

## NEUTRON SCATTERING STUDY OF SULPHUR-TELLURIUM LIQUID ALLOYS : STRUCTURAL EVIDENCE FOR A CLOSED LOOP MISCIBILITY GAP.

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The homogeneity of liquids at various length scales is a challenging question specially as far as liquid metals are concerned. In order to contribute to these kind of studies, we focused on the homogeneity of sulphur-tellurium liquid alloys. Pure tellurium is a twofold coordinated semiconductor in the solid state, and undergoes a transition to a metallic state upon melting. As shown by many neutron and x-rays experiments [1,2] as well as computer simulations [3], this transition is characterised by an increase of the number of first neighbours up to three in the liquid state when increasing the temperature. On the contrary, liquid sulphur remains essentially twofold coordinated and insulating [4]. When alloying these two elements, a closed loop miscibility gap is reported to appear in the liquid state [5]. This phase separation, a unique feature in a binary inorganic system, is assumed to occur in a very narrow temperature and concentration range around 40% at. sulphur and 700°C.

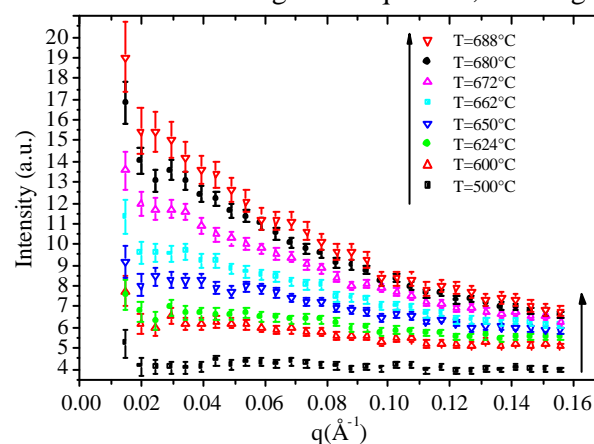
In previous works, we studied the local order of sulphur-tellurium melts by neutron scattering in a broad range of concentration and temperature. The results combined with a modelling of the structure factors allow to determine the evolution of the partial coordination numbers [6,7]. We could explain some of the mechanisms responsible of the phase separation : neglecting chain breaking effects, at 700°C, pure liquid tellurium is a mixture of 2- and 3- fold coordinated atoms. Adding sulphur reveals a phase separation between two phases with different coordination numbers. In order to explicit the link between structure and thermodynamics, we developed a regular solution model with multiple connectivity [8]. Using the measured coordination number, we could deduce the thermodynamic quantities of mixing in the melt. The mixing enthalpy displays a change in concavity when increasing the temperature, characteristic of the presence of two phases in equilibrium. However consistent with a tendency to phase separation, this previous work

does not provide a direct experimental proof of the closed loop miscibility gap.

Two kinds of experiments are reported here that try to give a structural evidence of the phase separation. First, small angle experiments were performed in order to reach gain a knowledge of the structure at large scale. Then, owing to the success of previous experiments, a first attempt in the determination of the local order of the two phases in equilibrium is reported.

Small angle scattering experiments were performed on PACE spectrometer. The wavelength was fixed to 5Å and the momentum transfer range was from 0.02 to 0.2 Å<sup>-1</sup>. The experiments were realised at the concentration of the miscibility gap (40% at. S), the temperature range between 450°C (temperature of the liquidus) and 688°C. The high vapour pressure of sulphur turned out to be the critical parameter of the experiment : the highest temperature that could be reached was measured as 688°C, just below the reported lower critical temperature of the closed loop miscibility gap.

Figure 1 shows the small angle intensities obtained after usual data corrections. Up to 600°C, the signal is flat on the whole q range, which is characteristic of a homogeneous liquid. Above this temperature, the small angle intensities are increasing at low q values, showing



**Figure 1** : Small angle scattered intensity versus q at various temperatures.

that the melt becomes inhomogeneous. In order to quantify the concentration fluctuations that develop in the liquid, an Ornstein-Zernike formalism was used. It consists in writing the intensity  $I(q)$  as a function depending on  $q^2$  and  $\xi$ , where  $\xi$  is the correlation length of the concentration fluctuations. We showed that the correlation length reaches a maximum value of  $16\text{\AA}$  in the temperature range that could be analysed [7].

Then, using a new experimental device (rotating furnace and diaphragm) developed on the 7C2 spectrometer, local order measurements of the two phases in equilibrium were performed. The sample consists in cylindrical quartz tube filled by powder of sulphur and tellurium at the desired concentration (40 % at. S) and is set-up vertically in the furnace. On the one hand, the rotating furnace allows *in situ* "shaking" of the sample and thus ensures the homogeneity of the melt. On the other hand, the automatically driven diaphragm enables one to measure separately the lower and the upper part of the sample which correspond respectively to the denser and the less dense phase in equilibrium.

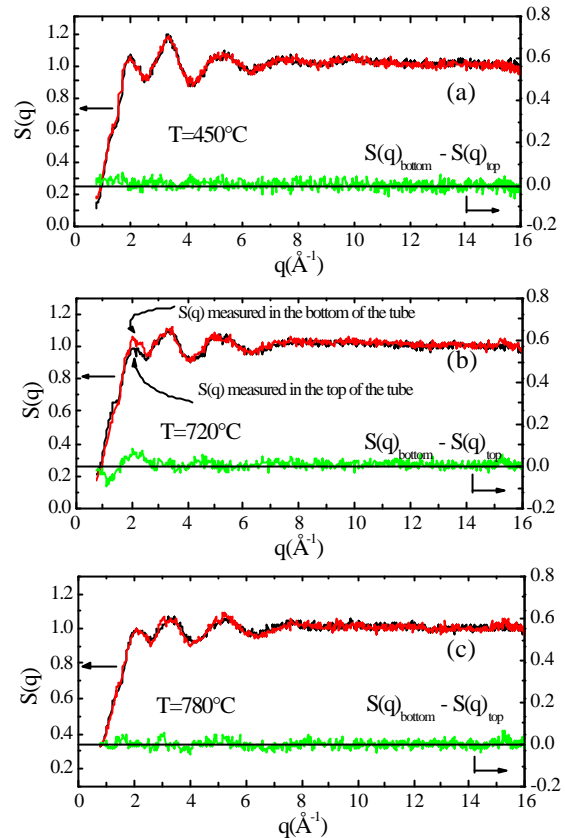
The sample was slowly molten until  $450^\circ\text{C}$  and homogenised by turning the furnace upside down. For each temperature the top and bottom parts of the sample were analysed in turn during the same experiment. The time evolution of the signal was checked by alternating small counting sequences on top and bottom parts.

Figure 2 shows the structure factors measured in the two parts of the tube at various temperatures. At a temperature below the miscibility gap (fig.2a), as shown by the difference plot, the two structure factors are the same within the statistical accuracy.

At  $720^\circ\text{C}$  (fig.2b), differences appear between the two spectra. They are predominant at low  $q$  values : in the upper part of the tube, the structure factor presents a shoulder around  $1.5\text{\AA}^{-1}$ , and the first peak around  $2\text{\AA}^{-1}$  is lower than the second. These features are characteristic of a sulphur rich phase as shown by our previous works [6]. If we look at the difference spectrum we can observe oscillations until  $8\text{\AA}^{-1}$ , the statistics being not sufficient to observe them at higher  $q$  values.

At even higher temperature ( $780^\circ\text{C}$ ), the two structure factors became the same again (fig.2c). Owing to entropy effects, the system is homogeneous again.

Although small, a difference is observed at  $720^\circ\text{C}$  between the structure factors measured in the top and bottom parts of the tube. Combined to the



**Figure 2** : Structure factors measured in the lower (red) and upper (black) part of the tube for various temperature. In green is represented the difference between the two spectra.

small angle scattering measurements, this work gives a direct structural proof of the existence of this closed loop miscibility gap. Concerning the mechanisms at the origin of this phenomenon, local order measurements together with a thermodynamic modelling allowed us to conclude [7] that structural changes undergone by the tellurium rich liquid when the temperature is increased are responsible of the miscibility gap.

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