X-ray and Neutron diffraction study of liquid Sb-Zn alloys

S. Knott[1], S. Gruner[2] ,J. Marczinke[2], A. Mikula[1], W. Hoyer[2]

[1]Institute of Inorganic Chemistry/Materials Chemistry, A-1090 Vienna, Austria
[2]Institute of Physics, Chemnitz University of Technology, D-09107 Chemnitz, Germany

Due to their outstanding thermoelectrical properties, antimony-zinc alloys have been in the focus of materials science for several years. Especially using the intermetallic compound Sb_3Zn_4 in thermoelectric devices yields a much higher thermoelectric efficiency than the commonly used PbTe alloy. The efficiency of the process of converting heat to electric tension or vice versa is ruled by thermophysical properties of the materials as heat conductivity, heat capacity and electrical conductivity.

It is clear, that the atomic structure in the solid state has a crucial impact on these properties and both have been investigated intensively. Besides, experimental data of the thermophysical properties of these alloys in the liquid state has been collected. These investigations include calorimetric studies [1], measurements of the electrical conductivity in the liquid state [2] as well as measurements of the dynamic viscosity [3]. All the mentioned studies find extreme values of the respective properties for the liquid Sb_3Zn_4 alloy: the excess heat of mixing as well as the excess entropy show a minimum, dynamic viscosity and electrical resistivity are highest for this composition. It is thus suggested that clusters of a similar stoichiometry are present in the liquid state, i.e. well above the liquidus line. To investigate this further, a structural study aiming to determine partial pair correlation functions has to be carried out.

In an earlier work [4], Neumann and Mikula performed neutron diffraction experiments at the D4 diffractometer at the ILL, Grenoble, for three selected Sb-Zn alloys: $Sb_{70}Zn_{30}$, $Sb_{43}Zn_{57}$, $Sb_{25}Zn_{75}$ (at.-%). Deviations from a statistical distribution of the atoms became obvious in this study, pointing to a preferred tetragonal arrangement of unlike atoms in the first co-ordination shell.

Additional high energy X-ray diffraction experiments for the same alloys have been carried out at the BW5 experimental station at HASYLAB at DESY, Hamburg. The choosen X-ray energy was 100 keV corresponding to a wavelength of $\lambda = 0.124$ Å. A high-temperature vacuum-heater which has been constructed and built at the Chemnitz University of Technology and which is suitable to perform both diffraction experiments (wide- and small angle) as well as EXAFS measurements was placed on top of the BW5 sample tower. In order to reduce background scattering the camber was equipped with Be-windows.

Figure 1 shows the total Faber-Ziman [5] structure factors obtained by X-ray and Neutron diffraction experiments at 843 K.

The reverse Monte Carlo (RMC) [6] modelling technique has been applied with both experimental total structure factors simultaneously in order to obtain partial pair correlation functions. A final configuration of 8000 atoms has been used for all three alloys under investigation and good agreement between experiment and model has been achieved. The partial pair correlation functions are depicted in figure 2.

The analysis of partial co-ordination numbers and short-range order parameters calculated from these curves confirms the tendency of unlike atoms to group together in these alloys. Taking the higher temperature into account, the radius of the first Sb-Zn co-ordination shell is comparable to the Sb-Zn distance in solid Sb_3Zn_4. However, due to the small difference in the S(Q), the Sb-Zn and Zn-Zn contribution can not be separated properly during RMC modelling. Therefore, further EXAFS experiments are scheduled, and the EXAFS-modulation measured at both Sb- and Zn-K-edge will be supplied to further RMC modelling.

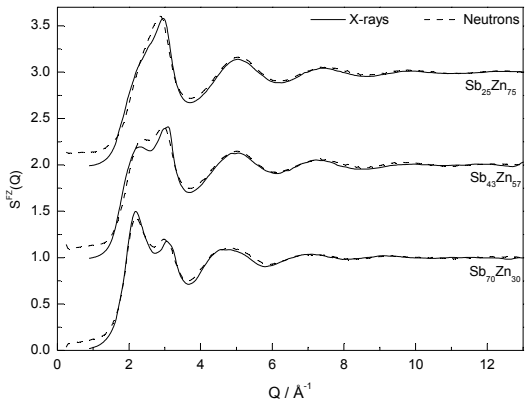

Fig. 1: Total Faber-Ziman structure factors obtained of the Sb-Zn alloys under investigation.

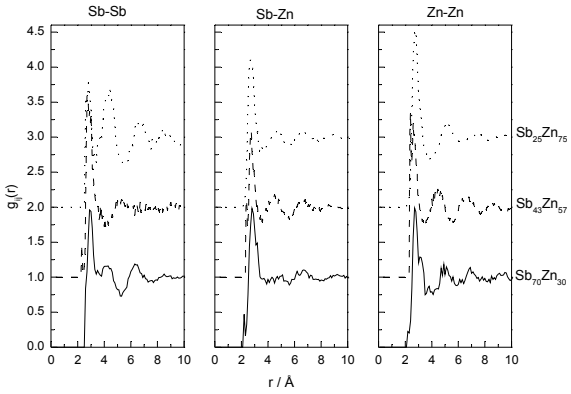

Fig. 2: $g_{ij}(r)$ obtained by RMC modelling of both experimental total structure factors. Note the composition dependence, especially in the g_{SbSb}.

References

[1] B. Rubin, K. L. Komarek, E. Miller, *Z. Metallkde.* **65** (1974) 191

[2] M. R. Mian, A. Mikula, K. L. Komarek, W. Neumann, *Z. Metallkde.* **77** (1986) 133

[3] C. Dong, *Viskosität metallischer Schmelzen und deren präzise Messung*, Dissertation, TU Chemnitz **2001**

[4] H. Neumann, A. Mikula, *J. Non-Cryst. Solids* **312 - 314** (2002) 30

[5] T. E. Faber, J. M. Ziman *Phil. Mag.* **11** (1965) 153

[6] R. L. McGreevy, L. Pusztai, Mol. Simul. 1 (1988) 359

Acknowledgement

Three of us (S.K., J.M, and S.G) gratefully acknowledge HASYLAB for the financial support under the project no. I-20060007 EC as well as the BW5 beamline staff for their help during the experiments.