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Structure and dynamics of glass-forming alloy melts investigated by application of levitation techniques

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Abstract: In this work results of studies on the short-range order and on the atomic dynamics in different stable and undercooled glass-forming metallic melts are reviewed. In order to undercool the melts deeply below the melting temperature and to avoid chemical reactions of the melts with crucible materials, the samples are containerlessly processed utilizing the electromagnetic or the electrostatic levitation technique. The short-range structure of the melts is studied by neutron diffraction, while the atomic dynamics are investigated by quasielastic neutron scattering. The relationship between short-range structure and atomic dynamics is discussed within the mode coupling theory of the glass transition. We will show that taking the time- and space-averaged structural information provided by measured partial structure factors as an input, mode coupling theory is able to explain the experimental results concerning the activation energies for self-diffusion and the coupling/decoupling behavior of the self-diffusion coefficients of the different alloy components.

Keywords: atomic dynamics; containerless processing; HTMC-XVI; short-range order.

Introduction

By use of suitable processing techniques, melts of metallic alloys may be undercooled below their glass transition temperature at which the melt freezes under formation of a metallic glass of amorphous structure. Open questions to understand the formation of glasses are concerned with the temperature and composition dependence of the different melt properties, with the relation between these properties and with their influence on the glass-formation process. Short-range structure and atomic dynamics of the liquids are atomic scale properties that determine the macroscopic properties of the melts and govern the solidification behavior as well as the glass-forming ability. Together with the structure of crystallizing solid phases the short-range order of the liquid phase determines the solid-liquid interfacial energy that is an important parameter that influences the crystal-nucleation behavior from undercooled liquids [1–3]. The atomic mobility influences both, crystal nucleation and subsequent crystal growth [2, 3]. Because glasses are formed, if the crystallization of undercooled melts is avoided, short-range order and atomic dynamics are key properties for understanding the mechanisms of glass-formation. In addition to the importance of both atomic scale properties for understanding the solidification and glass-formation behavior of undercooled melts the relation

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between short-range structure and atomic dynamics is of fundamental scientific interest. From the theoretical side the mode coupling theory (MCT) of the glass transition [4] establishes a firm relationship between the short-range order and dynamic properties of the melt like self-diffusion coefficients and viscosity. The only input parameters of MCT calculations are partial static structure factors and packing densities, which can be experimentally determined.

Concerning the short-range order of glass-forming melts, there are controversial discussions on the role of a possible icosahedral short-range order for the glass-forming ability. For monoatomic metallic melts an icosahedral short-range order has been predicted by Frank basing on estimations of the energy of different aggregates in systems with Lennard–Jones like interactions [5]. Diffraction experiments confirmed for melts of numerous pure metals [6–8] and some alloys with a moderate difference of the atomic radii of the components [9, 10] that the short-range order of the liquid is dominated by icosahedral aggregates. However, most glass-forming alloy systems are characterized by a large disparity of the atomic radii of the components. Moreover, for alloys also the interactions between the different atomic species vary. Both may result to the preference for aggregates of a structure different from the icosahedral one in glass-forming metallic melts [11]. Because of these reasons the short-range order of glass-forming alloys in the liquid and in the glassy state has been subject of considerable research effort, experimentally [12–15] or by molecular dynamics simulations [16–20]. While some authors [12, 13, 15–17, 21] report indications for a decisive degree of icosahedral short-range order in glass-forming alloy melts, other studies [18–20] suggest that their short-range order is not dominated by one type of aggregates but consists of a large variety of different structures. Most of the experimental studies on the short-range order in glass-forming melts suffer from the fact that only total X-ray structure factors were measured. However, for a conclusive analysis of the short-range structure of alloy melts partial structure factors must be determined. In this work results of experimental diffraction studies on binary glass-forming liquids consisting of an early and a late transition metal are reviewed, in which partial structure factors have been directly experimentally determined. We will show that the short-range order of these liquids is not dominated by an icosahedral short-range order.

Concerning the atomic dynamics in metallic melts, classical measurements of diffusion coefficients, e.g. using the long-capillary method [22], are often hampered by buoyancy-driven convective flow and chemical reactions of the melt with the capillary. For these reasons experimental diffusion data in liquid alloys are rare, especially over large temperature intervals. On the other hand also the metastable regime of an undercooled melt that is of special importance for glass-formation is not accessible by such techniques due to heterogeneous nucleation at container walls. Quasielastic neutron scattering (QENS) combined with containerless processing techniques enables the precise measurement of self-diffusion coefficients of incoherently scattering atoms even for deeply undercooled melts [23]. Here we present systematic measurement of self-diffusion coefficients for different metallic glass-forming melts measured by quasielastic neutron scattering.

In order to analyse the structure-dynamics relationship calculations in the framework of MCT are performed. We show that taking partial structure factors measured for binary glass-forming alloys, MCT is able to correctly predict relative changes of dynamical quantities like e.g. the temperature dependence of the self-diffusion coefficients or the coupling behavior of the self-diffusion coefficients of the different alloy components as a function of the alloy composition.

Experimental

Many glass-forming alloys consist of chemically highly reactive components like e.g. Zr or Hf. Therefore experiments in a container are often hampered by reactions of the sample with crucible materials. These problems can be circumvented by application of containerless levitation techniques [24–26] enabling studies of liquids in a broad temperature range. On the one hand high temperatures above 2500 K can be reached. On the other hand, by suppression of heterogeneous nucleation at container walls or impurity sites levitation techniques enable to access even the metastable regime of an undercooled liquid at temperatures several 100 K below the melting temperature. If utilized in scattering experiments, containerless processing offers the additional

advantage that the background signal is reduced due to the avoidance of scattering at crucible materials, resulting to an excellent signal to background ratio. For the scattering experiments on the short-range order and on the atomic dynamics of metallic melts that are described in this work, two different containerless processing techniques are employed, the electromagnetic and the electrostatic levitation technique.

Electromagnetic levitation

The scattering experiments on electromagnetically levitated melts were performed in a device that has been specially designed for this purpose [27, 28]. A roughly spherical, electrically conductive sample, 6–10 mm in diameter, is processed within an inhomogeneous electromagnetic radio frequency field of a levitation coil system. This leads to the induction of eddy currents into the specimen. The interaction of the eddy currents with the inhomogeneous magnetic field of the levitation coil creates a force that acts on the sample. In order to levitate the sample, this force is adjusted such that the gravitational force is compensated. Moreover, the eddy currents lead to an inductive heating of the specimen, which is utilized for melting of the sample. The levitation coil is powered by a semiconductor based RF-generator with a maximum power output of 5 kW and a typical frequency of about 150 kHz.

Sample and coil are located in a vacuum chamber, which is evacuated to a pressure of 10^{-7} mbar with a turbo-molecular pump. Afterwards the chamber is backfilled with inert gas (He, Ar or a He/(4 %)H₂ mixture) of 99.9999 % purity that is further purified using a Messer Griesheim Oxisorb cartridge and a liquid nitrogen cold trap.

The sample temperature is measured through a window from above by a pyrometer that is calibrated at the melting temperature of the sample. The accuracy of the temperature measurement is estimated to ± 5 K. The temperature of the sample is controlled by adjusting the power of the RF generator and/or by varying the flow of cooling gas over the sample surface. The gas flow is created by a nozzle of Al₂O₃ or fused silica that is installed below the sample and is regulated by a flow control valve.

The levitation chamber is equipped with an Aluminum window with 1.5 mm thickness through which the primary beam of neutron or high-energy synchrotron radiation enters into the chamber and the diffracted radiation leaves the chamber in order to be counted by a detector. The window covers an angle of 200° around the vertical axis of the levitation furnace. A system of slits and shields of absorbing materials is installed inside and outside the levitation chamber in order to reduce background scattering [27].

Electrostatic levitation

For performing scattering experiments with neutron- or synchrotron radiation also a dedicated electrostatic levitation furnace has been developed [26, 29]. Here a positively charged sample is levitated in the electrostatic field of two vertically arranged electrodes. Two pairs of side electrodes are employed to control the horizontal sample position. In order to ensure high purity environmental conditions, the electrode system is installed within an ultra-high vacuum (UHV) chamber that can be evacuated with a turbo molecular pump into the pressure regime of 10^{-8} mbar.

In order to monitor the sample position, the specimen is illuminated by two crossed expanded beams of red lasers. The shadow casted by the sample in the laser beams is detected by two-dimensional position sensitive Si-photodetectors. The sample position signals produced by these detectors are the input for a closed-loop sample position control algorithm [30] that regulates the high voltages supplied to the electrodes on a millisecond timescale. The main levitation force is generated utilizing a high-voltage amplifier with a maximum output voltage of 40 kV that powers the pair of vertical electrodes. For horizontal position control four horizontal electrodes are used that are driven by separate 3 kV bipolar high-voltage amplifiers. The specimen is heated by use of two 75 W infrared fiber-coupled diode laser with 810 nm wavelength. The sample temperature is measured with a pyrometer that is again calibrated at the melting temperature.

In order to compensate charge losses during heating up of the sample before charging by thermionic emission sets in at elevated temperatures, the specimen is illuminated by ultraviolet light, which recharges the sample by means of the photoelectric effect.

For performing scattering experiments with neutron- or high-energy synchrotron radiation, the facility is equipped with a window of Al through which the primary radiation can enter into the vacuum chamber and the scattered intensity can exit the chamber in order to be acquired with a detector. Similar as for the electromagnetic levitation facility, also here a system of slits and shields of absorbing materials is installed in order to reduce background scattering [29].

Scattering experiments

In order to investigate the short-range order of glass-forming melts that were processed by electromagnetic or electrostatic levitation, the static structure factors of the melts were measured by elastic neutron scattering or diffraction of synchrotron radiation. The elastic neutron scattering experiments were performed at the high-intensity two-axis diffractometer D20 of the Institut Laue–Langevin (ILL) in Grenoble, France, using a wavelength of the incident neutrons of $\lambda = 0.94 \text{ \AA}$. Information on the experimental setup is given in refs. [27–29] and on the data treatment procedure in ref. [27].

The atomic dynamics of containerlessly processed glass-forming melts processed by electromagnetic or electrostatic levitation were studied by quasielastic neutron scattering at the time-of-flight spectrometer TOFTOF [31] of the Munich research reactor (FRM II) in Garching, Germany. Depending on the investigated alloys, wavelengths in the range $5.1\text{--}7.0 \text{ \AA}$ were used. The instrumental energy resolution was in the range of $60\text{--}100 \text{ \mu eV}$.

X-ray diffraction studies on electrostatically levitated melts on the short-range order were performed at beamline BW5 of the Hasylab at the German electron synchrotron (DESY) using monochromatic X-rays of 100 keV energy and a two dimensional flat panel detector. One dimensional calibrated and dark current corrected intensity spectra have been determined from the measured two dimensional intensity data by application of the FIT2D [32, 33] software. From the intensity data the total structure factors are calculated after subtraction of the background measured with the empty levitator, and correcting for self-absorption, multiple scattering, Compton scattering, polarization, and oblique incidence by use of the PDFgetX2 [34] software package.

Results and discussion

Short-range order

As outlined before, for conclusive investigations of the short-range order of alloy melts partial structure factors are required. In order to determine the full set of partial structure factors, for the case of a binary alloy three diffraction experiments with a different scattering contrast of the alloy components are necessary. One possibility of varying the scattering contrast is offered by the isotopic substitution technique in combination with neutron scattering. Here the different neutron scattering lengths of the isotopes of one element are utilized for contrast variation. Another way to vary the scattering contrast is offered by the differences in the scattering cross-sections if different types of radiation are used for scattering experiments, e.g. neutrons or X-rays. A combination of neutron and X-ray diffraction was applied for instance for studies of the short-range order in Zr–Cu [35] and Zr–Pd [36] melts. As an example for isotopic substitution studies, here we present an investigation in which all partial structure factors of $\text{Zr}_{50}\text{Ni}_{50}$ melts are determined by elastic neutron scattering.

Samples of $\text{Zr}_{50}\text{Ni}_{50}$ alloys roughly 0.5 g in mass were prepared from the pure elements under an Ar-atmosphere (purity 99.9999%) by arc melting. The specimens were prepared using ^{60}Ni , ^{58}Ni , and Ni of natural isotopic composition in order to determine the partial static structure factors.

For investigation of the SRO in liquid $\text{Zr}_{50}\text{Ni}_{50}$ we have measured the total structure factors, $S(Q)$, of three $\text{Zr}_{50}\text{Ni}_{50}$ molten samples prepared with natural Ni, ^{58}Ni , and ^{60}Ni by elastic neutron scattering combined with electrostatic levitation at temperatures of 1445 K and 1665 K. These temperatures are below and above the liquidus temperature of $T_L = 1533$ K [37]. As shown in Fig. 1, significant differences between the three total structure factors are found, indicating a pronounced degree of chemical order in the liquids. In order to obtain information on the topological and chemical structure of the melts, partial static structure factors have been calculated from the total structure factors within the Bhatia–Thornton [39] and the Faber–Ziman formalism [40]. The Bhatia–Thornton formalism defines three partial static structure factors: $S_{NN}(Q)$ describes the topological short-range order of the melt, $S_{CC}(Q)$ the chemical short-range order, and $S_{NC}(Q)$ the correlation of number density and chemical composition. Within the Faber–Ziman formalism the three partial static structure factors $S_{\text{ZrZr}}(Q)$, $S_{\text{ZrNi}}(Q)$, and $S_{\text{NiNi}}(Q)$ describe the contributions to $S(Q)$ that result from the three different types of atomic pairs (Zr–Zr, Zr–Ni and Ni–Ni). The Bhatia–Thornton partial structure factors are shown in Fig. 2 and the Faber–Ziman partial structure factors in Fig. 3. Obviously, the prepeaks visible in the total structure factors of Fig. 1 below $2 \text{ \AA}^{-1}$ result from maxima of the partial structure factors S_{CC} and S_{NiNi} . Hence, they are a consequence of chemical ordering. The variation of the partial structure factors with the temperature is quite small.

Fig. 1: Total structure factors measured by neutron scattering for liquid $\text{Zr}_{50}\text{Ni}_{50}$ prepared with different Ni isotopes at a temperature of $T = 1665$ K [38]. The curves are shifted along the vertical axis.

Fig. 2: Partial Bhatia–Thornton structure factors S_{NN} , S_{CC} and S_{NC} for liquid $\text{Zr}_{50}\text{Ni}_{50}$ at $T = 1665$ K (red) and $T = 1445$ K (blue). The curves are shifted along the vertical axis.

Fig. 3: Partial Faber-Ziman structure factors S_{ZrZr} , S_{ZrNi} and S_{NiNi} for liquid $Zr_{50}Ni_{50}$ at $T=1665$ K (red) and $T=1445$ K (blue) [38]. The curves are shifted along the vertical axis.

The partial pair correlation functions, $g_{NN}(r)$, $g_{CC}(r)$, $g_{NC}(r)$, $g_{ZrZr}(r)$, $g_{NiNi}(r)$, and $g_{ZrNi}(r)$ are calculated by Fourier transformation from the partial static structure factors. These are shown in Figs. 4 and 5. Some small oscillations visible in the partial pair correlation functions are artifacts resulting from the limited Q -range available for Fourier transformation.

Noteworthy is the pronounced minimum of g_{CC} at $r \approx 2.7$ Å that becomes slightly more pronounced with decreasing temperature. This minimum indicates a chemical order that is characterized by a preference for the formation of heterogeneous Ni–Zr nearest neighbor pairs in the melt. The preference for the formation of heterogeneous nearest neighbor pairs is supported by the fact that the first maximum of the Faber–Ziman partial pair correlation function $g_{NiZr}(r)$ is considerably larger than the first maxima of $g_{ZrZr}(r)$ and $g_{NiNi}(r)$. The positions of the first maxima of $g_{NN}(r)$, $g_{ZrZr}(r)$, $g_{NiNi}(r)$, and $g_{ZrNi}(r)$ correspond to the nearest neighbor distances for the different types of atomic pairs. They are compiled in Table 1 for $Zr_{50}Ni_{50}$ and other binary glass-forming melts consisting of an early (Hf, Nb, Zr) and a late (Cu, Ni, Pd) transition metal.

When comparing the nearest neighbor distances with the atomic Goldschmidt radii of the elements ($R_G(Ni) = 1.24$ Å and $R_G(Zr) = 1.60$ Å) [43], we find that for $Zr_{50}Ni_{50}$ the nearest neighbor distance d_{ZrZr} is about 2% larger than twice the Goldschmidt radius of Zr. Moreover, the Zr–Ni nearest neighbor distances d_{ZrNi} are

Fig. 4: Partial Bhatia-Thornton pair correlation functions g_{NN} , g_{CC} and g_{NC} for liquid $Zr_{50}Ni_{50}$ at $T=1665$ K (red) and $T=1445$ K (blue). The curves are shifted along the vertical axis.

Fig. 5: Partial Faber-Ziman pair correlation functions g_{ZrZr} , g_{ZrNi} and g_{NiNi} for liquid $Zr_{50}Ni_{50}$ at $T=1665$ K (red) and $T=1445$ K (blue). The curves are shifted along the vertical axis.

smaller by about 5 % compared to $R_G(Ni) + R_G(Zr)$. This contraction of the Zr–Ni nearest neighbor distance d_{ZrNi} is reminiscent of a strong interaction between Zr and Ni atoms that gives rise to the observed chemical short-range order in liquid $Zr_{50}Ni_{50}$.

Table 1 also gives the nearest neighbor coordination numbers, Z_{AB} ($A, B=N, Hf, Nb, Ni, Zr$). Please note that, as in the nomenclature by Bhatia and Thornton [39], N refers to the particle number but not to the element nitrogen. The partial coordination numbers are calculated by integrating the first peak of the partial radial distribution function $4\pi c_B \rho_N r^2 g_{AB}(r)$ between its first and second minimum. Here ρ_N denotes the number density and c_B the concentration of the alloy component B . Measurements of the density of liquid $Zr_{50}Ni_{50}$ as a function of the temperature showed a linear temperature dependence of the density expressed by $\rho(T) = (7.67 - 3.77 \cdot 10^{-4} K^{-1} T) \text{ g cm}^{-3}$ [44], which gives the following expression for the temperature dependence of the number density: $\rho_N = (0.062 - 3.03 \cdot 10^{-6} K^{-1} T) \text{ at.}/\text{\AA}^3$.

The coordination numbers Z_{AB} determined from the Faber–Ziman pair correlation functions give the average number of nearest neighbors of type A around an atom of type B . The nearest neighbor coordination number Z_{NN} that is calculated from the Bhatia–Thornton pair correlation function g_{NN} describes the average number of nearest neighbors of an arbitrary atom without distinguishing the different types of atoms. Z_{NN} should equal the average coordination number $\langle Z \rangle = c_A(Z_{AA} + Z_{BA}) + c_B(Z_{BB} + Z_{AB})$ inferred from the Faber–Ziman partial coordination numbers. Minor deviations can be explained by errors resulting from the wiggly artifacts visible in the pair correlation functions as mentioned above.

In Table 1 nearest neighbor coordination numbers Z_{NN} are compiled for different binary glass-forming alloys consisting of an early and a late transition metal. In most cases the values of Z_{NN} are considerably larger than 13. This means that they are significantly higher than the typical values of $Z_{NN} \approx 12$ reported for melts of pure metallic elements such as Ni [6], Fe [6], Co [8], and Zr [6]. The high coordination numbers found for most of the binary glass-forming melts provide direct evidence that the short-range order of these liquids cannot be dominated by icosahedral aggregates, because a dominant icosahedral short-range order (as well as one of fcc- or hcp type) is characterized by a coordination number of 12. However, for $Zr_{50}Ni_{50}$ the coordination numbers are only slightly larger than the value of 12 ($Z_{NN} = 13.0$ at $T = 1445$ K and $Z_{NN} = 12.6$ at $T = 1665$ K). For a more detailed analysis of the topological SRO in melts beyond the simple determination of coordination numbers, one may model the measured $S_{NN}(Q)$ in the range of large momentum transfer Q by assuming that the short-range order is dominated by one type of structural units as described in detail in [45, 46]. An attempt to describe the measured S_{NN} of $Zr_{50}Ni_{50}$ at $T = 1445$ K under assumption of an icosahedral short-range order is shown in Fig. 6. Here, the model parameters have been adjusted such that the oscillation at about $8 \text{ \AA}^{-1}$ is reasonably well reproduced. Nevertheless, the other oscillations are out of phase, demonstrating that also liquid $Zr_{50}Ni_{50}$ is not characterized by a predominant icosahedral short-range order. Also for a dodecahedral,

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 ($A = \text{N, Hf, Nb, Zr; B = N, Cu, Ni, Pd}$).

	$T [\text{K}]$	$d_{AA} [\text{\AA}]$	$d_{AB} [\text{\AA}]$	$d_{BB} [\text{\AA}]$	$d_{AB} [\text{\AA}]$	Z_{AA}	Z_{BB}	Z_{AB}	Z_{BA}	$\langle Z \rangle$	Ref.
$\text{Hf}_{33}\text{Ni}_{65}$	1510	2.62 ± 0.02	3.15 ± 0.02	2.56 ± 0.02	2.65 ± 0.02	13.3 ± 0.5	6.2 ± 0.5	5.6 ± 0.5	10.4 ± 0.5	13.2 ± 0.5	[41]
	1615	2.62 ± 0.02	3.18 ± 0.02	2.56 ± 0.02	2.66 ± 0.02	13.1 ± 0.5	6.3 ± 0.5	5.4 ± 0.5	10.1 ± 0.5	13.0 ± 0.5	[41]
$\text{Nb}_{40.5}\text{Ni}_{59.5}$	1495	2.61 ± 0.02	3.00 ± 0.02	2.51 ± 0.02	2.64 ± 0.02	14.3 ± 0.5	6.8 ± 0.5	6.6 ± 0.5	9.6 ± 0.5	14.4 ± 0.5	[42]
$\text{Zr}_{66.7}\text{Cu}_{33.3}$	1325	2.95 ± 0.01				13.7 ± 0.5					[35]
$\text{Zr}_{50}\text{Cu}_{50}$	1175	2.79 ± 0.01				13.8 ± 0.5					[35]
	1280	2.79 ± 0.01				13.6 ± 0.5					[35]
$\text{Zr}_{41.2}\text{Cu}_{58.8}$	1110	2.75 ± 0.01				13.8 ± 0.5					[35]
	1260	2.74 ± 0.01				13.6 ± 0.5					[35]
$\text{Zr}_{64}\text{Ni}_{36}$	1375	2.80 ± 0.02	3.20 ± 0.02	2.55 ± 0.02	2.69 ± 0.02	13.8 ± 0.5	2.5 ± 0.5	8.8 ± 0.5	5.0 ± 0.5	13.9 ± 0.5	[14]
$\text{Zr}_{50}\text{Ni}_{50}$	1445	2.69 ± 0.02	3.26 ± 0.02	2.54 ± 0.02	2.69 ± 0.02	13.0 ± 0.5	3.4 ± 0.5	7.1 ± 0.5	7.1 ± 0.5	13.0 ± 0.5	[38]
	1665	2.68 ± 0.02	3.25 ± 0.02	2.52 ± 0.02	2.68 ± 0.02	12.8 ± 0.5	3.4 ± 0.5	6.9 ± 0.5	6.9 ± 0.5	12.6 ± 0.5	[38]
$\text{Zr}_{36}\text{Ni}_{64}$	1385	2.63 ± 0.02	3.31 ± 0.02	2.51 ± 0.02	2.70 ± 0.02	13.8 ± 0.5	6.3 ± 0.5	5.9 ± 0.5	10.4 ± 0.5	13.8 ± 0.5	[38]
$\text{Zr}_{66.7}\text{Pd}_{33.3}$	1105	2.97 ± 0.01				13.8 ± 0.5					[36]
	1375	2.95 ± 0.01				13.8 ± 0.5					[36]

Fig. 6: Measured (blue dots) and modelled (red line) S_{NN} of liquid $Zr_{50}Ni_{50}$ at a temperature of $T=1445$ K in the regime of large momentum transfer. For the modelling an icosahedral short-range order is assumed to prevail in the melt and the method described in refs. [45, 46] is used. It is shown that the measured S_{NN} is not well described under the assumption of a dominant icosahedral short-range order.

fcc, hcp or bcc type of SRO the modeled S_{NN} disagree with the experimental data. Obviously, a more complex type of SRO prevails in liquid $Zr_{50}Ni_{50}$. The same conclusions are drawn by a similar analysis for the short-range order in other binary glass-forming melts like $Zr_{50}Cu_{50}$, $Zr_{66.7}Cu_{33.3}$ and $Zr_{41.2}Cu_{58.8}$ [35] and $Zr_{64}Ni_{36}$ [14].

From the partial coordination numbers also the average coordination numbers around the A and B atoms can be calculated: $Z_A = Z_{AA} + Z_{BA}$ and $Z_B = Z_{BB} + Z_{AB}$. For $Zr_{50}Ni_{50}$ melts at $T=1445$ K, for instance, this shows that the smaller Ni atoms are characterized by a nearest neighbor coordination number of $Z_{Ni} = Z_{NiNi} + Z_{ZrNi} = 10.5$, while the larger Zr atoms show a considerably higher coordination number of $Z_{Zr} = Z_{ZrZr} + Z_{NiZr} = 15.5$. This directly implies that the short-range order around the Ni atoms differs from that around the Zr atoms. A similar disparity of the coordination around the different alloy components is found also for the melts of $Zr_{64}Ni_{36}$, $Zr_{36}Ni_{64}$ [41], $Hf_{35}Ni_{65}$ [41] and $Ni_{59.5}Nb_{40.5}$ [42]. This highlights that these glass-forming liquids cannot be characterized by one single type of short-range order. This is confirmed by several molecular dynamics simulations for Zr-based binary glass-forming liquids [18–20] that suggest a large variety of different types of aggregates prevailing in the melt. The structural frustration associated with different types of short-range structures may impede crystallization of the melt and by means of this promote the formation of a metallic glass.

Atomic dynamics

In order to investigate the atomic dynamics, a large variety of glass-forming alloys melts processed by electromagnetic or electrostatic levitation has been investigated by quasielastic neutron scattering. As an example, Fig. 7 shows the quasielastic range of the scattering law $S(Q, \omega)$ for liquid $Zr_{36}Ni_{64}$ at two different temperatures ($T=1350$ K and $T=1650$ K) and at a momentum transfer of $Q=1.0$ Å⁻¹. The quasielastic signals are well described by a Lorentzian function convoluted with the instrumental energy resolution function measured on Vanadium at room temperature (lines in Fig. 7). At constant Q , the full width at half maximum, Γ , of the Lorentzian function decreases with decreasing temperature. If $S(Q, \omega)$ is measured at constant temperature but different Q , a decrease of Γ is found with decreasing Q (see Fig. 8). In the hydrodynamic limit ($Q \rightarrow 0$) the mean self-diffusivity of the incoherently scattering atoms in the melt is related with Γ by $D = \Gamma Q^{-2}/2\hbar$ [47, 48]. For Zr–Ni alloys the measured signal at small Q is dominated by the incoherent scattering of the Ni atoms (incoherent scattering cross sections: $\sigma_{inc}(Ni) = 5.2$ barn, $\sigma_{inc}(Zr) = 0.02$ barn) such that here the Ni self-diffusion is investigated by quasielastic neutron scattering. Hence, a plot of Γ as a function of Q^2 shows a linear behavior at small momentum transfer (Fig. 9) and the slopes of the

Fig. 7: Scattering law $S(Q, \omega)$ of liquid $\text{Zr}_{36}\text{Ni}_{64}$ for $Q = 1.0 \text{ \AA}^{-1}$ at $T = 1350 \text{ K}$ (blue symbols) and $T = 1650 \text{ K}$ (red symbols). The black dashed line gives the instrumental energy resolution.

Fig. 8: Scattering law $S(Q, \omega)$ of liquid $\text{Zr}_{36}\text{Ni}_{64}$ at $T = 1650 \text{ K}$ for momentum transfers of $Q = 0.5 \text{ \AA}^{-1}$ (blue symbols) and $Q = 1 \text{ \AA}^{-1}$ (red symbols). The black dashed line gives the instrumental energy resolution.

linear fits give the Ni self-diffusivities. Deviations from the linear behavior at larger Q result from coherent contributions to the scattered intensity that significantly increase when approaching the maximum of the structure factor.

Figure 10 shows the temperature dependence for the (mean) self-diffusivities of the incoherently scattering alloy components (e.g. Ni, Cu, Ti, or Hf) determined by quasielastic neutron scattering for different glass-forming alloys. At temperatures well above the glass-transition temperature the temperature dependence of the self-diffusivities can be well described by an Arrhenius law $D(T) = D_0 \exp(-E_A/k_B T)$, where E_A is the activation energy for self-diffusion and D_0 the diffusion coefficient in the limit of infinite temperature. As an example the black line in Fig. 10 shows an Arrhenius fit to the Ni self-diffusion data measured for liquid $\text{Zr}_{64}\text{Ni}_{36}$ giving values of $E_A = (0.64 \pm 0.02) \text{ eV}$ and $D_0 = (2.1 \pm 0.3) \times 10^{-7} \text{ m}^2/\text{s}$. At the highest undercoolings, however, deviations from the Arrhenius behavior are visible for $\text{Zr}_{64}\text{Ni}_{36}$ [29]. Even stronger deviations from the Arrhenius behavior are found for melts of the multi-component glass-forming alloy $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ (Vitreloy 1) [50]. Such deviations from the Arrhenius law are predicted by the mode coupling theory (MCT)

Fig. 9: Full width at half maximum, Γ , of the Lorentzian fits to the quasielastic lines as a function of Q^2 for liquid $\text{Zr}_{36}\text{Ni}_{64}$ at four different temperatures.

Fig. 10: Temperature dependence of the (mean) self-diffusion coefficients of the incoherent neutron scatterers (e.g. Ni, Cu, Ti, Hf) in melts of different glass-forming alloys [29, 41, 49–51]. The black solid line is an Arrhenius fit to the data for $\text{Zr}_{64}\text{Ni}_{36}$ at high temperatures with $E_A = (0.64 \pm 0.02)$ eV and $D_0 = (2.1 \pm 0.3) \times 10^{-7}$ m²/s. The gray solid line represents a fit of a potency law to the data for $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ with $T_c = 850$ K and $\gamma = 2.5$ [50].

of the glass transition [4] when the temperature approaches a critical temperature T_c . According to MCT the temperature dependence of the self-diffusivity is described by a potency law: $D(T) \sim [(T - T_c)/T_c]^\gamma$. The mean Ni, Ti and Cu self-diffusivity in $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ is well described by such a potency law with $T_c = 850$ K and $\gamma = 2.5$ [50] (gray line in Fig. 10).

When comparing the diffusivity values measured for Zr–Ni and Zr–Cu, it is noteworthy that at same temperatures the Cu self-diffusivities in the Zr–Cu alloy melts are higher than the Ni self-diffusivities in the corresponding Zr–Ni melts, despite the fact that Zr–Cu shows a better glass-forming ability than Zr–Ni. While in general it is accepted that a low atomic mobility favors glass-formation, this clearly shows that the diffusivity is only one parameter amongst others that influences the glass-forming ability.

The diffusivity values shown in Fig. 10 are measured by quasielastic neutron scattering and consequently these are the (mean) self-diffusivities of the incoherently scattering alloy components (e.g. Ni, Cu, Ti, Hf).

Fig. 11: Temperature dependence of the Ni, Zr, and Hf self-diffusion coefficients measured by a radio tracer technique (RT) [52] or by quasielastic neutron scattering (QENS) [38, 41] for melts of Zr–Ni and Hf–Ni alloys. In case of the $\text{Hf}_{35}\text{Ni}_{65}$ alloy prepared with natural Ni the mean Ni and Hf self-diffusion coefficient is measured, which is however dominated by the Ni self-diffusion. Also shown are the Ni, Zr and Hf self-diffusion coefficients calculated in the framework of the mode coupling theory (MCT) with measured partial structure factors as an input [38, 41].

Because the incoherent neutron cross-sections of Zr and Al are negligible, for the Zr–Ni(–Al) melts these are essentially the Ni self-diffusivities and for the Zr–Cu melts these are the Cu self-diffusivities. In case of Vitreloy 1 a mean value of the self-diffusivity of the incoherently scattering components Ni, Ti and Cu is measured. For the $\text{Hf}_{35}\text{Ni}_{65}$ alloy, both elements show a significant incoherent scattering cross-section ($\sigma_{\text{inc}}(\text{natNi}) = 5.2$ b; $\sigma_{\text{inc}}(\text{Hf}) = 2.6$ b). Nevertheless, because the incoherent scattering cross-section of natural Ni is approximately twice as large as that of Hf and because Ni is also the majority-component, here the measured mean diffusivity is dominated by the Ni self-diffusion.

Due to the vanishing incoherent neutron scattering cross-section of Zr, the Zr self-diffusion coefficients are not accessible by quasielastic neutron scattering. Here a radio tracer technique can be applied for measurements of the self-diffusion coefficients [52]. Recently the Zr and Ni self-diffusion in liquid $\text{Zr}_{64}\text{Ni}_{36}$ and $\text{Zr}_{36}\text{Ni}_{64}$ has been studied using a radio tracer technique by Basuki et al. [52] using ^{57}Co (as a substitution for Ni) and ^{95}Zr atoms as tracers. In Fig. 11 these results are compared with the results obtained for the Ni self-diffusivity obtained by QENS. The values of the Co/Ni self-diffusion coefficients measured with the radio tracer technique are in good agreement with the neutron scattering data. For $\text{Zr}_{64}\text{Ni}_{36}$ the Ni and Zr self-diffusion coefficients are equal, which means that the diffusion of Zr and Ni atoms is coupled. As discussed in ref. [53], this coupling may be explained by the pronounced chemical order experimentally observed by elastic neutron scattering [14]. For the Ni-rich alloy $\text{Zr}_{36}\text{Ni}_{64}$, however, as shown in Fig. 11, the diffusion coefficient determined by the ratio tracer technique for the Zr self-diffusion is considerably smaller than the Ni self-diffusion coefficient [52]. A ratio of $D_{\text{Ni}}/D_{\text{Zr}} = 1.4$ is reported at a temperature of 1388 K. Obviously, there is a decoupling of the dynamics of Zr and Ni when increasing the Ni composition of the alloy, despite the fact that also the Ni-rich alloy shows a pronounced chemical short-range order in the melt.

Due to the fact that Hf shows a non-vanishing incoherent neutron scattering cross-section, QENS allows measuring the Hf self-diffusion in Hf–Ni melts, if the alloys are prepared using the Ni isotope ^{60}Ni that is characterized by a vanishing incoherent scattering cross-section as well as by a small coherent one. As outlined before, if the samples are prepared using natural Ni, the measured mean diffusivity is mainly governed (to about 80 %) by the Ni self-diffusion. Results of such measurements [41] at two different temperatures are also shown in Fig. 11. Similar as for $\text{Zr}_{36}\text{Ni}_{64}$, for $\text{Hf}_{35}\text{Ni}_{65}$ a dynamical decoupling is observed with a ratio of the self-diffusivities of $D_{\text{Ni}}/D_{\text{Hf}} \approx 2$ [41].

Structure-dynamics relationship

In order to analyse the structure-dynamics relationship, the partial static structure factors measured for $\text{Zr}_{64}\text{Ni}_{36}$, $\text{Zr}_{50}\text{Ni}_{50}$, $\text{Zr}_{36}\text{Ni}_{64}$, $\text{Nb}_{40.5}\text{Ni}_{59.5}$ and $\text{Hf}_{35}\text{Ni}_{65}$ were used as an input for MCT to calculate transport coefficients [38, 41]. The Hf, Zr and Ni self-diffusion coefficients calculated by MCT for the Zr–Ni and Hf–Ni alloys are compared in Fig. 11 with the measured values. As discussed in ref. [38], the deviation of the MCT results from the measured data on the absolute scale results from the fact that the temperature enters only as an indirect parameter in MCT calculations. It is however remarkable that the self-diffusivities calculated by MCT for $\text{Zr}_{50}\text{Ni}_{50}$ and $\text{Hf}_{35}\text{Ni}_{65}$ show a similar temperature dependence as the corresponding experimental results. 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 (for $\text{Zr}_{50}\text{Ni}_{50}$ see e.g. Fig. 3), this ability of MCT to reproduce accurately the activation energies for self-diffusion is a remarkable result. The sensitivity to small changes of the partial structure factors also implies that precise measurements of the structure factors are required which can be achieved by utilization of containerless processing techniques that guarantee an excellent signal to background ratio.

In addition to the activation energies for self-diffusions, also the observed coupling/decoupling behavior of the diffusion coefficients is well reproduced by the MCT calculations. For $\text{Zr}_{64}\text{Ni}_{36}$ MCT predicts equal Zr and Ni self-diffusion coefficients (see Fig. 11) as experimentally observed in the radio tracer experiments [52]. For $\text{Zr}_{36}\text{Ni}_{64}$ the radio tracer experiments show a decoupling of the diffusivities with a ratio of the self-diffusion coefficients of $D_{\text{Co}}/D_{\text{Zr}} = 1.4$ (see upper part of Fig. 12). Here also MCT predicts a dynamical decoupling with a slightly higher ratio of $D_{\text{Ni}}/D_{\text{Zr}} = 1.8$. For $\text{Hf}_{35}\text{Ni}_{65}$ the decoupling suggested by the MCT calculations ($D_{\text{Ni}}/D_{\text{Hf}} = 1.8$) is close to the QENS results, which reveal a ratio of the self-diffusivities of $D_{\text{Ni}}/D_{\text{Hf}} \approx 2$ [41].

Static partial structure factors provide only space- and time-averaged structural information of the alloy melt. Nevertheless, this information is sufficient to reveal the dynamical decoupling of the diffusion coefficients as well as the activation energy for self-diffusion when serving as an input for MCT. Hence by a closer inspection of the partial structure factors and of functions (like e.g. the partial pair correlations functions) and parameters inferred from these one may identify structural features that give rise to observed trends for the coupling or decoupling behavior of the diffusion coefficients or for the activation energies. In general the atomic dynamics of alloy melts will not be determined by only one single parameter, but there will be an interplay of different effects. In order to separate different mechanisms that influence the atomic dynamics

Fig. 12: Upper part: Composition dependence of the ratios $D_{\text{Ni}}/D_{\text{Zr}}$, $D_{\text{Ni}}/D_{\text{Hf}}$ and $D_{\text{Ni}}/D_{\text{Nb}}$ for melts of Zr–Ni, Hf–Ni and Nb–Ni as determined by radio tracer measurements (RT) [52], quasielastic neutron scattering (QENS) [41] and MCT calculations [38, 41]. Lower part: Fractions N_{AB} ($A, B = \text{Zr, Hf, Nb, Ni}$) of the different nearest neighbor pairs determined from the partial coordination numbers (Table 1) for melts of Zr–Ni, Hf–Ni and Nb–Ni as a function of the Ni-composition c_{Ni} [38, 41].

it is favorable to compare systems where some important characteristics and properties are similar. $\text{Hf}_{35}\text{Ni}_{65}$ and $\text{Zr}_{36}\text{Ni}_{64}$ nearly have the same stoichiometry, and are characterized by a similar packing fraction, which is known to be a macroscopic property that has a decisive impact on the atomic dynamics [49]. Moreover also the atomic radii of Hf and Zr are similar. Nevertheless, the activation energy for Ni self-diffusion (slope of the curves in Fig. 11) is nearly twice as large for $\text{Hf}_{35}\text{Ni}_{65}$ ($E_A = 1.31 \pm 0.06$ eV [41]) as compared with $\text{Zr}_{36}\text{Ni}_{64}$ ($E_A = 0.76 \pm 0.11$ eV [49]). When comparing the structural characteristics of both melts provided in Table 1, the most striking difference is that the distance of nearest Hf–Hf neighbors ($d_{\text{HfHf}} = 3.15$ Å at $T = 1510$ K) is considerably shorter than the distance of nearest Zr–Zr neighbors ($d_{\text{ZrZr}} = 3.31$ Å). This might be interpreted as a locally higher density of packing of the Hf atoms in $\text{Hf}_{35}\text{Ni}_{65}$ as compared to the Zr atoms in $\text{Zr}_{36}\text{Ni}_{64}$, providing a structural explanation for the higher activation energy for self-diffusion. This demonstrates that not only the macroscopic packing fraction influences the atomic dynamics, but also differences of the atomic packing on the atomic length-scale as described by the partial pair correlation functions must be considered.

Promising parameters that may provide an explanation for the observed composition dependence of the coupling behavior of the self-diffusion coefficients of the alloy components are the fractions of the different atomic nearest-neighbor pairs. These are calculated from the atomic concentrations c_A and the partial coordination numbers Z_{AB} ($A, B = \text{Ni, Zr, Hf, Nb}$) by: $N_{AA} = c_A Z_{AA} / \langle Z \rangle$; $N_{AB} = (c_A Z_{BA} + c_B Z_{AB}) / \langle Z \rangle$. As shown in the lower part of Fig. 12 for the Zr–Ni melts, N_{ZrZr} decreases roughly linearly with increasing Ni concentration from about 48 % for the $\text{Zr}_{64}\text{Ni}_{36}$ melt to about 16 % for the $\text{Zr}_{36}\text{Ni}_{64}$ melt. N_{ZrNi} , however, first increases, but then when a percentage of heterogeneous pairs of about 55 % is reached a saturation is observed. N_{NiNi} increases continuously with increasing Ni content from a rather low value of 7 % for $\text{Zr}_{64}\text{Ni}_{36}$ to a more than four times larger value of 30 % for the $\text{Zr}_{36}\text{Ni}_{64}$ alloy. When increasing the Ni concentration also the ratio $D_{\text{Ni}}/D_{\text{Zr}}$ increases (upper part of Fig. 12). This can be explained by the weaker interaction between Ni–Ni nearest-neighbor pairs as compared with Zr–Ni pairs [54]. When the Ni concentration is increased, the fraction of strongly interacting Zr–Ni pairs N_{ZrNi} is saturated above a certain concentration because the number of Zr atoms is limited. Only the fraction of Ni–Ni pairs N_{NiNi} can increase further. Hence, the saturation of the fraction of heterogeneous nearest neighbor pairs at higher Ni concentrations leads to an increased number of excess less-strongly interacting Ni atoms, which exhibit a higher mobility. This explains the observed decoupling of the self-diffusion coefficients. Similar values for the fractions of the different nearest neighbor pairs as found for the $\text{Zr}_{36}\text{Ni}_{64}$ melt were observed for liquid $\text{Hf}_{35}\text{Ni}_{65}$ [41] (Fig. 12), highlighting that the same mechanism is able to explain also the dynamical decoupling in Hf–Ni. For melts of the glass-forming alloy $\text{Nb}_{40.5}\text{Ni}_{59.5}$ no experimental values for the Nb self-diffusion coefficients are available. Nevertheless, when using measured partial structure factors [42] as an input for MCT calculations, these suggest a dynamical decoupling of the diffusion coefficients with a ratio of $D_{\text{Ni}}/D_{\text{Nb}} = 1.4$ [41]. Also here the fractions of the different neighbor pairs are similar as those found for $\text{Zr}_{36}\text{Ni}_{64}$ and $\text{Hf}_{35}\text{Ni}_{65}$ (Fig. 12), highlighting that the saturation of the fraction of strongly interacting nearest neighbor pairs may provide an explanation for the dynamical decoupling observed also in melts of other systems, including bulk metallic glasses [55].

Conclusions

The application of containerless processing techniques, like electromagnetic or electrostatic levitation, allows performing scattering experiments with an excellent signal to background ratio even for chemically reactive melts and in the metastable regime of an undercooled liquid at temperatures below the melting temperature.

We have determined partial structure factors of different levitated melts of binary glass-forming alloys consisting of an early and a late transition metal by neutron diffraction using the technique of isotopic substitution or by a combination of X-ray and neutron scattering. The melts are characterized by large nearest neighbor coordination numbers and exhibit a pronounced chemical short-range order with affinity for the formation of heterogeneous nearest neighbor pairs. Different from melts of pure metals, we found that the short-range order of the investigated glass-forming liquids is not dominated by icosahedral aggregates. There are indications that the short-range order is characterized by various types of aggregates, including structures

of high coordination numbers. The pronounced chemical order, the large local density of packing and structural frustration, amongst others, may be key properties promoting glass-formation.

The atomic dynamics of various glass-forming melts has been studied by means of quasielastic neutron scattering. Interestingly, Zr–Cu melts show larger diffusivity values at same temperatures as compared with the corresponding Zr–Ni melts, despite the better glass-forming ability of the Zr–Cu alloys. While in general it is accepted that a low atomic mobility favors glass-formation, this clearly shows that the diffusivity is only one parameter amongst others that influences the glass-forming ability.

For an analysis of the relation between short-range structure and atomic dynamics, MCT calculations were performed using measured partial structure factors as an input to calculate transport coefficients. The MCT results show a remarkably good agreement with the experimental results concerning the activation energies for self-diffusion and the coupling/decoupling behavior of the diffusion coefficients of the different alloy components. This highlights that the time- and space-averaged structural information provided by measured partial structure factors is sufficient to describe the temperature dependency of self-diffusion coefficients as well as the relative dynamical behavior between the different alloy components.

We have identified that the increased activation energy for self-diffusion observed for $\text{Hf}_{35}\text{Ni}_{65}$ as compared with $\text{Zr}_{36}\text{Ni}_{64}$ can be explained by a higher local density of packing for the Hf atoms in $\text{Hf}_{35}\text{Ni}_{65}$ compared to that of the Zr atoms in $\text{Zr}_{36}\text{Ni}_{64}$, although the overall average packing fraction of the melts is similar. As a generic effect in the Ni-rich binary Zr–Ni, Hf–Ni and Nb–Ni melts, we find a dynamical decoupling of the diffusivities of the alloy components although the investigated melts show pronounced chemical ordering. This dynamical decoupling at high Ni concentrations can be explained by a saturation of the fraction of strongly interacting heterogeneous neighbor pairs accompanied by an increased amount for less strongly bound and thus faster diffusing Ni atoms. This mechanism is not restricted to special atomic interactions or a specific type of short-range order and thus might be extended to other metallic melts with preferred heterogeneous nearest-neighbor pairs.

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