Experimental report

13/02/2019

Proposal: **6-03-439** **Council:** 4/2016

Title: Structural investigation of binaryglass-forming metallic melts usingelectrostatic levitation and isotopic substitution

Research area: Physics

This proposal is a continuation of 6-03-433

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Samples: Hf-Ni, Ni-B, La-Ni

Instrument	Requested days	Allocated days	From	To
D20	6	6	20/06/2016	27/06/2016

Abstract:

Metallic glasses are of great scientific and technological interest. They are formed when a deeply undercooled alloy melt freezes in an amorphous structure at the glass transition temperature instead of crystallizing. In order to understand the glass formation process on a microscopic scale, knowledge of the short-range structure in the liquid and of the atomic dynamics is of fundamental importance especially also in the metastable regime of the undercooled melt.

In preceding studies we have systematically investigated the short-range order in binary glass-forming alloys consisting of Zr and late transition metals like Ni, Cu, Co and Pd. We now propose such investigations on binary melts consisting of Ni and the early transition metals Hf and La as well as of the metalloid B. We are planning to determine partial structure factors at D20 by using an isotopic substitution technique (samples prepared with natural Ni, 58Ni and 60Ni). These structural investigations are complemented by studies on the atomic dynamics by quasi-elastic neutron scattering experiments at FRM-II and by calculations within mode coupling theory aiming to find a relation between structure and atomic dynamics.

The aim of experiment 6-03-439 was the investigation of the short-range order of binary alloy melts that are forming metallic glasses. During the beamtime we have successfully measured structure factors of melts of $Hf_{35}Ni_{65}$, Ni_2B, and $La_{60}Ni_{40}$ utilizing our electrostatic levitation furnace at the diffractometer D20.

As an example, here we present results obtained from our isotopic substitution experiments for melts of $Hf_{35}Ni_{65}$. The measured total static structure factors for $Hf_{35}{}^{58}Ni_{65}$, $Hf_{35}{}^{nat}Ni_{65}$, and $Hf_{35}{}^{60}Ni_{65}$ at 1510 K and 1615 K are shown in Fig. 1.

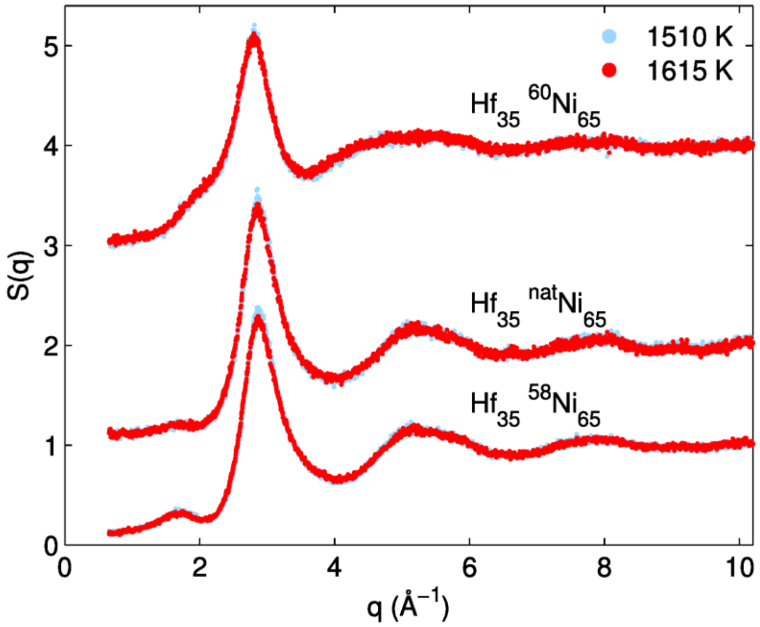

FIG. 1. Measured total static structure factors for $Hf_{35}{}^{60}Ni_{65}$, $Hf_{35}{}^{nat}Ni_{65}$, and $Hf_{35}{}^{58}Ni_{65}$ at 1510 K and 1615 K [1].

The results illustrate a weak temperature dependence for a temperature increase of 105 K. The measurement at lower temperatures shows slightly stronger oscillations, however the differences are very small. Partial static structure factors have been calculated from the total static structure factors within the Faber-Ziman and Bathia-Thornton formalisms, respectively. These are shown in Fig. 2. The partial static structure factors for $Zr_{36}Ni_{64}$ at 1385 K are shown for comparison [2]. The Bathia-Thornton partial structure factors S_{NN} of $Hf_{35}Ni_{65}$ at 1510 K and $Zr_{36}Ni_{64}$ at 1385 K are roughly equal, indicating a similar topological SRO.

The Bathia-Thornton partial structure factor S_{CC}, describing the chemical SRO (CSRO), shows strong oscillations for both alloys, which implies a pronounced chemical order. The amplitude of the oscillations observed for $Hf_{35}Ni_{65}$ is slightly lower as compared with $Zr_{36}Ni_{64}$, particularly in the q range of the second oscillation around 3 to 4 Å^{-1}. The Bathia-Thornton partial static structure factor S_{NC}, which describes the correlation between number density and chemical composition, is almost identical for all three measurements. For a further analysis of the SRO, we have calculated the Faber-Ziman partial static structure factors, which describe the different contributions of each of the atomic pairs (Ni-Ni, Hf/Zr-Ni, and Hf-Hf/Zr-Zr) to the total static structure factor $S(q)$.

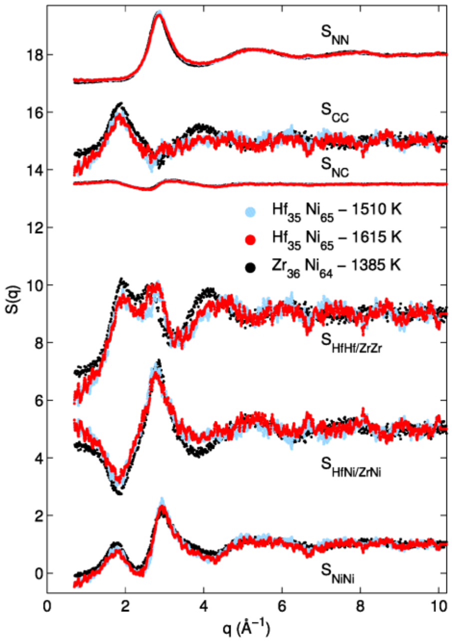

FIG. 2. Partial static structure factors calculated using the Faber-Ziman and Bathia-Thornton formalism for $Hf_{35}Ni_{65}$ at 1510K and 1615 K and $Zr_{36}Ni_{64}$ at 1385 K [1,2].

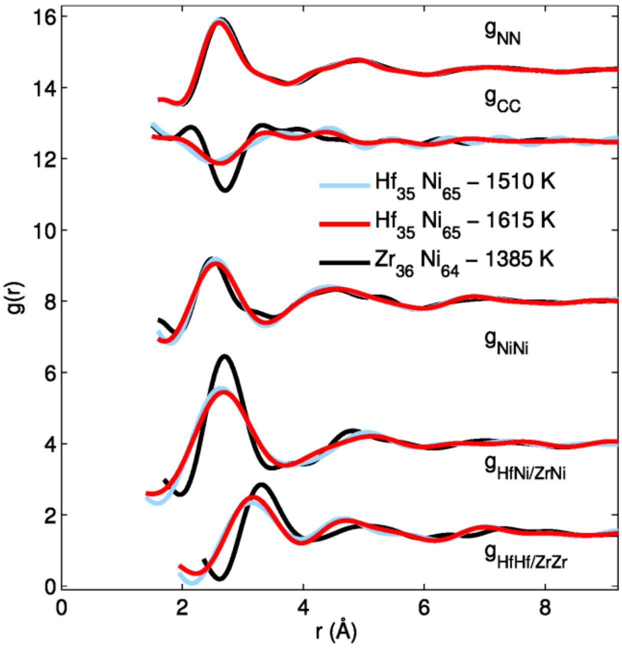

FIG. 3. Partial pair correlation functions calculated using the Faber-Ziman and Bathia-Thornton formalism for $Hf_{35}Ni_{65}$ at 1510K and 1615 K and $Zr_{36}Ni_{64}$ at 1385 K [1,2].

Partial pair-correlation functions were determined through Fourier transformation of the partial static structure factors. Results for $Hf_{35}Ni_{65}$ and $Zr_{36}Ni_{64}$ are plotted in Fig. 3. The pair-correlation function g_{NiNi} is almost identical for both alloys. The first maximum of g_{ZrNi} is sharper compared to g_{HfNi}, which implies a broader distribution of Hf-Ni nearestneighbor distances in comparison to Zr-Ni distances. The fact that the first maxima of g_{ZrNi} and g_{HfNi} are larger than the first maxima of g_{NiNi} and g_{ZrZr} (g_{HfHf}), respectively, implies that heterogeneous nearest-neighbor pairs are preferred in both alloy melts. The same conclusion can also be drawn from the observation of the minima in the Bathia-Thornton pair-correlation function g_{CC} around 2.6 Å. Moreover, it is remarkable that the first and second peaks of g_{HfHf} are shifted to smaller interatomic distances compared to g_{ZrZr}. This fact cannot be explained by a temperature effect since the shift of the first peak positions of g_{HfHf} between 1510 and 1615 K is very small in comparison to the difference between g_{HfHf} and g_{ZrZr}. For a more quantitative description, we have calculated coordination numbers and nearest-neighbor distances. The nearest-neighbor distances correspond to the positions of the first maxima in the pair-correlation functions. The coordination numbers have been determined by integrating the first peak in the radial distribution function between its first and second minima. The results are compiled in Table 1 together with those for $Zr_{36}Ni_{64}$ [2]. The coordination numbers for $Hf_{35}Ni_{65}$ and $Zr_{36}Ni_{64}$ are equal within the error of the measurement, which underlines a similar topological SRO for both alloys.

Table 1: Distances of atomic nearest neighbors (d_{AB}) and partial nearest neighbor coordination numbers, Z_{AB}, for melts of different binary glass-forming alloys (A = N, Hf, Zr; B = N, Ni).

	T [K]	**d_{NN} [Å]**	**d_{AA} [Å]**	**d_{BB} [Å]**	**d_{AB} [Å]**	**Z_{NN}**	**Z_{AA}**	**Z_{BB}**	**Z_{AB}**	**Z_{BA}**	**<Z>**	**Ref.**
$Hf_{35}Ni_{65}$	1510	2.62±0.02	3.15±0.02	2.56±0.02	2.65±0.02	13.3±0.5	5.3±0.5	6.2±0.5	5.6±0.5	10.4±0.5	13.2±0.5	[1]
	1615	2.62±0.02	3.18±0.02	2.56±0.02	2.66±0.02	13.1±0.5	5.5±0.5	6.3±0.5	5.4±0.5	10.1±0.5	13.0±0.5	[1]
$Zr_{36}Ni_{64}$	1385	2.63±0.02	3.31±0.02	2.51±0.02	2.70±0.02	13.8±0.5	6.2±0.5	6.3±0.5	5.9±0.5	10.4±0.5	13.8±0.5	[2]

The SRO around larger Hf and Zr atoms, respectively, is considerably different compared to smaller Ni atoms since the partial coordination numbers for Hf ($Z_{\mathrm{HfHf}} + Z_{\mathrm{NiHf}} \approx 16$) and Zr ($Z_{\mathrm{ZrZr}} + Z_{\mathrm{NiZr}} \approx 17$), respectively, are larger in comparison to Ni ($Z_{\mathrm{NiNi}} + Z_{x\mathrm{Ni}} \approx 12$). The most striking observations are smaller nearest-neighbor distances $d_{\mathrm{HfHf}} = 3.15$ Å as well as smaller second nearest-neighbor distances $d_{\mathrm{HfHf,2}} = 4.66$ Å (derived from the position of the second maximum in g_{HfHf}) at 1510 K compared to the distances of $d_{\mathrm{ZrZr}} = 3.31$ and $d_{\mathrm{ZrZr,2}} = 5.02$ Å. The smaller interatomic distance between Hf-Hf compared to Zr-Zr might be interpreted as a locally higher packing density of Hf atoms in $Hf_{35}Ni_{65}$ in comparison to Zr atoms in $Zr_{36}Ni_{64}$. This may lead to a more sluggish diffusion in $Hf_{35}Ni_{65}$ as compared to $Zr_{36}Ni_{64}$, hence explaining the higher activation energy for Ni self-diffusion in $Hf_{35}Ni_{65}$ that was experimentally observed by quasielastic neutron scattering experiments [1].

In order to analyse the structure-dynamics relationship, the measured partial static structure factors were used as an input for calculations in the framework of the mode coupling theory (MCT) of the glass transition [3] in order to calculate transport coefficients [1]. While some deviations of the MCT results from the measured data on the absolute scale may be explained by the fact that the temperature enters only as an indirect parameter in MCT calculations, it is remarkable that the self-diffusivities calculated by MCT for $Hf_{35}Ni_{65}$ show a similar temperature dependence as the corresponding experimental results [1]. Hence the activation energies for self-diffusion predicted by MCT are in good agreement with the experimentally determined ones. In the light of the very small variations of the partial static structure factors associated with the temperature change (see Fig. 2), this ability of MCT to reproduce accurately the activation energies for self-diffusion is a remarkable result. In addition to the activation energies for self-diffusions, also the coupling/decoupling behavior of the diffusion coefficients of the different alloy components is well reproduced by the MCT calculations [1].

References

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