscibility gap from high temperature.

In the l-Rb–Se mixture there exists a miscibility gap in the concentration range between 0 and 20 at.% Rb [2,11]. Hoshino and Endo [1] found that the miscibility gap disappears by applying pressure of over 1060 bar. It is interesting to note that the electrical conductivity of l-Se increases upon the addition of Rb by three or four orders of magnitude [1].

In the present paper, we report the results of EXAFS, neutron diffraction and RMC simulation for l-Rb–Se mixtures near the miscibility gap and discuss how the local structure is associated with the occurrence of the liquid–liquid phase separation.

2. Experimental

EXAFS measurements of l-Rb20Se80 were performed using a spectrometer installed at the BL-10B station of Photon Factory in the KEK. Spectra at Se and Rb K-absorption edges were obtained in a transmission mode using Si(311) monochromator. The intensity of the incident beam and transmitted beam were monitored by ionization chambers with ArN2 and Ar gas, respectively. The samples were inserted into a gap between two X-ray windows made of the quartz glass which were polished to 0.3 mm thickness to increase the efficiency of X-ray transmission [7].

The elastic ND measurements for l-Rb10Se90, l-Rb15Se85 and Rb20Se80 in the wide temperature range were carried out by using the HIT-II spectrometer at the KENS spallation neutron source in KEK. The sample was sealed in a cylindrical fused silica cell (inner diameter 8 mm and wall thickness 0.3 mm) [12]. Before the measurements, each sample was heated up to 500 °C in order to get a homogeneous solution. Then the scattering intensity was accumulated for about 8 h by using the ‘time of flight’ method with decreasing temperature step by step. The counts of scattered neutrons at the Q position except for Q < 1 Å⁻¹ exceed 10⁵ typically, which gives a sufficient statistical quality.

The RMC method used in the present study is essentially similar to that adopted by McGreevy [10]. A brief summary of the procedure is as follows. The number of Rb and Se atoms is 8000 in total, which are initially arranged in a rock salt structure. The size of a cell was about 60 x 60 x 60 Å³. A randomized configuration of Rb and Se atoms was created with an atomic closest-approach constraint. 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, excellent agreement between experimental data and RMC calculation was obtained.

3. Results

EXAFS measurements at l-Rb20Se80 mixture have been carried out in the temperature range from 250 to 500 °C. Fig. 1(a) and (b) show the results for the k-weighted Se and Rb K-edge spectra k₂(κ) of l-Rb20Se80 mixture. As seen in Fig. 1(b) the amplitude of the EXAFS oscillation around Rb atoms is extremely small and damps rapidly above κ = 6.0 Å⁻¹ compared with that around Se atoms in Fig. 1(a), which suggests that the interaction between Rb and Se atoms is weak.

Fig. 2 shows the temperature variation of structure factor S(Q) for the l-Rb15Se85 mixture whose composition is close to the critical solution concentration (10 at.% Rb) [1,2,11]. 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 referred to as ‘the first sharp diffraction peak’ [13], a well-known signature of intermediate-range order. The pre-peak in l-Rb15Se85 is more distinctly separated from the first peak of S(Q) compared to that for l-Se at 300 °C plotted together in this figure. Interestingly, 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.

![Figure 1](image_url)
with decreasing temperature in the normal manner expected by the Debye–Waller (DW) factor.

Fig. 3 shows the temperature variation of the pair distribution function $g(r)$ for the l-Rb$_{15}$Se$_{85}$ mixture. The first peak of $g(r)$ at $r \sim 2.4$ Å corresponds to the nearest neighbor intra-chain distance of Se atoms. The height of the first peak for the l-Rb–Se mixture is nearly independent of temperature, while the height of the second peak increases with decreasing temperature. The first peak of $g(r)$ is separated clearly from the rest of neighbors as temperature is lowered. In Fig. 4, the $g(r)$ curves for l-Se at 300 °C, Rb$_{10}$Se$_{90}$, Rb$_{15}$Se$_{85}$ and Rb$_{20}$Se$_{80}$ mixtures at 280 °C are compared. The height of the first peak of $g(r)$ for l-Se decreases upon the addition of Rb, which implies an increase in the number of one-fold coordinated defects created by Se–Se bond breaking. The lower $r$ side of the second peak is enhanced by the addition of Rb to l-Se. This is attributable to the appearance of the Rb–Se correlation.

RMC simulation is useful for aiding our understanding of the atomic arrangements in the liquid mixture. The curves in Fig. 5 show the experimental structure factor $S(Q)$ (circles) for l-Rb$_{15}$Se$_{85}$ at 280 °C and the corresponding fit (solid line) produced in the RMC simulation.

Fig. 2. Temperature variation of the structure factor $S(Q)$ for l-Rb$_{15}$Se$_{85}$ obtained by ND measurements together with $S(Q)$ for l-Se at 300 °C.

Fig. 3. Temperature variation of the pair distribution function $g(r)$ for l-Rb$_{15}$Se$_{85}$ derived from the Fourier transformation of $S(Q)$.

Fig. 4. Composition variation of $g(r)$ for l-Rb–Se mixtures at 280 °C together with $g(r)$ for l-Se at 300 °C.

Fig. 5. Experimental structure factor $S(Q)$ (circles) for l-Rb$_{15}$Se$_{85}$ at 280 °C and the corresponding fit (solid line) produced in the RMC simulation together with the partial structure factors $S_{ij}(Q)$ at 280 °C (dashed lines) calculated from the largest RMC configuration. The curve at lower part of the figure shows concentration–concentration structure factor $S_{cc}(Q)$ at 280 °C.
The partial structure factors \( S_{ij}(Q) \) (dashed lines) are also shown in the figure.

Of particular interest, the pre-peak at about 1.3 Å\(^{-1}\) in the experimental \( S(Q) \) is caused by the peak of \( S_{\text{Se-Se}}(Q) \) at the same \( Q \). The curve at the lower part of Fig. 5 shows the concentration-concentration structure factor \( S_{\text{cc}(Q)} \) (in the Bhatia-Thornton formalism [14]) divided by \( c_1 c_2 \) \((c_1 \text{ and } c_2 \text{ denote } \text{Rb and Se concentration in mole fraction, respectively})\). A rise in \( S_{\text{cc}}(Q) \) in the low \( Q \) region is observed. Fig. 6(a) and (b) show the computed \( g(r) \) from the RMC model (full line) compared with the experimental \( g(r) \) (circles) and the neutron-weighted partial pair distribution functions \( g_{\text{Se-Se}}(r) \), \( g_{\text{Se-Rb}}(r) \) and \( g_{\text{Rb-Rb}}(r) \) (dashed lines). The peak of \( g_{\text{Se-Se}}(r) \) lies around 3.5 Å. The \( g_{\text{Rb-Rb}}(r) \) curve contains a large statistical noise because of low Rb concentration. The curves for \( g'_{\text{Rb-Rb}}(r) \) without neutron- and concentration-weight near the first peak are compared in the inset of Fig. 6(b). The data show that the bond length of Rb-Rb is nearly the same as that of Rb-Se.

4. Discussion

EXAFS signal for l-Rb\(_{20}\)Se\(_{80}\) mixture near Rb K-edge is weak compared with that near Se K-edge as seen in Fig. 1(a) and (b). The analysis shows that DW factor for the Rb-Se bond is one order of magnitude smaller than that for the Se-Se bond. This indicates that the interaction between Rb and Se atoms is very weak. Although the quality of the experimental data at the Rb K-edge is low, a rough estimation gives nearly the same bond length for Rb-Se and Rb-Rb.

The position of the first peak of \( g(r) \) for l-Se is nearly unchanged by the addition of Rb, while the height decreases. Assuming that the first peak of \( g(r) \) is composed of only Se-Se correlations in the Se chains, the Se coordination number around Se atoms in l-Rb\(_{15}\)Se\(_{85}\) at 280 °C is estimated to be 1.85, which suggests that the two-fold coordinated Se chains are shortened into the chains formed by less than 10 Se atoms on average. As seen in Fig. 4, the lower \( r \) side in the second peak of \( g(r) \) is enhanced by the addition of Rb to l-Se, which is attributed to the appearance of the Rb-Se correlation. The above evidence is consistent with RMC simulation results. The inset of Fig. 6(b) reveals that the peak position for \( g_{\text{Rb-Se}}(r) \) lies around 3.5 Å which is close to that of the first peak of \( g_{\text{Rb-Rb}}(r) \), suggesting that the interaction between Rb and Se atoms is weak and the Rb atoms at the Se chains ends come close together. From the EXAFS and ND results we find that there exist relatively short Se chain-molecules in l-Rb-Se mixtures and the Rb atoms do not randomly substitute for Se atoms in the chain.

We see a small pre-peak near \( Q \sim 1.3 \text{ Å}^{-1} \) in the \( S(Q) \) of l-Rb\(_{15}\)Se\(_{85}\) in Fig. 2, which is a signature of intermediate-range order. The pre-peak in l-Se merges with the first peak and is only seen as a shoulder. The RMC simulation results shown in Fig. 5 demonstrate that only \( S_{\text{Se-Se}}(Q) \) contributes to the appearance of the pre-peak in total \( S(Q) \). The stabilization of Se chain-molecules by the addition of Rb is responsible for the appearance of the relatively intense pre-peak for the Rb-Se mixtures. Fig. 7 shows the snapshots of atomic configurations at 500 °C and 280 °C, respectively. The figures present a 10 Å thick slice of a part of the largest RMC configuration. The gray and black circles are Se and Rb atoms, respectively. The neighboring Se atoms are connected by the gray bond. The bonds between the Se atoms and the Rb atoms adsorbed to the Se chain ends, whose distance apart is smaller than 3.1 Å, are denoted by black bond. The figures demonstrate that the chain-like or ring-like Se segments are separated by interstices or voids and the Rb atoms adsorbed to Se chain ends at high temperature (see Fig. 7(a)). The short Se chain-molecules link up with each other and the Rb atoms segregate in voids when one approaches the boundary of miscibility gap by lowering temperature (see Fig. 7(b)).

Many papers [12,15] have been reported for the structural origin of the pre-peak in chalcogen liquids. Elliott [15] proposed that the pre-peak in the structure factor of network glasses and liquids is a pre-peak in the concentration-concentration structure factor due to the chemical ordering interstitial voids around cation-centered clusters in the structure. We found that the pre-peak in total \( S(Q) \) around 1.3 Å\(^{-1}\) is caused by Se-Se correlation, \( S_{\text{Se-Se}}(Q) \), and the chain-like or ring-like Se segments are separated by interstices or voids. The pre-peak observed for l-Rb-Se mixtures can be explained in terms of weak
ordering between locally aligned segments of Se separated by voids. Such a quasi-periodicity has been proposed in several of the model for explanations of the pre-peak [13,16]. The average distance between Se–Se segments is related to the position of the pre-peak. However, it is noticed that the ordering is weak and local. The degree of ordering between Se segments decreases with increasing concentration of Rb atoms in the voids, which results in a decrease of pre-peak intensity. In summary, the structure of l-Rb–Se mixtures can be viewed as consisting of shortened Se chains which are terminated by Rb atoms. The liquid mixture is not microscopically homogeneous. The segregation of Rb atoms in the voids induces large concentration fluctuations near the miscibility gap.

5. Conclusion

The local structure of l-Rb–Se mixtures near the miscibility gap has been investigated from EXAFS and ND measurements. The DW factor for Rb–Se bond determined from EXAFS analysis is one order of magnitude smaller than that for Se–Se bond. In the structure factor $S(Q)$ of l-Rb-Se mixtures obtained by ND measurements there exists a small pre-peak at $\sim$1.3 Å$^{-1}$ which is referred to as a signature of intermediate-range order. The pre-peak exhibits a decrease in intensity with decreasing temperature. The first peak of $g(r)$ for l-Rb–Se mixtures is less intense compared to l-Se, and the Rb–Se correlation appears in lower $r$ side (3.0–3.5 Å) of the second peak of $g(r)$. The mixtures are composed of short Se chain-molecules whose chain ends are terminated by Rb atoms and the interaction between Rb and Se atoms is very weak.

We have carried out detailed structural modeling studies using RMC simulation. The results give some new insights into the atomic configurations in the mixtures. The chain-like or ring-like Se segments are separated by voids and Rb atoms are adsorbed to Se chain ends. The Rb atoms segregate in the voids and the short Se chain-molecules link up each other when one approaches the boundary of the liquid–liquid phase separation by lowering temperature. The segregation of Rb atoms in the voids induces large concentration fluctuations. We find that the pre-peak of $S(Q)$ at 1.3 Å$^{-1}$ is caused by the pre-peak of $S_{\text{Se-Se}}(Q)$. The pre-peak can be explained in terms of weak ordering between locally aligned segments of Se separated by voids. The degree of ordering decreases with segregation of Rb atoms in voids, which results in a decrease of pre-peak intensity.

References