

Cranfield University



Martin E. Stiehler

**Caught in the act: The structural pathway of liquid
metals to vitrification monitored in situ by
synchrotron X-ray diffraction**

School of Aerospace, Transport and Manufacturing

PhD Thesis

Supervisors:

Dr. Konstantinos Georgarakis
Prof. Mark R. Jolly

September 2021

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This thesis is submitted in partial fulfilment of the requirements for the
degree of
Doctor of Philosophy

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Abstract

When a metallic melt is undercooled fast enough below its liquidus temperature, crystallisation can be avoided and a metallic glass, i.e. a metallic solid with amorphous structure, be formed. This kind of solidification is called vitrification. The prerequisites for this phenomenon are still not clear. An extensive review of the available relevant literature was carried out. To reveal the structural changes taking place at the atomic scale during undercooling and vitrification, data obtained by ultrafast synchrotron X-ray diffraction during aerodynamic-levitation experiments of different metallic-glass forming liquids was analysed. The complete pathway from temperatures well above the liquidus temperature during undercooling and vitrification down to temperatures well below the glass-transition temperature T_g was studied. During undercooling, a non-linear evolution of structural metrics in real as well as in reciprocal space takes place. Especially the height of the first maximum in the structure factor can be described by a structural analogue to the Curie-Weiss law. This behaviour was also found in published data re-analysed here. Indications of universal behaviour among the investigated alloys below a certain temperature as well as for a liquid-liquid crossover in $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ were found. Small differences in the temperature dependence of the structural behaviour among the different alloys are possibly related to their different glass-forming abilities. To facilitate the analysis of the real-space structure the novel concept of the anti-shell was introduced. Temperature affects different length scales differently. Below T_g the structural behaviour is dominated by the Debye-Waller factor as well as by normal thermal-expansion behaviour. Above T_g an apparent negative thermal expansion of the first nearest-neighbour distance can be attributed to the influence of the structure-forming processes. In addition to short- and medium-range order, a third structural range for distances beyond the third nearest-neighbour is proposed. A disordering of the atomic structure of metallic glasses by the introduction of further alloying elements, facilitated by emergent effects among the components, could be demonstrated. The importance of the influence of global electronic interactions on structure formation was shown as well as their limitation to distances beyond the third nearest-neighbour.

Keywords

Aluminium alloys, Titanium alloys, Zirconium alloys, metallic glasses, ultrafast diffraction, synchrotron diffraction, electronic structure, global electronic effects, pseudogap, glass-forming ability, undercooling, glass transition, liquid-liquid transitions, emergence, anti-shell, negative thermal expansion

Acknowledgements

This thesis has been made possible by the support of many people. First and foremost, my special thanks go out to my supervisors Dr. Kostas Georgarakis and Prof. Mark Jolly. Despite mile-long todo lists Kostas was always available for a discussion. I'm not really sure how he managed to do that as he had to supervise many other students in parallel. His knowledge in the field of metallic glasses was always inspiring.

Experimental support during synchrotron X-ray-diffraction by the teams of beamlines ID11, ID13 and ID15 at the ESRF as well as beamline I15-1 at the Diamond Light Source is gratefully acknowledged.

Thanks goes also to Steve Pope, Tracey Roberts and Christine Kimpton for sample cutting, mounting as well as their support with in-house XRD measurements, to Nikos Panagiotopoulos and Yurii Ivanov at the University of Cambridge for DSC and TEM measurements as well as to John Alissandratos and Rylan Cox for letting me use equipment for sample preparation in their laboratory.

For their help in turning sketches into real parts I'd like to thank Graham Hartwell, Paul Wakefield and Derek Brown.

I also want to acknowledge Alan Heaume, Tim Pryor, Tony Gray, Kevin Green, Fred John, Marion Collinson, Ian Hakon and Tony Parker who facilitated working in the CRIMSON laboratory.

Many thanks also go to Liz Wade, Claire Steed and Charmaine Bassindale for their invaluable support in bureaucratic matters as well as to Emanuele Pagone, Michalis Papanikolaou, Kostas Salonitis, John Patsavellas, Osama Elzoubi, Yousef Haddad and Anjy Alzrigat who helped making life in B50 enjoyable.

The Engineering and Physical Sciences Research Council (EPSRC) is acknowledged for financial support of my project "Bulk Metallic Glasses: Revealing the Structural Pathway of Liquid Metals to Vitrification" (ref. 2043971) in the framework of the EPSRC Doctoral Training Partnership with Cranfield University (EP/N509450/1).

Finally, I would like to thank my parents for their constant support over the years.

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Nomenclature

Acronyms

Acronyms used in this thesis are listed below together with their definitions. Chemical elements are abbreviated by their usual symbols and not shown in the list.

2D	two-dimensional
3D	three-dimensional
a	amorphous
AAC	amorphous-to-amorphous crossover
AAPT	amorphous-to-amorphous phase transition
AAT	amorphous-to-amorphous transition
AIMD	ab initio molecular dynamic (simulation)
a.m.	arc-melting
AS	anti-shell
AXS	anomalous X-ray scattering
b.m.	ball milling
BMG	bulk metallic glass
c	crystalline
Cb	cuboctahedral clusters
CCD	charge-coupled device
CNL	conical-nozzle levitation
CNT	classical nucleation theory
CRR	cooperatively rearranging region
CSRO	chemical short range order
d.c.	results obtained from a data collection
DFT	density functional theory
DOI	digital object identifier
DOS	density of states
DSC	differential scanning calorimetry
EDX	energy dispersive X-ray spectroscopy
EML	electromagnetic levitation
ERO	extended range order
ESL	electrostatic levitation
ESRF	European Synchrotron Radiation Facility
EXAFS	extended x-ray fine structure
EXELFS	extended electron energy loss fine structure
f.e.	flash evaporation (as production method)
FEL	free-electron laser
FIB	focussed ion beam
FSC	fragile-to-strong crossover
FST	fragile-to-strong transition
FT	FOURIER transform
FWHM	full width at half maximum (symbol Γ)
GFA	glass forming ability

gl	glassy
HAADF	high-angle annular dark-field imaging
HTL	high temperature liquid
i.c.	injection casting (as production method)
ICO	icosahedral clusters
IPES	inverse photo electron spectroscopy
ISS	International Space Station
L	laser (as heating method)
l	liquid
LAMMPS	large-scale atomic/molecular massively parallel simulator
LDA	local density approximation
LLC	liquid-to-liquid crossover
LLPT	liquid-to-liquid phase transition
LLT	liquid-to-liquid transition
LTL	low temperature liquid
MCT	mode-coupling theory
MD	molecular dynamics (simulation)
MG	metallic glass
MGG	metallic glacial glass
MRO	medium range order
m.s.	melt spinning (as production method)
NMR	nuclear magnetic resonance
NN	nearest neighbour
PDF	pair distribution function
PES	photo electron spectroscopy
RDF	radial distribution function
RhC	RhD and Cb clusters
RhD	rhombic dodecahedral clusters
RMC	reverse Monte-Carlo (simulation)
RT	room temperature
SANS	small-angle neutron scattering
SAXS	small-angle X-ray scattering
SNR	signal-to-noise ratio
SPO	spherical periodical order
SRO	short range order
UCL	undercooled liquid
VP	VORONOI polyhedr(onal)
TM	transition metal
TTT	time temperature transformation
WANS	wide-angle neutron scattering
WAXS	wide-angle X-ray scattering
XRD	X-ray diffraction
XFEL	X-ray free-electron laser

Symbols

The nomenclature used in this thesis generally follows that commonly used in condensed-matter physics, especially in the field of metallic glasses.

C	quasi CURIE-constant [Ryu19]
c	speed of light (in vacuum)
c_i	concentration of component i in an alloy
D	fragility parameter in the VOGEL-FULCHER-TAMANN equation
d_{at}	interatomic distance of an elemental pair
d_c	critical casting diameter (a measure of GFA)
δ_{ij}	KRONECKER delta
E	energy
E_A	activation energy
E_F	FERMI energy
E_i	energy of incident X-ray beam
e	elementary charge
e	EULER's constant
η	viscosity
η_0	viscosity at infinite temperature
f_i	X-ray atomic form factor of component i in an alloy
$f(x)$	generic (structure) function
Γ	FWHM of a peak
$G(r)$	reduced pair distribution function
$G(r, T)$	temperature-dependent reduced pair distribution function
$g(r)$	pair correlation function
$g(r, T)$	temperature-dependent pair correlation function
h	PLANCK's constant
$\hbar$	reduced PLANCK's constant
$\Delta H_{\text{mix}}, \Delta H^{\text{mix}}$	enthalpy of mixing (taken from [Tak05])
H_X	enthalpy of crystallisation
$\vec{k}$	wavevector
k	wavenumber
k_B	BOLTZMANN constant
$\vec{k}_i$	wavevector of an incident beam
k_F	FERMI wavenumber
$k_i = \vec{k}_i $	modulus of the wavevector of an incident beam
$\vec{k}_s$	wavevector of a scattered (diffracted) beam
$k_s = \vec{k}_s $	modulus of the wavevector of a scattered (diffracted) beam
Λ	measure of asymmetry of a peak
λ_i	wavelength of incident X-ray beam
λ_{Fr}	FRIEDEL wavelength
M	molar mass
m	fragility
m_e	mass of the electron
m_{str}	structural fragility
n	number of NN shell
$N(E_F)$	electronic density of states at the FERMI energy
$N_0(E_F)$	electronic density of states at the FERMI energy (nearly free electron model)
N_C	coordination number

Ω_0	atomic volume
$\bar{\Omega}_0$	average atomic volume
P	pair probability
$\vec{Q}$	scattering vector
$Q = \vec{Q} $	modulus of the scattering vector
Q_1	position of the peak for the first halo of $S(Q)$
$Q_{1,\text{at}}$	Q_1 estimated from atomic radius
$Q_{1,\text{c}}$	position of the centroid of the peak for the first halo of $S(Q)$
$Q_{1,\text{m}}$	position of the maximum of the peak for the first halo of $S(Q)$
Q_{max}	upper integration limit for FOURIER transform
r	distance from a centre atom
$R_{A/B}$	ratio of atomic size of atoms A and B
r_A	radius of atom A
r_{at}	atomic radius (taken from [Mir10])
r_B	radius of atom B
r_n	distance of the n -th NN shell from $r = 0$ Å
$r_{n,\text{c}}$	distance of the centroid of the n -th NN shell
$r_{n,\text{m}}$	distance of the maximum of the n -th NN shell
$R(r)$	radial distribution function
ρ_0	average particle number density
$\rho(r)$	local atomic pair density (atomic pair density function)
$S(Q)$	static structure factor
$S(Q, T)$	temperature-dependent static structure factor
σ^2	variance (second moment) of a peak
T	temperature
$T_A = 2 T_g$	onset temperature for cooperativity [Blo15]
$T_D = 1.4 T_g$	backbone temperature [Sok16]
T_{end}	end temperature of the pathway in an experiment
T_g	glass-transition temperature
T_{IG}	ideal-glass temperature [Ryu19]
T_l	liquidus temperature
T_{LLC}	temperature of an LLC
T_m	melting temperature
T_{max}	highest temperature of the sample
$T_{\text{rg}} = T_g / T_l$	<i>reduced</i> glass-transition temperature
T_{start}	start temperature of the pathway in an experiment
T_X	crystallisation temperature
$\Delta T_X = T_X - T_g$	undercooled-liquid region
$T(t)$	time-dependent sample temperature
$\dot{T}(t)$	temperature rate
θ	scattering angle
$\bar{\Theta}_D$	composition-averaged DEBYE-temperature
$\Theta_{D,\text{g}}$	quasi DEBYE-temperature in the glassy state
$\Theta_{D,\text{l}}$	quasi DEBYE-temperature in the liquid state
V	volume
W_{ij}	FABER-ZIMAN weight factor for atomic pairs i - j
ξ_s	structural coherence length
Z	valence
$\bar{Z}$	average valence

1 Introduction

Unaware of their amorphous atomic structure humankind has used glasses for various purposes since millennia. Compared to other glassy materials metallic glasses have been discovered only recently [Buc54, Kle60, Bre63]. It was found that they often exhibit properties like high mechanical strength, high hardness, large elastic strain and high corrosion as well as wear resistance usually being superior to those of their conventional crystalline counterparts [Gre09, Kha18]. Together with the feasibility of near net-shape casting of metallic glasses or the shapeability of metallic-glass sheets e.g. by blow moulding [Sch07] this special class of metallic alloys offers a high potential for numerous applications in many different industrial fields [Gre09, Kha18]. However, the broader application was and still is hampered by their low glass-forming ability (GFA), i.e. only small parts can be cast homogeneously amorphous. Metallic glasses with critical diameters exceeding 1 mm are called bulk metallic glasses (BMG). Even after extensive research over the past decades rules for the assessment and prediction of GFA of metallic glasses are practically only empirical [Ino00, Mir04, Law15]. Many criteria for high GFA [Cha16, Ren21] can only be evaluated after the glass has already been made since characteristic temperatures of the alloy are needed as input parameters. Machine-learning methods are about to be employed as well [Sun17, Ren18, Liu21, Sam21]. Still, even the diameter of the biggest BMG to date does not exceed 8 cm [Nis12]. The critical size can also be expressed in terms of a critical cooling rate; the smaller it is the bigger the metallic glass can be. Solidification of a melt into a glass is called *vitrification*. Together with the transition in the opposite direction it is also referred to as glass transition. Although the focus of the present thesis is on glasses quenched from a liquid the term "glass" will be used to refer to all homogeneously amorphous solids irrespective of their method of production. Furthermore, in literature, the term "amorphous" is often used synonymously with the term "glass", i.e. to denote solids only. However, both liquids and glasses are amorphous materials – the term "amorphous" relates to a structure, not a phase, and is used here accordingly. Along the *pathway* of the melt from above the liquidus temperature T_l down to vitrification at the glass-transition temperature T_g the viscosity of the liquid alloy increases by more than 12 orders of magnitude while the changes at the atomic structure are only very subtle. To understand this discrepancy and to gain knowledge on how to extend the critical sizes of metallic glasses the processes taking place at the atomic scale along the pathway need to be investigated in more detail. For the sake of brevity, the

pathway of a liquid metal from temperatures well above its T_l during undercooling and through vitrification down to temperatures below T_g will simply be referred to as "pathway" for the remainder of this thesis. An increased understanding of how and why some liquid metallic alloys can be quenched into glasses while others crystallise upon cooling would deeply impact basic research and engineering alike. New alloys with increased GFA and tailor-made properties are expected to open completely new fields of applications.

Only a few studies of the atomic structure along the complete pathway have been published to date. This scarcity of experimental data on structural changes along the pathway is one of the major gaps in metallic glass research. On the one hand this is caused by the high critical cooling rates necessitating setups capable of ultrafast monitoring of the structure at the atomic scale. On the other hand the avoidance of heterogeneous nucleation caused by the reaction of the sample with containers calls for setups involving containerless levitation techniques. Both are not readily available. The aim of the present thesis is to gather deeper insights into the structural evolution along the pathway and during vitrification. Additionally, anomalies along that pathway, so-called liquid-liquid crossovers (LLC), that seem to be a common feature in many glass-forming systems [Tan20], will also be addressed. The main methodological approach is the analysis of diffraction data obtained using high-energy synchrotron X-ray diffraction of containerlessly, aerodynamically levitated samples of Zr- and Ti-based multinary alloys along their individual pathways. The alloys chosen exhibit high bulk-GFA. Due to the small experimental acquisition times in the millisecond-range large amounts of high-resolution diffraction data needs to be processed. The temperature-dependence of structure functions like the static structure factor $S(Q)$ in reciprocal space and the reduced pair-distribution function $G(r)$ in real space as well as of several structural metrics derived from them can give valuable insights along the pathway. While many steps of the analysis are facilitated by existing software packages several routines to handle $S(Q, T)$ and $G(r, T)$ data were devised here. Although the temperature-dependent measurements are in the centre of the present thesis several objectives are related to the investigation of structural aspects at constant temperature. This includes the effect of global electronic interactions on the structure of binary metallic glasses containing Zr which are the base alloys for the BMGs in focus. Insights obtained will be used to interpret temperature dependences of structural features along the investigated pathways of the multinary alloys. The effect of small compositional changes, instead of a changing temperature, on the structure is used to investigate

the validity of some of the empirical rules for GFA and as means to distinguish length scales with different structural behaviour. The main objective is the investigation and comparison of the structure of different metallic alloys along the pathway to identify universal behaviour but also differences that may help to explain their different GFAs.

The remainder of this thesis is organised as follows. Chapter 2 acts as a more detailed introduction to this thesis and also contains a review of all available publications to date presenting data on in-situ monitoring of the atomic structure of metallic-glass forming alloys along their pathways. It also discusses results of related simulations. In Ch. 3 suitable experimental methods to map the pathway are described, including an outlook to future developments in the field. Chapter 4 contains the investigation of the influence of global interactions between the electronic system and the atomic structure by analysing data for binary and ternary Zr-containing metallic glasses. The effect of small changes of composition by adding Ni or Co to $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ is scrutinised in Ch. 5 which yields clues about distinct distance ranges in real space which are governed by different influences. In Ch. 6 $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ was analysed in detail along its pathway. Chapter 7 compares these results to those for $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ and $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$, analysed in the same way, to identify possible universal behaviour during undercooling and vitrification. Chapter 8 presents a summarising conclusion of the previous chapters. It also gives an outlook to future work based on the present results which complements the outlook contained in Ch. 3.

2 Traces of the pathway – A literature review

Although ubiquitous in nature and technology a deep understanding of glass formation and glass transition is still missing. It is assumed that the remarkable slowdown of kinetics towards vitrification can be traced back to structural changes in the undercooled liquid. Therefore, a continuous monitoring of the atomic structure during cooling from the equilibrium liquid down to the glassy state is inevitable. However, the high critical cooling rates usually necessary for vitrification of metallic alloys make this a difficult, but at the same time very exciting, endeavour. Only in recent years it has been technologically possible to achieve in-situ monitoring of the evolving structure for a small number of metallic-glass forming alloys. Currently, only high-energy X-rays from synchrotron sources and free-electron lasers as probe in combination with fast two-dimensional detectors are able to capture diffraction images from usually containerlessly levitated samples with the necessary scattered intensity as well as resolution in space and time. The present chapter reviews the results for those materials where in-situ monitored vitrification has been experimentally accomplished and compares the approaches of experiment and data processing. Insights into the structural behaviour during vitrification derived from these experiments are discussed. Results from accompanying simulations are also included. In addition to the in-situ observation of vitrification structural indications of possible liquid-liquid crossovers in the alloys under consideration are part of this chapter as well.

2.1 Introduction

When undercooled fast enough below its liquidus temperature T_l crystallisation of a melt can be avoided and a solid with amorphous structure, known as glass, can be formed. This implies that at least three phases, i.e. liquid, glass and crystal, need to be considered in order to be able to conclude which phase is favoured under given circumstances. While in terms of the atomic structure a relatively easy distinction between crystal and liquid can be made, the difference between a glass and a liquid is not equally as straightforward. It can be speculated that, 25 years ago, it was this structural similarity between glass and liquid that led P.W. ANDERSON to consider the glass transition one of the deepest unsolved problems in solid state theory [And95]. Despite considerable progress many aspects of the puzzle remain unsolved till today. Due to their growing technological relevance [Gre09] the origin of the high glass-forming ability (GFA) of bulk-metallic glasses (BMG) is of great interest.

Although a glass can be formed from a melt by rapid temperature decrease (quenching), rapid pressure increase (crushing) or a combination of both (crunching) [Wen78] this chapter addresses glass formation and glass transition by quenching a metallic melt only. The glass transition, taking place at the glass-transition temperature T_g , in the direction from high to low temperatures is referred to as *vitrification* (liquid-to-glass transition). It should be noted that, although logically sound, the transition in the opposite direction, i.e. the transition from the glass to the liquid, is generally *not* called “devitrification”. This term is usually reserved for the crystallisation of a glass by ageing or other influences. More general, the term “glass” will be used here for an amorphous solid irrespective of its origin, i.e. not only when originated from a liquid. The term “amorphous” does not relate to a phase but to the atomic structure and is therefore applicable for the equilibrium liquid above T_l , the undercooled liquid below T_l as well as the glass.

To get deeper insights into subtle structural differences between liquid and glass data with high resolution in space as well as time are needed. The high temporal resolution is necessary since experiments need to be carried out under rapid cooling dictated by the high critical cooling rates to bypass crystallisation. Furthermore, since important processes related to glass formation already take place above T_l [Jai16], the structural investigation should commence at sufficiently high temperatures.

To avoid heterogeneous crystallisation containers have to be abandoned in the most cases and levitation techniques need to be employed. As will be discussed in more detail in Ch. 3 from several levitation techniques available *only* electrostatic levitation (ESL) and aerodynamic levitation, the latter usually in the form of conical nozzle levitation (CNL), is used for the study of metallic glasses. From the palette of structural probes (electron, neutron and X-ray diffraction) *only* X-ray diffraction (XRD) is currently able to serve the necessary speed, intensity and resolution for monitoring the structural changes along the pathway in the systems under investigation. The underlying reasons will be elaborated on in Ch. 3.

In combination, the aforementioned prerequisites mandate that the complete pathway (or at least major parts of it) starting from the equilibrium liquid, during undercooling and vitrification down to the glassy state (Fig. 2.1) of containerlessly levitated samples has to be continuously monitored in situ by high-energy synchrotron X-ray diffraction in transmission mode. In what follows the term *pathway* refers to the sequence just described. In particular, wide-angle X-ray scattering (WAXS) is used to

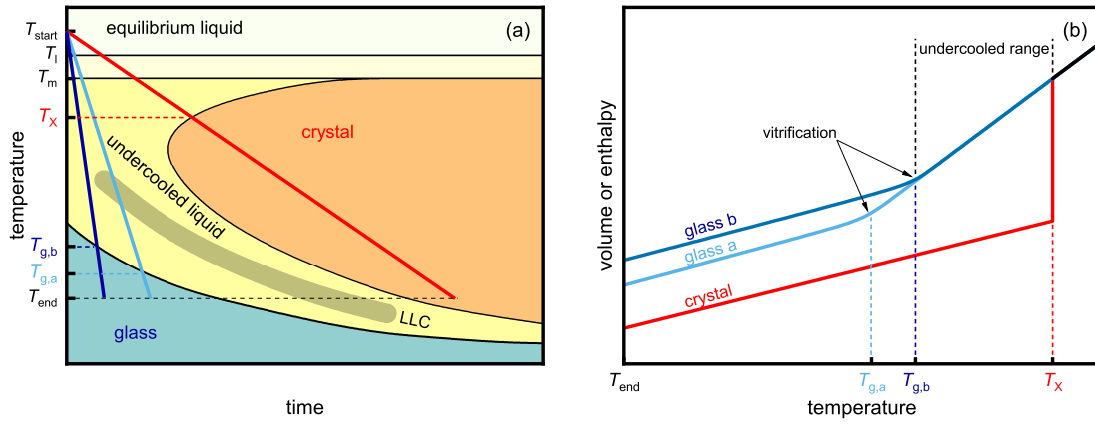


Figure 2.1: Schematic time-temperature-transformation (TTT) diagram of a model alloy quenched from T_{start} with three different cooling rates (a) and the temperature dependence of its volume or enthalpy at constant pressure (b). The model experiment ends at T_{end} . Depending on the cooling rate the (undercooled) liquid can crystallise at T_x or vitrify at different glass transition temperatures $T_{g,a}$ or $T_{g,b}$ yielding glasses with slightly different properties. Pathway b passes through a possible liquid-liquid crossover (LLC). Its range of existence and transition region is often only insufficiently known and, therefore, only roughly sketched in (a) (shaded in grey). The effects of LLCs on the macroscopic sample volume are controversial [Li11, Ben13, Wei13, Sto16] and have been omitted in (b).

resolve the structure in appropriate detail. This chapter seeks to review the key results of studies that investigated metallic alloys in this manner. In parallel to the metallic melts several oxides have been monitored in the same way [Hen07, Byt10]. Despite some similarities with metallic materials oxides will not be discussed in detail here. More information can be found in recent review articles [Ben12, Ben17]. The feasibility of other spectroscopic techniques to monitor the pathway, e.g. SAXS (Small-angle X-ray scattering), AXS (anomalous X-ray scattering) and EXAFS (Extended X-Ray Absorption Fine Structure) as well as e.g. electron scattering is briefly discussed in Ch. 3. Further quantities like electrical resistivity [Hoe19, Moh19] or specific heat [Sto16] have also been monitored in situ in levitation experiments and show typical changes around T_g .

Along this pathway it is not only the in-situ observation of vitrification itself that is of interest, but also other phenomena which are possibly linked to liquid-liquid crossovers (LLC) and are often associated with so-called fragile-to-strong¹ crossovers (FSC) [Zha10a, Alv19, Luc19]. Here, LLCs only as they may show in in-situ structural

¹The reader is advised that the terms "fragile" and "fragility" in the current context are used to describe the temperature dependence of the viscosity of (undercooled) liquids [Ang88, Deb01]. As introduced by ANGELL, the more the latter departs from ARRHENIUS behaviour the more fragile the liquid is. The opposite is called "strong". The viscosity of strong liquids like SiO_2 is close to ARRHENIUS behaviour.

measurements will be addressed rather than providing an in-depth investigation of their still not well-understood nature in general as well as in metallic-glass forming liquids in particular. LLCs have recently been reviewed [Wei13a, Wan17, Luc19, Luc20] and a lot of theoretical work has been dedicated to the possible descriptions of LLCs in a unified manner [Tan00, Ang08, Tan20]. Different designations found in literature like liquid-liquid transitions (LLT) or liquid-liquid phase transitions (LLPT) will be summarised under the more circumspect term LLC since it is unclear as to what extent they can be considered thermodynamic transitions. The possible location of an LLC in a TTT (time-temperature-transformation) diagram is roughly sketched in (Fig. 2.1a).

The first in-situ diffraction study along the complete pathway for metallic alloys was reported for $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ in 2003 by URIARTE et al. in the group of A.R. YAVARI in Grenoble [Uri03] (Fig. 2.2). Although since then a few further in-situ monitored vitrifications of BMGs were reported (Tab. 2.1) a first detailed analysis including many structural metrics derived from the experimentally obtained structure functions and supporting comprehensive results from computer simulations, was not published until 2015 for $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ [Geo15].

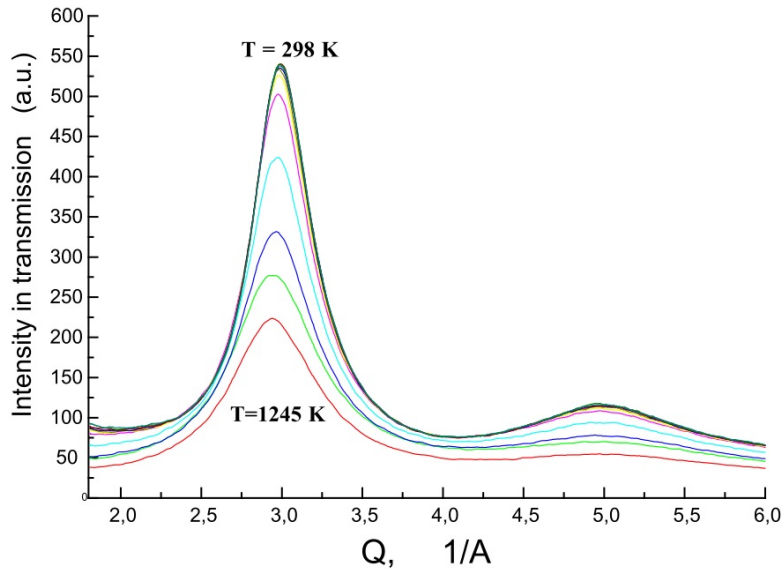


Figure 2.2: Intensity distribution $I(Q)$ acquired using high-energy synchrotron X-ray diffraction in transmission at various temperatures for the first reported in-situ monitoring of the complete pathway from the equilibrium liquid down to the glassy state for metallic alloys ($\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$) [Uri03] (figure reproduced from ref. Yav04).

alloy	T interval K	T_g K	T_1 K	$\frac{T_g}{T_1}$	T_{LLC} K	$\frac{T_{LLC}}{T_g}$	mount/heat	cooling rate K/s	E_i (λ_i) keV ($\text{\AA}$)	year/ref.
Pd ₄₀ Cu ₃₀ Ni ₁₀ P ₂₀	1270...600	569 [Mat03]	864 [Mat03]	0.659	–	–	amp/l	30...10 (a)	90 (0.138)	2003 [Uri03]
Pd ₄₀ Cu ₃₀ Ni ₁₀ P ₂₀	910...298	569 [Mat03]	864 [Mat03]	0.659	–	–	amp/l	8.33 avg. (n)	92.5 (0.134)	2011 [Geo11, Lou11]
Pd _{42.5} Cu ₃₀ Ni _{7.5} P ₂₀	1100...420	575 [Nis12]	836 [Nis12]	0.688	–	–	ESL/L	5...0.5 (f)	131 (0.095)	2019 [Ryu19]
Zr ₅₀ Cu ₄₀ Al ₁₀	1700...700	712 [Paj18]	1159 [Paj18]	0.614	–	–	CNL/L	120 avg. (f)	113.4 (0.109)	2010 [Wat10]
Zr _{50.7} Cu ₂₈ Ni ₉ Al _{12.3}	1673...673	– [†]	1167	–	–	–	CNL/L	84 avg. (c)	61.67 (0.201)	2012 [Qu12]
Zr _{51.9} Cu _{23.3} Ni _{10.5} Al _{14.3}	1673...673	776	1132	0.686	–	–	CNL/L	97 avg. (c)	61.67 (0.201)	2012 [Qu12]
Zr ₅₅ Cu ₃₀ Ni ₅ Al ₁₀	1346...388	683 [Har10]	1150 [Har10]	0.594	–	–	CNL/L	85 avg. (f)	100 (0.124)	2020 [Lou20]
Zr ₅₇ Cu _{15.4} Ni _{12.6} Al ₁₀ Nb ₅	1389...577 [§]	682	1115	0.612	1000	1.47	ESL/L	4.3 avg. (f)	129 (0.096)	2016 [Lan16]
Zr _{58.5} Cu _{15.6} Ni _{12.8} Al _{10.3} Nb _{2.8}	1473...673	708 ^{†,‡} [Wei15]	1170	0.605	~ 860	1.21	ESL/L	5 avg. (f)	100 (0.124)	2016 [Sto16]
Zr ₆₀ Cu ₃₀ Al ₁₀	1471...372	671	1207	0.556	1070	1.59	CNL/L	100 avg. (f)	100 (0.124)	2015 [Geo15]
Ti ₄₀ Cu ₃₄ Pd ₁₄ Zr ₁₀ Sn ₂	1473...487	689	1176	0.586	940	1.36	CNL/L	80 avg. (f)	100 (0.124)	2021 (Ch. 6)

[†] T_g not identifiable in metrics

[‡] vitrification not discussed

^{||} cooling started at 1678 K

[§] minor crystallinity below 850 K

Table 2.1: Some key data for the metallic alloys that have been successfully vitrified under in-situ structural monitoring by high-energy synchrotron X-rays: the temperature interval during which in-situ monitoring took place, the glass-transition temperature T_g , the liquidus temperature T_l , the reduced glass-transition temperature T_g/T_l , the onset temperature of a possible LLC T_{LLC} (this quantity may be denoted differently in the individual references), the ratio T_{LLC}/T_g , the method of sample mounting (amp: quartz ampoule), the method of heating (L: laser, I: inductive heating), the achieved cooling rates and method as given in the reference and (a: air jet on outside of quartz ampoule after stopping induction current; n: using liquid nitrogen instead of air; f: free cooling after switching-off laser causing a strongly temperature-dependent cooling rate; c: controlled cooling using the heat source to achieve a particular cooling rate), the energy E_i and wavelength λ_i of the incident monochromatic high-energy X-ray beam and the year of the report as referenced.

It is necessary to mention that in parallel to in-situ monitoring of structural metrics during cooling also that during annealing of metallic glasses progressed [Mat02, Mat03, Mat04, Yav04, Yav05, Mat07b, Jia10, Mat12, Joh14]. Mainly performed on melt-spun samples, these investigations complement the in-situ cooling experiments especially when performed for the same composition. The major drawback of experiments in annealing mode is the wide temperature range in which the alloy cannot be monitored in an amorphous state due to the intervention of crystallisation (i.e. $T_X < T < T_l$). If the sample is annealed to temperatures above T_g , but below T_X , technically in-situ vitrification ("re-vitrification" for that matter) can be monitored on cooling to temperatures below T_g [Yav04a, Bed11, Eve14, Hec18, Kue18]. Since this chapter is dedicated to studies of the complete pathway reports on re-vitrification are not reviewed here. Nevertheless, re-vitrification studies can help investigating cooling-rate dependencies of the structure for deeply undercooled samples [Kue18]. Furthermore, being able to perform heating and cooling, i.e. cycling the same sample, in the same setup, opens the opportunity to explore possible hystereses of the temperature-dependent structural changes. Crystallisation of metallic glasses upon heating (and slow cooling) is in itself of utmost interest and the occurrence of different phases depending on the heating or cooling rate is of relevance for basic research as well as for possible applications of metallic glasses [Yav99, Geo13, Kos20]. Comparing the structure of an alloy slightly above and below T_g structural changes seem to be extremely minute. However, tracing the structure in a certain temperature interval around and during the glass-transition (in either direction) marked changes ("kinks") in the temperature-dependence of structural metrics become clear indicating its structural basis. Despite a lot of progress in experimental techniques still only a few BMG-forming alloys have been analysed in-situ along the complete pathway to date. These alloys are listed in Tab. 2.1 together with the studied temperature range and some key experimental parameters.

2.2 The Pathway

An experiment for in-situ monitoring the pathway should be designed to commence at a temperature sufficiently higher than the alloy's T_l , ideally even overheated to several hundred kelvin above T_A , the temperature that marks the onset of cooperative reorganisation of atoms and the beginning of glass-formation in the liquid alloy [Jai16]. From

the overheated state, after passing milestones like possible (maybe even mandatory) LLCs, vitrification takes place and yields an amorphous solid called a glass. Structure and properties of the latter are not unique but depend on the overheating as well as the cooling rate [Deb01, Muk04a]. When the alloy stays liquid below its T_l it is referred to as undercooled liquid (UCL). The frequently used term "supercooled" is misleading and somewhat contradictory since "super" has the meaning of above but not below. It may hint at the necessary *superfast* cooling to obtain glass from the undercooled liquid alloy at T_g .

Figure 2.3a exemplarily shows $S(Q, T)$ for $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ [Geo15] along the pathway in a three-dimensional way using a so-called "waterfall plot" [Uri03, Geo11, Geo15, Ryu19]. The same information can be illustrated in a contour plot (Fig. 2.3b). After FOURIER transform all real-space structure functions, most importantly $G(r)$, can be visualised in the same way. Figure 2.3c shows the corresponding reduced pair-distribution functions $G(r, T)$ for $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ [Geo15] as 2D projection where T -dependent trends can be followed with the help of an appropriate colour scale. All these T -dependent plots can be supplemented by movies showing the structural evolution in about the real experimental time (cf. e.g. Ch. 6).

In the following a closer look will be taken at the milestones along the pathway and how they may show in structural data gathered by in-situ high-energy synchrotron X-ray diffraction experiments. Paralleling the experiment, the discussion starts at high temperatures and follows the pathway towards lower temperatures.

2.2.1 Undercooling

After the alloy has successfully passed the first step of the pathway towards vitrification by entering the UCL state structural changes at the atomic scale, that finally lead to vitrification, could now be identified. Contrary to experiments investigating the structural changes of metallic glasses on heating or during isothermal holds [Mat02, Mat03, Mat04, Yav04, Yav05, Mat07b, Jia10, Mat12, Mau13, Mau13a, Mau14, Joh14], respectively, rapid cooling experiments have the potential to continuously probe the sample in an amorphous state down to T_g and enable the determination of the functional relations of the T -dependence of structural metrics. The intervention of crystallisation prevented the latter during the experiments in heating or at isothermal holds. Due to initial limitations of detector speed, the density of data-points of the early studies on cooling

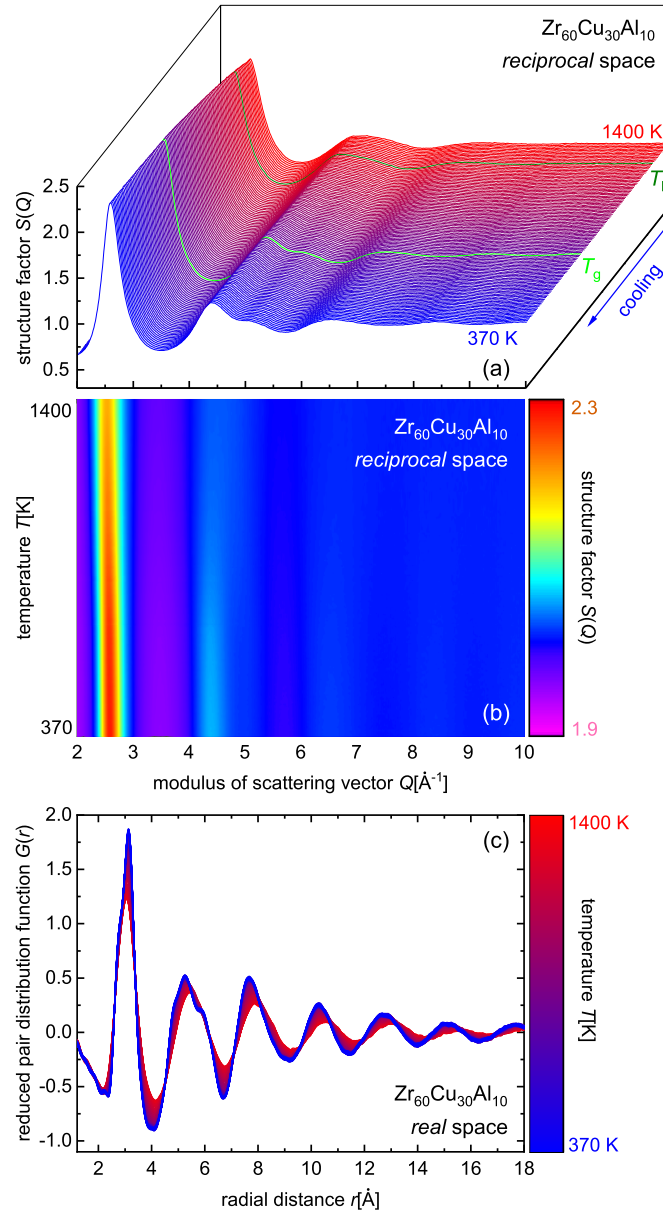


Figure 2.3: The evolution of structure functions along the pathway exemplarily for $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ during cooling from 1400 K (red) to 370 K (blue) (data taken from ref. Geo15). This also showcases different ways of visualising structure function along the pathway. In (a) the T -dependence of the structure factor $S(Q, T)$ is shown in a three-dimensional way as waterfall plot. Highlighted in green are the functions for the liquidus temperature $T_l = 671$ K and the glass-transition temperature $T_g = 1207$ K. Alternatively, in (b) the T -dependence of the structure factor $S(Q, T)$ is shown as contour plot. The corresponding reduced pair-distribution functions $G(r, T)$ are shown in (c) as 2D plot. Here T -dependent trends in the in the large amount of data can be followed with the help of the colour coding.

that achieved in-situ vitrification was low and details of the functional dependence still could not be resolved yet [Uri03, Geo11, Lou11]. QU et al. were the first to publish quasi-continuous sets of structural data over a wide temperature range along the pathway in form of the position of the principal maximum in the diffraction intensity

$I(Q, T)$ [Qu12]. Despite the relatively strong scatter, a non-linear behaviour became visible for temperatures above T_g in Zr-based metallic glasses (Tab. 2.1). Data with a high density of data points and at the same time much higher signal-to-noise ratio was presented by GEORGARAKIS et al. [Geo15] for $Zr_{60}Cu_{30}Al_{10}$, including the additional step to obtain $S(Q, T)$ from $I(Q, T)$ (Sec. 3.5). Of $S(Q, T)$ the position $Q_1(T)$ of the principal peak as well as its height $S(Q_1, T)$ was analysed, showing the non-linear temperature-dependence above T_g much clearer (Fig. 2.4). Recently, RYU et al. demonstrated the curvature of $S(Q_1, T)$ with high clarity for $Pd_{42.5}Cu_{30}Ni_{7.5}P_{20}$ [Ryu19]. The latter study showed that a CURIE-WEISS-like function, originally known from the description of magnetic ordering phenomena [Ash76], can be fitted to $S(Q_1, T) - 1$ with a negative characteristic temperature (quasi-CURIE temperature) that has been associated with a proposed hypothetical "ideal-glass" state that possesses long-ranged (non-decaying) density correlations [Ryu19, Ryu20]. In MD simulations for several other metals (elements and alloys) a comparable behaviour could be observed [Ryu19]. Further experimental studies have to validate the generality of this behaviour but it seems to be more common than expected (exemplified by the red dashed curve for $Ni_{62}Nb_{38}$ in Fig. 2.4; cf. also Ch. 7). Compared to $S(Q_1, T)$ the non-linear behaviour for $Q_1(T)$ is less pronounced [Mat02, Mat03, Mat07b, Qu12, Wei13, Geo15, Sto16, Jon19]. In any case the presence of curvature casts doubt on results derived from fitting linear functions or tangents to temperature-dependent structural metrics especially since their slope depends on the T -range they are fitted to [Mat03, Mat07a, Mat07b, Mau13, Mau13a, Mau13b, Geo15]. The latter is either strongly influenced by subjectivity or insufficiently known due to experimental constraints (accessible T -range).

A curvature (Fig. 2.4) with increasing (negative) slope upon cooling indicates an acceleration of the structural evolution upon increasing undercooling [Mau13, Mau13a, Mau14, Geo15, Lan16]. Anomalies in the way this acceleration takes place may be related to LLCs (Sec. 2.2.2) reflecting changes in fragility. In real space non-linear changes of structural metrics with temperature were observed as well [Mat03, Mat07b, Wei13, Geo15, Lan16, Sto16], probably related to the same effects as in reciprocal space (see also Ch. 7), showing that the accelerated ordering spans various length scales belonging to short- (SRO) as well as medium-range order (MRO).

MD simulation data accompanying the experimental results suggest that during progressing undercooling more and more atoms are gathered in clusters [Che08, Che09, Sok13, Geo15, Lan16]. This enhancement of the SRO is often predominantly characterised by icosahedral-like symmetry with strong covalent bonding (hybridisation

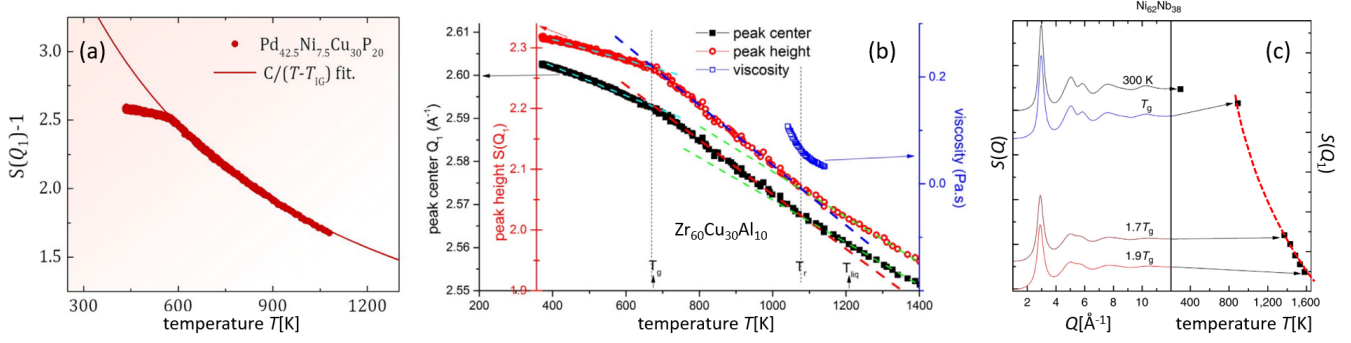


Figure 2.4: Non-linear temperature dependence of structural metrics in reciprocal space for different metallic glasses. A CURIE-WEISS-like behaviour has been proposed recently and was fitted to the experimentally obtained height $S(Q_1) - 1$ of the first peak of the structure factor of $\text{Pd}_{42.5}\text{Cu}_{30}\text{Ni}_{7.5}\text{P}_{20}$ (a, reproduced from ref. Ryu19). For the height $S(Q_1)$ and position Q_1 of $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ the continuous non-linear shape has been approximated discontinuously using two linear functions each whose intersection was associated with a stark increase in the viscosity $\eta(T)$ (b, reproduced from ref. Geo15). A lack of data for wide T regions severely hampers a correct fit as in the case of $\text{Ni}_{62}\text{Nb}_{38}$ (c, adapted from ref. Mau14) but again allows for a non-linear dependence over the complete T region down to T_g as sketched by the red dashed line while originally a linear approximation [Mau14] was used for the high- T region only.

effects) [Che08, Che09, Sok13, Geo15]. The number of icosahedral-like clusters shows a non-linear behaviour comparable to the metrics discussed above highlighting again the accelerated structural evolution in the UCL corroborating the finding in reciprocal space mentioned above (Fig. 2.8). Icosahedral SRO is associated with the stabilisation of the amorphous structure against nucleation of crystalline phases [Fra52] and the covalent bonding character to a shortening of interatomic distances or increased packing efficiency [Lek09, Lou11, Kab13, Geo15]. Both aid the significant slowing-down of the relaxation kinetics related to the sharp increase in viscosity towards vitrification [Ino98, Lou11]. Experiments also revealed that the first NN shell seems to exhibit negative thermal expansion [Mat03, Jia10, Geo11, Gan14a, Geo15]. After demonstrating this clearly for $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ upon cooling by GEORGARAKIS et al. [Geo11] the same behaviour has been reported numerous times for other alloys as well [Gan14a, Geo15, Sto16]. Further results showed that this effect is not limited to alloys but even occurs in liquid elements [Lou13]. An explanation was given in terms of the developing clusters along the pathway. At high temperatures only the strongest bonds survive and clusters are relatively small, i.e. the coordination number N_c is low. The developing bonds on cooling cause more atoms to enter the clusters, causing their radius (roughly the first NN distance) as well as N_c to increase [Geo11, Lou13]. At the same time the packing density increases which, in turn, is beneficial for high GFA [Ino98]. This behaviour stops abruptly at T_g highlighting that it is caused by

structural changes in the UCL and not a "real" negative expansion (Ch. 6 and 7). All higher NN shells exhibit a positive expansion [Mat03, Gan14a] with NN shells two and three expanding even stronger than observed macroscopically (cf. also Ch. 6 and 7). This illustrates that it is the MRO that determines the macroscopic thermal expansion. Since MRO also determines the position of Q_1 in $S(Q)$ [Car75, Ryu20] highlights the importance of the YAVARI equation [Yav04, Yav05] for the description of thermal expansion. Since atoms located on NN shells belonging to the MRO are at the centre of their own SRO both should be describable on common grounds. However, the MRO seems to be governed by its own emergent many-body effects [Ryu20]. Global electronic interactions have been invoked to describe the characteristic distances of the MRO [Hau92, Hau05, Sti19] (cf. also Ch. 5 and 6). It remains to be seen if such a global description will be able to aid a deeper understanding of glass formation and glass transition. Interestingly, during undercooling it is not only the clusters constituting the first NN shell that "absorb" atoms, but it could be shown quite generally that atoms are transferred from anti-shells to shells (Fig. 2.5) which can be interpreted as signature of increasing structural order along the pathway [Geo15] (cf. also Ch. 5 and 6).

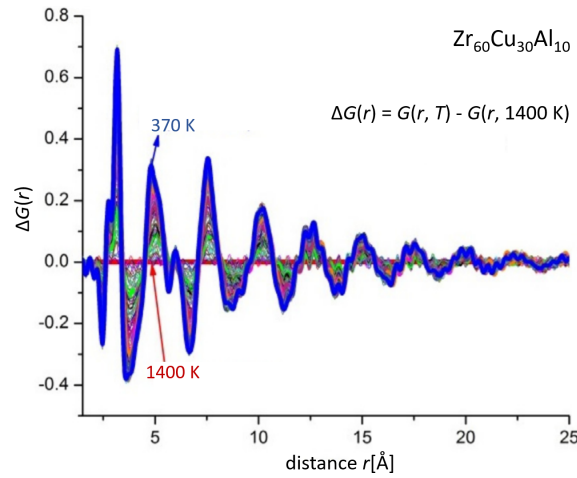


Figure 2.5: The function $\Delta G(r, T) = G(r, T) - G(r, 1400 \text{ K})$ for $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ shows the transfer of atoms from the anti-shells to the shells upon undercooling, i.e. an increasing height of the peaks of $\Delta G(r, T)$ accompanied by a decreasing depth of the troughs (reproduced from ref. Geo15).

Apart from analysing distances, other real-space metrics have been used to underline the structural changes during undercooling and their relationship with the slowdown of kinetics [Lou11, Lou20]. The evolution of clusters and their interconnection changes the activation energy for viscous flow. In this respect the intensity ratio of two sub-peaks, fitted to describe the first NN shell for $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ [Lou11]

and $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ [Lou20], has been considered. Not only is this metric showing the accelerated evolution again, but their curved T -dependence parallels $\eta(T)$ for $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ remarkably well [Lou11]. This was interpreted as the CSRO providing the structural basis for the stark increase of $\eta(T)$ in the UCL region towards vitrification [Lou11]. Comparing the evolution of the intensity ratio for both $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ and $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ a relation to fragility seems to be encoded in this metrics [Lou11, Lou20]; the stronger the structural changes upon cooling the more fragile the alloy is. Further attempts to find structural signatures for fragility have been made by constructing metrics that are able to emphasise small details. Contrary, or perhaps additionally, to the findings of LOUZGUINE et al. [Lou11, Lou20], it could be shown that fragility is connected to the structural evolution in the MRO on distances around the fourth NN shell [Wei15, Sto16]. In the following signatures of structural crossovers, maybe related to changes in fragility, are discussed.

2.2.2 Liquid-liquid crossovers

The experiments that were able to monitor the vitrification in situ (Tab. 2.1) show changes in slope, frequently called "kinks" (Fig. 2.4; cf. also Ch. 7), in several structural metrics which is ascribed to the glass transition at T_g (Sec. 2.2.3). However, additional anomalies along the pathway were reported by several authors. To get reliable results, data for a temperature range as wide as possible is necessary, which is not always provided. Even if a putative kink is close to the centre of the measured temperature interval its determination is not always without doubt. Sometimes kinks are identified with the help of "tangents" (Fig. 2.4). However, this approach is somewhat subjective and may cause the detection of transitions or crossovers where there may actually be none [Geo15, Lan16]. Step-like "double-kinks" were found in the temperature-dependent position $Q_1(T)$ of the first maxima of Zr-based alloys (Vitreloy 1 and 106a) [Wei13, Sto16, Jon19]. The associated change in behaviour takes place over relatively small temperature intervals and was ascribed to LLCs (Fig. 2.6). Interestingly, these step-like kinks can point "downstairs" (Fig. 2.6a) or "upstairs" (Fig. 2.6b) where no explanation for the different direction was reported [Jon19]. Difficulties in interpretation may arise from the evolution of the different partial structure factors of these multi-component alloys during the LLC which cannot be disentangled easily [Jon19]. The macroscopic density remains virtually unchanged across the LLC in Vitreloy 1 and 106a and the slow transition kinetics was found incompatible with

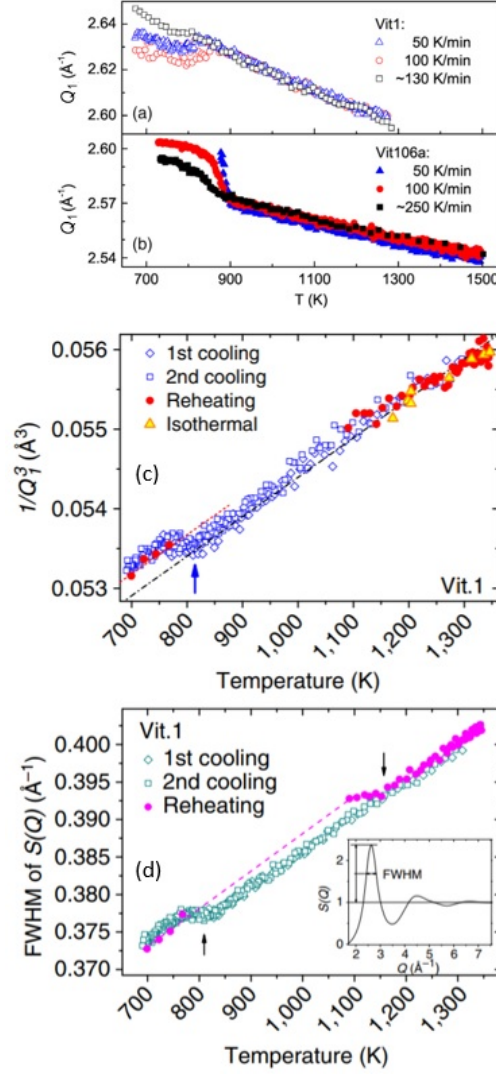


Figure 2.6: Kinks in structural metrics in reciprocal space during supposed LLCs and their temperature dependence. (a) The position Q_1 of the first peak of $S(Q)$ of Vitreloy 1 ($\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$) for three different cooling rates [Jon19], (b) the same for Vitreloy 106a ($\text{Zr}_{58.5}\text{Cu}_{15.6}\text{Ni}_{12.8}\text{Al}_{10.3}\text{Nb}_{2.8}$) [Jon19], (c) $1/Q_1^3$ (which is supposed to be a microscopic measure (esp. MRO) of the volume of the alloy) for Vitreloy 1 [Wei13], (d) FWHM $\Gamma(T)$ of the first peak of $S(Q)$ of Vitreloy 1 showing indications of a hysteresis [Wei13].

only local structural changes [Wei13, Sto16, Jon19]. Additionally, a strong cooling rate dependence was found (Fig. 2.6a,b). The higher the cooling rate the less pronounced the kinks are [Jon19]. While the results shown in Fig. 2.6 were taken by an ESL setup [Wei13, Sto16, Jon19] CNL was used for $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ (Fig. 2.4). Given the about 50 times higher cooling rates for the latter (Tab. 2.1) and the trend observed in ref. Jon19 (Fig. 2.4a,b) LLCs may almost be invisible in CNL experiments without elaborate data treatment (possible ways of enhancing the visibility of LLCs in structural metrics have

been proposed, cf. e.g. refs. Wei15, Sto16 and Ch. 6). To clarify this important issue alloys with pronounced kinks found in ESL would need to be investigated in a CNL setup additionally. For $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ (in $\Gamma(T)$) additionally to a kink at lower temperature during cooling a similar kink at higher temperature on heating was reported (Fig. 2.4d) which was taken as an indication for a hysteresis [Wei13]. However, the lack of data for the sample in an amorphous state during heating between T_x and T_m makes the clear identification of the hysteresis difficult. Further investigations are necessary to see whether a hysteresis can be seen in other (structural) metrics and other alloys as well. Indications for the latter were recently reported [Kha19]. Furthermore, it is not clear whether T_{LLC} itself depends on the cooling rate [Jon19]. The existence of both non-linear behaviour and kinks in the same alloy (Fig. 2.7) highlights that the accelerated evolution probably is the "normal" behaviour and LLCs are occurring additionally under certain circumstances. Finally, a possible LLC may be bypassed completely during rapid undercooling (path b in Fig. 2.1a) not unlike possible crystalline phases [Lan17, Kos20, She20] and will be visible only upon heating the vitrified sample. Such a behaviour would bear similarities with recent reports of a possible "glacial-glass" phase² in metallic alloys [She20].

To increase the confidence for a surmised LLC it should be reflected in non-structural quantities as well. Such quantities can for instance be the temperature-dependent viscosity $\eta(T)$ [Geo15], density (back projection of the levitating drop) [Wei13] or thermodynamic properties like the specific heat [Sto16]. Anomalies in the specific heat have been shown, which were discussed in relation to a possible first-order nature of LLCs [Wei13, Sto16, Tan20]. However, this is not readily observed in the cooling curves $T(t)$ for metallic glasses [Geo15, Sto16] (a possible kink in $T(t)$ was reported for oxide glasses though [Hen07]). Viscosity, on the other hand, is virtually never known over the complete T -range of the pathway, since the huge change in its magnitude cannot be measured by with a single method.

The proposed origins of LLCs are probably diverse and also controversial. However, an LLC should originate in intrinsic structural changes. Competing explanations have been put forward as well as attempts for a unified description [Mil07, Ang08, Tan20]. That the aforementioned kinks in the structural metrics can "bend" in both directions [Jon19] makes it even harder to determine the underlying reason and hints at possibly

²The authors of ref. She20 chose the name "metallic glacial-glass" in analogy to the observation of a distinct amorphous phase in the molecular liquid/glass triphenyl phosphite [Coh96, Ha96] which exhibits an LLC when quenched into a deeply undercooled state and afterwards transforms slowly, "glacially", into a new amorphous state during annealing for several hours.

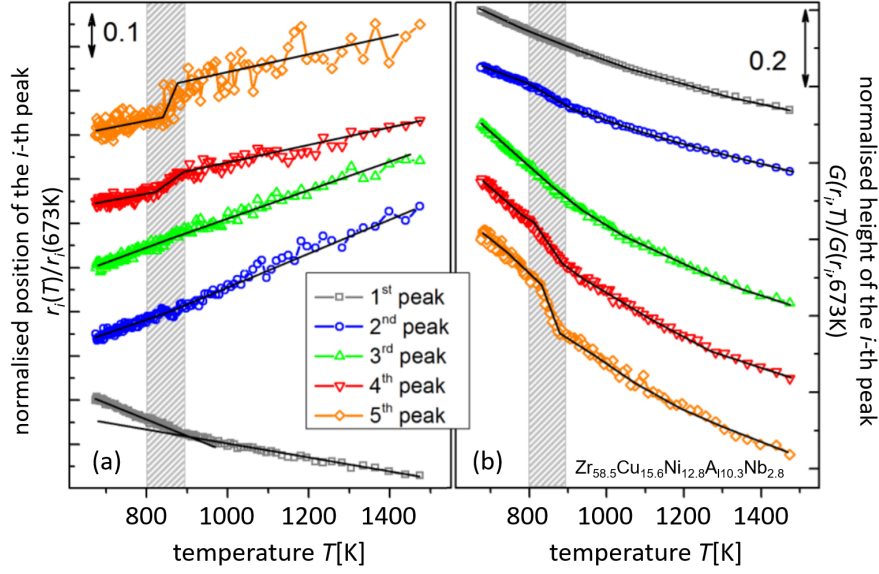


Figure 2.7: Kinks in the normalised position $r_i(T)/r_i(673\text{ K})$ and height $G(r_i, T)/G(r_i, 673\text{ K})$ of the first five peaks ($i = 1 \dots 5$) during an LLC (hatched region) of Vitreloy 106a ($\text{Zr}_{58.5}\text{Cu}_{15.6}\text{Ni}_{12.8}\text{Al}_{10.3}\text{Nb}_{2.8}$) upon cooling [Sto16]. Curves are shifted on the y-axes for clarity and the solid lines are a guides to the eyes. Note the combined occurrence of kinks and non-linear behaviour.

different reasons and underlying mechanisms for LLCs. With respect to the opposite evolution of distances for the first NN shell compared to that of the higher NN shells, as discussed above (Sec. 2.2.1), it could be possible that at some T the clusters approach a critical size triggering a reconfiguration on the length scale of the MRO during the LLC [Wei13]. Such changes at the level of the SRO are related to an increased number density and packing efficiency of locally preferred clusters [Geo15, Sok16, Sto16]. Furthermore, clusters increasingly tend to form backbones (MRO correlations) during undercooling which are going to percolate the sample at a specific temperature which may be related to T_{LLC} [Lad12, Zho15, Lan16, Sok16]. These backbones may be interpreted as partial solidification of the sample [Lan16]. Using MD simulations of $\text{Cu}_{64}\text{Zr}_{36}$ this percolation was found to take place at about $1.4T_g$ and is also related to the onset of glassy dynamics [Sok16]. Since percolation affects the dynamical properties LLCs are often associated with fragile-to-strong transitions or crossovers (FSC) [Alv19, Luc19]. Backbone formation has been connected to the onset of glassy dynamics [Lad12, Wan12, Sok16] making LLCs maybe precursors, or even necessary prerequisites, for vitrification. With energy barriers lower than for the liquid-crystal transformation [Wei13] LLCs may be likened to OSTWALD steps [Ang08, Ang08a, Xu09], however not necessarily towards a crystal but towards a glass. The (possibly kinetically

stronger) liquid below T_{LLC} can resist crystallisation better what may be key to increased undercoolability [Wei13] and eventually high GFA.

Since T_{LLC} is often close to the critical temperature $T_{\text{C}} \approx 1.25T_{\text{g}}$ of the mode-coupling theory (MCT) [Lan16, Jan18] it is tempting to identify both temperatures [Lan16], but only the temperatures being close is not sufficient to make this assertion without further validation [Lan16], if MCT is applicable for metallic glasses at all [Ega20a]. Nevertheless, it is not unreasonable that a connection between the dynamical crossover of the MCT or similar theories and a crossover observable in structural metrics exists. It remains to be seen how close developing backbones [She12, Wan12, Zho15, Sok16], collectively moving atoms in MCT [Jan18] or so-called cooperatively rearranging regions [Ada65, Ste06] of the ADAM-GIBBS description of the relaxation dynamics in undercooled liquids [Ada65] are related. The ratio $T_{\text{LLC}}/T_{\text{g}}$ may not be fixed for all classes of metallic liquids and LLCs may even occur above T_1 , multiple transitions may appear at different T in the same undercooled liquid [Lad12, Tan20] and a LLC may even be in competition with vitrification [Hec18].

Possible chemical decomposition involving long-range mass transport [Jon19] or nanoscale demixing into different liquids, as surmised in oxide glasses, have also been put forward in connection to LLCs [Gre08]. Temperature-dependent changes in the electronic structure have been proposed too [Kha19].

The increasing cooperativity during cooling begins with atoms forming clusters or associates in the equilibrium liquid way above T_1 and leads to the aforementioned formation of percolating backbones [She12, Wan12, Zho15, Sok16, Gan17]. In a sense the connection of clusters to backbones can be seen in analogy to the formation of polymers from monomers and the formation of the monomers from single atoms. A polymer has to be considered a different material than the individual monomers from which it emerges. In this respect, the interpretation of fragile-to-strong crossovers can be seen as a chemical transition. It is not a single material showing a change in the temperature dependence of the viscosity, but a mixture of the polymer as well as remaining monomers and individual atoms, where more and more polymer with $\eta(T)$ different from that of the monomers is created upon cooling. Following this view it needs to be investigated why polymerisation preferable takes place at the observed T_{LLC} and how close the relationship to "traditional" polymers is.

Besides temperature-dependent LLCs also so-called "polyamorphic" transitions, that happen during compression of metallic glasses, are frequently reported. They mainly occur in alloys containing rare-earth metals where f-electron states play a role, most prominently Ce [She07, Zen07, Li17, Dzi18, Yin21]. Other similar transitions based on pressure-dependent changes related to other electronic states (e.g. s-d-interactions) have been reported as well [Lou12, Du19, Kha19]. Following the definition of "amorphous", spanning the glassy as well the liquid states, the term "polyamorphic" is actually misleading since in literature usually reserved for transitions within the glassy state, sometimes even called amorphous-amorphous transitions (AAT) [Tan20] or amorphous-amorphous phase transitions (AAPT) [Kha19]. To be more precise, these transitions should be referred to by a more specific designation like "polyvitrific" (involving glass-to-glass transitions). Complementary, LLCs should be named "polyliquid" (involving liquid-to-liquid transitions) and the term "polyamorphic" (involving AATs in general) would be the genus comprising both. On the other hand, it is questionable whether the mentioned pressure-induced transitions are polyamorphic (polyvitrific) transitions at all since they are of extrinsic origin, i.e. forced utilising the special electronic properties of the rare-earth atoms [She07, Zen09, Zen10, Zen10a, Li17] and not related to specific properties or characteristics of the amorphous structure. Under pressure Ce and other 4f-metals are effectively turned into "different elements" with smaller size allowing denser packing. However, recent reports of the occurrence of a temperature-induced LLC and pressure-induced glass-glass transition in the same metallic glass points to a relationship or common ground for both [Kha19].

Another possible LLC is the already mentioned first-order transition into a glacial-glass state in $\text{La}_{32.5}\text{Ce}_{32.5}\text{Co}_{25}\text{Al}_{10}$ [She20]. Similar indications can be seen for $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ [Zhe10, Cal12, Kos20] and $\text{Pd}_{42.5}\text{Ni}_{42.5}\text{P}_{15}$ [Che21], where in the latter the new state was entered by varying the conditions of the high-temperature melt before quenching. Other recent observations may fall under this scope as well [An20, An20a, Na20, An21]. It is, however, not yet clear whether the glacial-glass state is really of amorphous structure [Tan20].

Other alleged LLCs should be more aptly called pseudo-LLCs. Those could be related to experimental artifacts (reviewed in [Kha10]) or transitions occurring above T_1 that can be associated with dissolving solid-like remainders on heating [He19]. In other cases [Li11] crystallisation was probably mistaken for an LLC [Ben13, Wei13]. For other transitions that have been called glass-to-glass transitions, like a H-induced transition in Mg-Ce-Ni-based glasses [Lin16], it is open into which category they fall.

2.2.3 Vitrification

That upon annealing of metallic glasses the temperature dependence of in-situ-obtained structural metrics, mainly those in reciprocal space, shows a kink close to T_g (known from thermo-analytical methods) has been shown and discussed in the literature galore [Mat03, Mat04, Yav04, Yav05, Mat07a, Mat07b, Li09, Pin09, Jia10, Zhe10, Bed11, Mat12, Eve14, Eve17, Hec18, Kue18]. Similar observations were made for oxide glasses [Bot08]. The studies investigating the glass transition of metallic-glass forming liquids on cooling from the high-temperature equilibrium liquid found comparable kinks at T_g . Detailed discussions of the evolving structural metrics across vitrification showed similar kinks in reciprocal as well as real space [Geo11]. Again, similar results for oxide glasses on cooling were reported as well [Hen07, Byt10, Dre19].

Below T_g , for annealing as well as cooling experiments and simulations, structural metrics show mostly linear or even constant temperature dependence [Mat02, Mat03, Yav04, Mat07b, Jia10, Mat12, Ryu19] (cf. also Ch. 6 and 7). This can be interpreted to result from ordinary thermal expansion of the glass, after the structural changes in the undercooled liquid have ceased to dominate. Especially the almost constant FWHM Γ_1 of the first halo points to mainly the DEBYE-WALLER factor acting (cf. also Ch. 7) and shows that the increase of the structural correlation length $\propto 2\pi/\Gamma_1$ during undercooling has stopped. Although it is beneficial to be principally able to identify the glass transition from structural results via the kink, a direct comparison of structure functions somewhat above as well as below T_g yields almost no differences highlighting again ANDERSON's puzzle. Since to date no partial structures have been experimentally resolved in pathway studies, for an insight on what causes the liquid to freeze into a glass at T_g simulation results are inevitable.

Several MD simulation studies clearly replicate the kink at or around T_g (Fig. 2.8), where the rapid increase in numbers of clusters abruptly stops [Che08, Men10, Zha11, She12, Geo15]. Non-structural results like diffusion coefficients derived from MD simulations show abrupt changes close to T_g as well [She12, Alv19]. The developing backbones in form of networks of clusters [She12, Wan12, Zho15, Sok16, Gan17] mentioned above seem to be the responsible entity that slows down the kinetics and cause the large increase in the activation energy and viscosity [Ega20a]. Arrest occurs close to or at T_g and vitrification takes place. The addition of relatively small quantities of alloying elements, Al to Zr-Cu-based metallic glasses being a prominent example [Geo09, Geo15], can enhance cluster formation as well as their interconnection

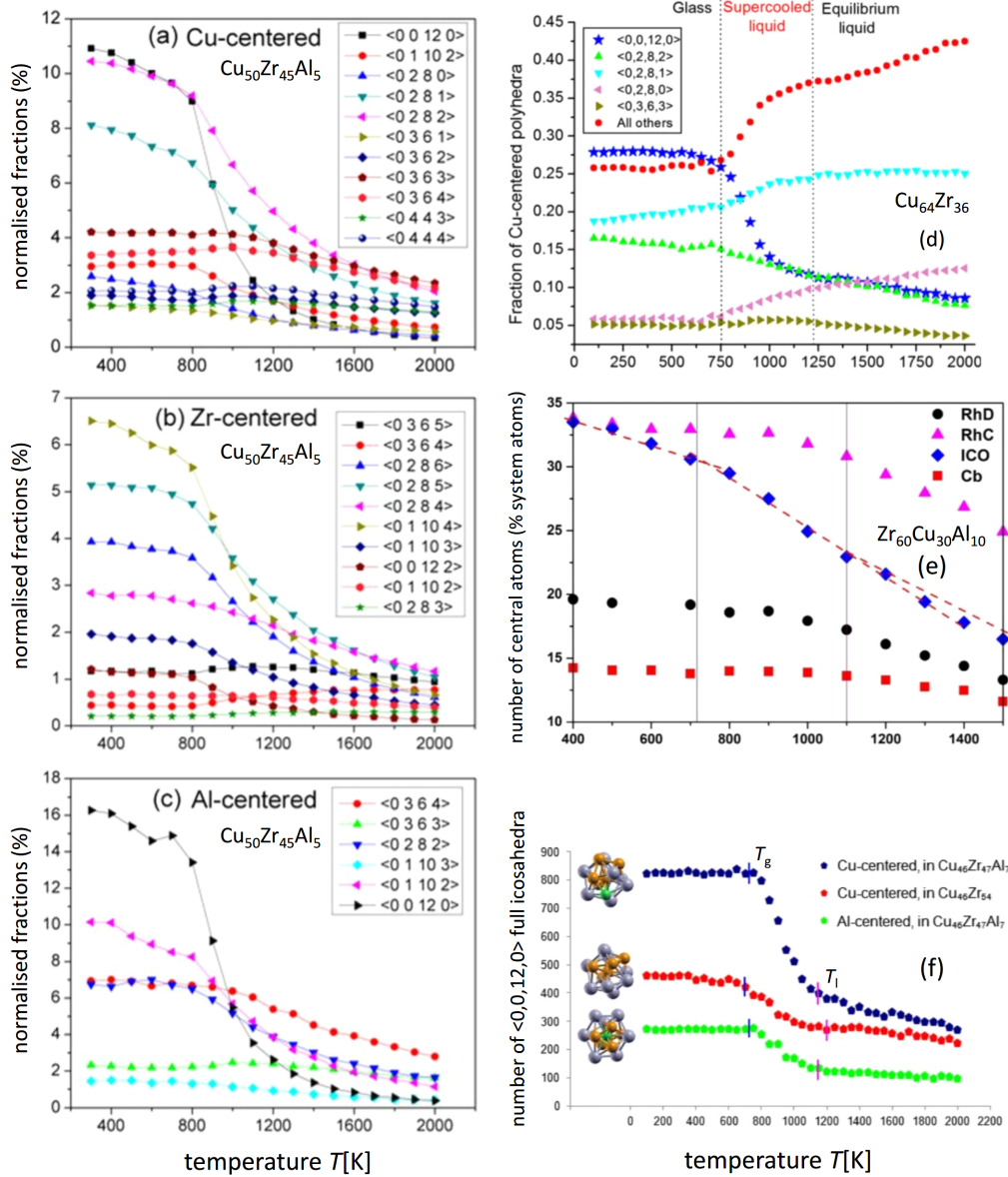


Figure 2.8: Results from MD simulations of various metallic glass forming liquids upon cooling. A rapid acceleration of cluster formation in the undercooled regime is clearly visible. This is especially the case for clusters with icosahedral-like symmetry. In (a), (b), (c), (d) and (f) so called VORONOI indices [Ste93, Ma15] are given where $\langle 0,0,12,0 \rangle$ relates to perfect icosahedral symmetry, i.e. central atoms enclosed by VORONOI polyhedra (VP) with 12 pentagonal facets. **(a,b,c)** Shows the cluster evolution around the different elemental species in $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ (reproduced from ref. Zha11). For $\text{Cu}_{64}\text{Zr}_{36}$ the growth of the $\langle 0,0,12,0 \rangle$ VP on the expense of clusters with other symmetries is highlighted in **(d)**, reproduced from refs. Che09a and Che11, respectively). In **(e)** cluster populations with rhombic dodecahedral (RhD), icosahedral (ICO) and cuboctahedral (Cb) shapes as well as the sum of the population of RhD and Cb clusters (RhC) are shown for $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ (reproduced from ref. Geo15). A comparison of the population of $\langle 0,0,12,0 \rangle$ clusters in $\text{Cu}_{46}\text{Zr}_{47}\text{Al}_7$ and $\text{Cu}_{46}\text{Zr}_{54}$ is shown in **(f)**, reproduced from ref. Che08). As in the experimentally obtained metrics (Fig. 2.4) mainly continuous non-linear dependences of the populations between T_i and T_g are visible.

leading to increased GFA [Che08, Che09, Wan12, Sok13, Geo15]. Although, thermodynamically, the glass transition is commonly considered a second order transition some indications for possible first-order glass transitions have been reported [Bus95, Na20]. Recalling that not only the glass, but also the liquid and undercooled liquid belong to amorphous materials, the glass-transition itself has to be considered an AAT as well, i.e. belong to polyamorphic transitions as LLCs do. This may offer a possible framework to describe the glass transition as well as (some of) the LLCs described above in a generalised and common way.

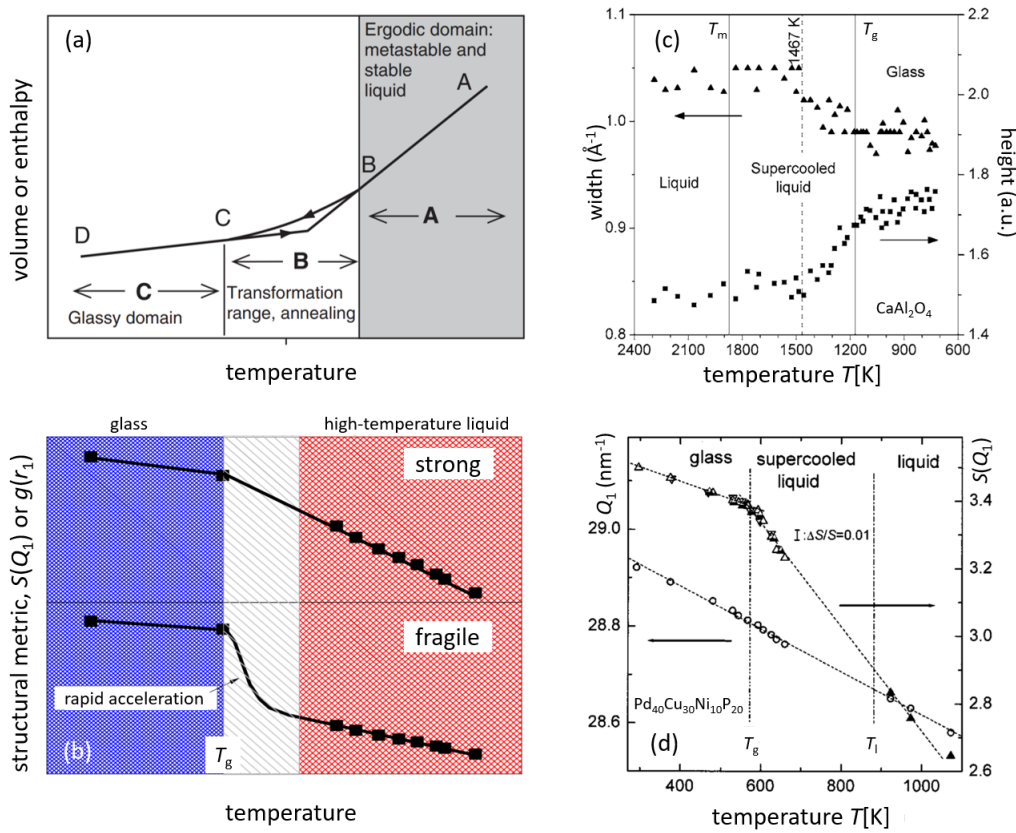


Figure 2.9: The pathway of liquids to vitrification can be separated into three different regimes. This subdivision is not unique and not agreed upon. Parallels to ANGELL's three domains of interest [Ang00, Ang08] can be drawn (a, adapted from ref. Ang08). MAURO et al. (cf. e.g. ref. Mau13a) hinted at three regimes, where the evolution of structural metrics in the region between high-temperature liquid and glass supposedly depends on the materials fragility (b, adapted from ref. Mau13a). Three regimes have also been pointed out for oxide melts (c, here CaAl_2O_4 adapted from ref. Hen07; mind the flipped temperature scale). A possible LLC in the undercooled ("supercooled") regime ($T_{\text{LLC}} = 1467$ K) and not T_m (or T_l) maybe the actual border of the first two regimes on cooling. Three regimes (glass, undercooled ("supercooled") liquid and liquid) have also been discussed for heating experiments (d, here $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ adapted from ref. Mat03; note how position Q_1 and height $S(Q_1)$ are affected very differently across the glass transition).

Using T_m or T_l and T_g the pathway can be divided into the three regimes (Fig. 2.9d). However, considering possible LLCs at T_{LLC} , another possible way of a division, again into three regimes, is possible (Fig. 2.9b,c). Now the regime of the high- T liquid (HTL) on cooling not necessarily ends at T_l or T_m , but may extend down to T_{LLC} . The second regime between T_{LLC} and T_g , that may be called low- T liquid (LTL) [Sto16, Che21], which is followed by the glassy regime below T_g . A division in this way has been pointed out for metallic glasses in simulation and experiment as well as for oxide glasses [Hen07, Mat07b, Jia10, She12, Geo15, Sto16, Alv19]. The three regimes have also been likened [Geo15] to ANGELL et al.'s three "domains of interest" (Fig. 2.9a) during cooling of glass-forming materials [Ang00, Ang08]. Future investigations have to validate this possible correspondence as well as if the existence of three regimes along the pathway is a general phenomenon. Together with further characteristic temperatures like T_A in the high-temperature liquid [Jai16] even more domains or regimes may be distinguished depending on the details of the topology of the potential energy landscape of the particular material [Alv19]. Several results from MD-simulations show accelerated structural ordering in the second regime, mainly ascribed to the formation of clusters of icosahedral-like geometry (Fig. 2.8) [Che08, Zha11, Sok13, Geo15]. This is supposed to be especially the case the more fragile the melt is (Fig. 2.9b). It is worthwhile mentioning that in an alternative view the dominance of the icosahedral structural motif is to be considered a sign of nano-crystallisation rather than one of glass formation [Ega20].

In summary, a large number of important pieces, experimental as well as theoretical, of the jigsaw puzzle "glass formation" has been accumulated over the past decades. However, it is the *continuous* experimental acquisition of structural data along the complete pathway of a liquid metal from temperatures well above its liquidus temperature during undercooling and vitrification down to temperatures well below the glass-transition temperature that possesses the capability needed to combine those pieces to the final picture and thereby closing an important research gap. Therefore, the foremost aim of the present thesis is to analyse and interpret data taken by ultrafast synchrotron X-ray diffraction during aerodynamic-levitation experiments of metallic-glass forming alloys along their complete pathways.

3 Mapping the pathway – Methodology

The experimental methods outlined in Ch. 2 are described here in some more detail including a brief description of the theoretical background for elastic scattering (Sec. 3.3). It will be discussed why only electrostatic levitation and aerodynamic levitation (Sec. 3.1) in combination with ultrafast X-ray diffraction can be used to study the atomic structure of metallic glasses (Sec. 3.2) along their pathways. Section 3.4 presents information about processing raw data and the necessary software while Sec. 3.5 describes further steps of data treatment, how structural metrics can be obtained from the experimental data, fitting and ways of presenting data. In Sec. 3.6 an outlook to possible improvements of the experimental methods, necessary to answer some of the open questions about the structural evolution along the pathway, is given. Detailed reviews of the experimental methods to date can be found in the literature [Hen11, Ben12, Ben17, Hen17].

3.1 Levitation techniques

In order to accomplish in-situ vitrification sufficiently high cooling rates as well as the exclusion of all sources of heterogeneous nucleation need to be achieved. The necessary cooling rate is dictated mainly by the critical cooling rate of the material itself. The cooling rate can be reduced by actively heating the sample during otherwise free cooling. A higher cooling rate can be achieved by a smaller sample size which, however, may be detrimental to sample handling. Heterogeneous nucleation can only be avoided by the omission of a sample container. This immediately implies the need for a means of levitation of the sample during (ground-based) experiments as well as the avoidance of any other reactive environment. For the same reason, temperature measurements need to be taken contactlessly. Therefore, one or more optical pyrometers are used [Kri97, Gan05, Hen07, Hen11, Geo15]. At low temperatures they become ineffective and can be replaced by infrared pyrometers [Kri97, Mau13b, Ben17]. Alternatively, an extrapolation to lower temperatures can be made by assuming and fitting an exponential function to the temperature profiles $T(t)$ (time-dependent surface temperature of the sample) measured at high temperatures [Geo15]. These methods can be used for all levitation methods discussed here. Of the possible levitation techniques [Mil06] three are usually used for structural studies on macroscopic metallic-glass samples, which are electromagnetic levitation (EML), electrostatic levitation (ESL) and aerodynamic levitation, the latter mainly in the form of conical nozzle

levitation (CNL). Detailed reviews can be found in the literature [Her93, Hye08, Pri10, Egr11, Par14, Ben17]. Each method has certain advantages and disadvantages in relation to the measurements taken and not all are suitable for in-situ monitoring of temperature-dependent fast structural changes. The method used also depends on the material to be investigated, especially its GFA, as well as sample size. While ESL and CNL allow for the diameters of about 3 mm, EML can be used for diameters twice as big [Mil06].

The oldest of these techniques is *electromagnetic levitation* (EML) [Okr52]. Its relatively simple basic construction consists of a coil-shaped water-cooled metallic pipe (Fig. 3.1). A traversing alternating electrical current generates an electromagnetic field which, in turn, will induce currents inside a conductive material (sample) placed in the centre of the coil. These currents will generate a secondary magnetic field which causes the sample to levitate inside the coil (LENZ's law). At the same time the

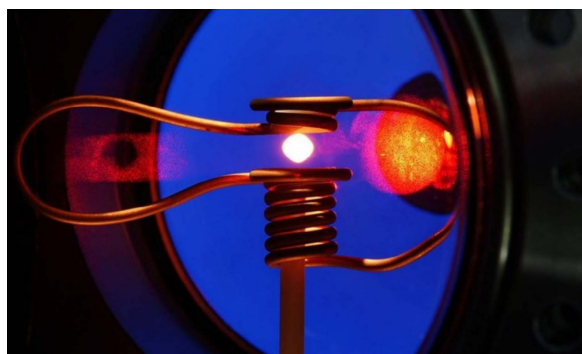


Figure 3.1: The coil responsible for levitation and heating of metallic samples (centre), reproduced from ref. Hen07.

induced currents also heat the sample beyond T_l . What seems to be convenient at first glance prevents this method from being used for the desired temperature-dependent measurements of the necessary wide temperature range considered here since heating and stable levitation would not be as independent of each other as necessary. Especially at low temperatures (e.g. below T_g) levitation is still necessary while heating is not. Although there are ways to mitigate this issue, e.g. by a combination with aerodynamic levitation [Mat05, Egr11] this method has not been used for any of the metallic glasses considered in this thesis (Tab. 2.1). Due to the need of electrical conductive materials EML cannot be used for oxide glasses either. Other problems like sample deformation need to be taken into account as well [Mat05] which may hamper accurate temperature measurements or even prevent the desired deep undercooling by premature nucleation [Rhi93].

Electrostatic levitation (ESL) in principal dates back to the experiments of MILLIKAN published in 1911 where small levitated charged oil drops were used to determine the elementary electrostatic charge [Mil11]. Studying undercooling and recalescence of large samples of high-temperature materials ESL was used only about 80 years later [Rhi93] followed by the first X-ray scattering studies on electrostatically levitated metallic liquids another decade thereafter [Kel03]. Finally, temperature-dependent measurements over a wide temperature range and in-situ vitrification was performed using ESL only recently (Tab. 2.1). Compared to EML the use of ESL has some key advantages. The range of materials that can be studied with this method spans metals, semiconductors and insulators, since the only requirement to generate a levitation force is a sufficient surface charge which is created by the photoelectric effect [Hen17] using ultraviolet light or by thermionic emission [Par05]. For ESL sample heating and levitation are independent of each other making a wide temperature range accessible while feedback control provides a stable sample positioning throughout the experiments [Cla80]. Furthermore, no distortion of molten samples occurs. While for EML

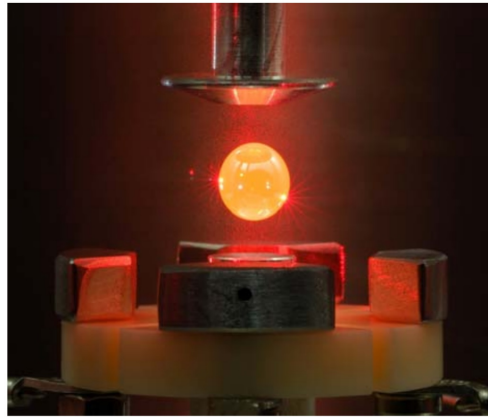


Figure 3.2: Electrostatic levitation exemplified for 0.6 g of liquid $\text{Ti}_{39.5}\text{Zr}_{39.5}\text{Ni}_{21}$ at 1150 K, reproduced from ref. Egr11.

the heating and levitation coil blocks the unrestricted view to the sample from the majority of angles, for ESL an open view for a plethora of instruments around the sample is possible allowing a variety of measurements and diagnostics to take place simultaneously [Rhi93, Aok03]. Those experiments can comprise density and thermal expansion by measuring the temperature-dependent size of the levitated ball using cameras and appropriate lighting [Ish01, Li11, Wei13], measuring the temperature-dependent specific heat and emissivity utilizing the STEFAN-BOLTZMANN law [Bus95, Gan17a], or even measurements of the viscosity or surface tension by adding a sinusoidal electric field to the levitation field for a short time [Rhi99, Par05] and observing the time-

dependent ring-down of the surface oscillations. Alternatively the shape change of the drop upon rotation can be analysed to determine surface tension [Rhi01, Mil04].

The independence of levitation and heating requires an independent source for sample heating for which different types and numbers of lasers are used. By varying their output power the temperature of the sample can be adjusted without impeding sample levitation. In-situ vitrification usually demands a cooling rate as high as possible if not only materials with exceptionally high GFA are to be investigated. Since ESL needs to take place in vacuo in order to prevent electrical breakdowns [Cla80], cooling is possible by radiation only which limits the possible cooling rates $\dot{T}(t)$. The highest $\dot{T}$ is achieved by free cooling after switching of the lasers completely. Despite many advantages this considerably limits the numbers of alloys for which in-situ monitoring of vitrification is possible in an ESL setup to those with exceptionally high GFA. Especially at low temperatures the small cooling rates cause cooling to become slow, i.e. the cooling curve $T(t)$ becomes very flat and a reliable assignment of a temperature to a diffraction image is hampered. In this case even for samples with low critical cooling rates in-situ vitrification was not described although no crystallisation took place [Wei13, Sto16].

The lasers used for heating vary in type, number and position relative to the sample [Mil04] where wavelengths in the infrared part of the spectrum are preferred. Asymmetric heating, e.g. by using only one laser beam on top of sample, can be used for interesting effects like "polyamorphic rotors" in connection with LLCs [Gre08]. With isotropic laser heating sample temperatures of 3000 K and beyond can be reached [Par05, Hen06, Ish17]. However, this may cause evaporation of sample material and possible changes in composition which needs to be verified by weighing the sample and chemical analysis after the experiment. Furthermore, coating of the pyrometer window in the vacuum chamber with sample material and possibly distorted temperature readings need to be taken into account and measures to mitigate them to be employed [Hen17]. Aerodynamic levitation suffers less from this issue than EML and ESL.

Figures 3.3 and 3.4 show the shape of nozzle that provided the name *conical nozzle levitation* (CNL) for this almost exclusively used design in state-of-the-art *aerodynamic levitation* setups [Hen11, Kri97, Neu14, Cue14, Web16, Web17, Hen17]. Based on the early works of WINBORNE et al. [Win76] the nozzle design has improved over time to allow increasingly bigger portions of the sample being visible to the neutron or

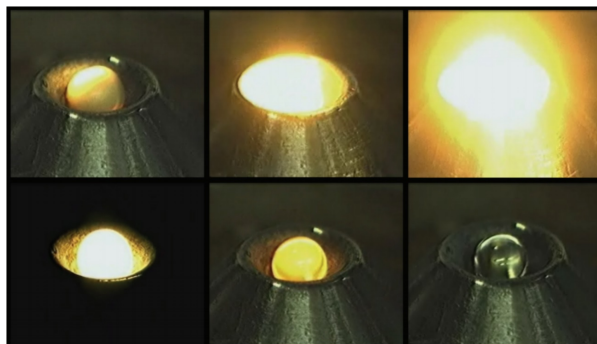


Figure 3.3: In-situ vitrification in a CNL setup showcased for an oxide melt (reproduced from ref. Ben12). From top left to bottom right the sample is heated and melted and subsequently vitrifies during cooling.

X-ray beam as well as to diagnostic instruments [Ben17]. Metallic-glass samples are stably levitated by a regulated flow of inert gas, usually Ar, through a convergent-divergent conical nozzle channeled upwards to counteract gravity [Hen17]. Levitation can be acoustically stabilized [Web94, Nor12]. Technically, CNL is not a containerless method. However, the use of noble gases should sufficiently exclude reactions causing heterogeneous nucleation. Like for ESL, levitation and heating are independent of each other for CNL as well and laser heating is performed in a virtually identical way as compared to ESL. The big difference and major advantage compared to e.g. ESL is that the levitation gas also provides a drastic increase in cooling rate making it possible to observe in-situ vitrification for a much wider range of liquids compared to the other levitation methods. Although He would provide an even higher thermal conductivity and subsequently higher cooling rates [Moh19, Gan21] it is less suitable for CNL [Ald17], mainly due to small atomic mass. Furthermore, the levitation gas also reduces sample evaporation (and coating of windows and other components) [Ben17]. Minor drawbacks of CNL can be seen in additional scattering from the levitation gas and the lower suitability for experiments that involve oscillations of the molten material (e.g. for surface tension). However, if the main goal of the investigation is to acquire structural information over a wide temperature range along the pathway including deep undercooling and vitrification CNL can be considered the best choice.

Containerless processing would be eminently facilitated if the need to counteract gravity is largely reduced or completely removed. Accordingly, experiments in microgravity have been performed during parabola flights, on board sounding rockets, the Space Shuttle or the International Space Station (ISS) [Her93, Egr99, Cla80,

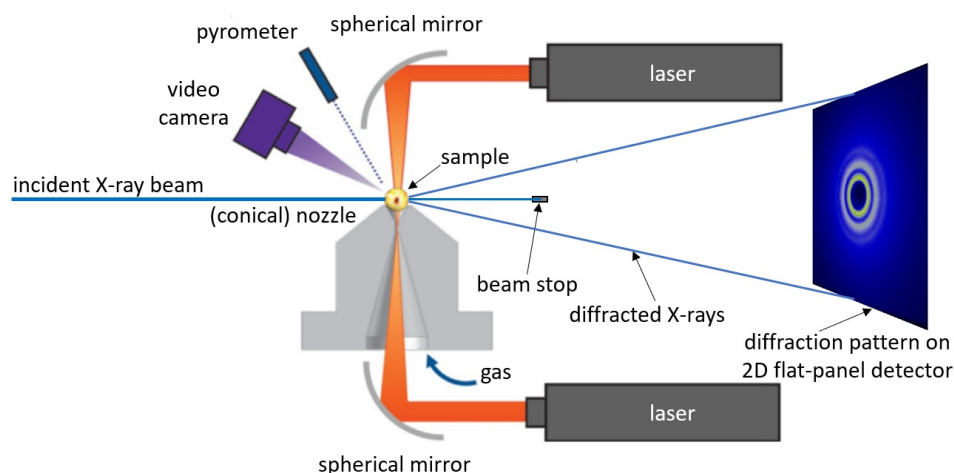


Figure 3.4: Schematic representation of conical-nozzle levitation and laser heating for synchrotron X-ray diffraction (adapted from ref. Hen17).

Loh02, Loh05, Egr08, Hoe19, Moh19, Moh20, Gan21]. For sample stabilisation and positioning combinations with the aforementioned techniques are possible [Loh05]. Microgravity, furthermore, allows to measure bigger samples than in ground-based setups [Loh02, Loh05, Par14], the spherical shape and surface of the droplets is less disturbed and convection greatly reduced [Hoe19]. However, due to the lack of compact radiation sources with the necessary characteristics, it is currently not possible to perform structural investigation in these environments [Egr99, Wun11, Bra19, Moh19a]. Measurements in reduced gravity are therefore restricted to containerless measurements of density, thermal expansion, viscosity, surface tension, heat capacity or electrical resistivity – the latter being at least an indirect scattering experiment using the conduction electrons as probe.

Ground-based levitation setups were first used to determine aforementioned macroscopic quantities like density, thermal expansion coefficient, heat capacity, emissivity, surface tension and viscosity [Par99, Ish01] that can be inferred directly by observing the entire levitated sample e.g. by using cameras. For the observation of the atomic structure and its evolution probes sensitive to interatomic distances are necessary. To gain insights into the bulk of the sample, rather than their surface, appropriate diffraction experiments are needed which, however, yield information in *reciprocal space* only. *Real space* information needs to be reconstructed subsequently which is connected with several challenges on its own as outlined in Sec. 3.3. The methods for determination of the atomic structure are briefly discussed in the following.

3.2 Scattering techniques

The scattering techniques commonly used in condensed-matter science are X-ray, neutron and electron diffraction. In order to gain information not only on the average structure, but also on the compositionally resolved *partial structure factors* or *pair correlation functions* in non-monatomic materials the same sample would need to be investigated by more than one of these probes [Ega03]. Given the usually high number of elements in BMGs with high GFA not enough independent scattering techniques may be available. The situation becomes even more aggravated since the high critical cooling rates demand an ultrafast operation and detection mode with a high frame rate for all of them. A single frame captured needs to contain a complete diffraction pattern. However, the higher the frame rate the less "light" enters the detector per frame and the lower the signal-to-noise ratio (SNR) becomes. All these considerations favour a transmission geometry with source, sample and (two-dimensional) detector being in one line and stationary (Figs. 3.4 and 3.5).

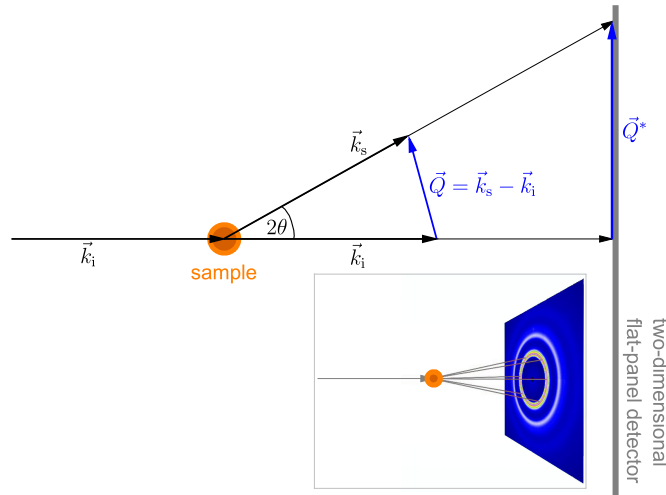


Figure 3.5: Geometry for elastic scattering methods in transmission. In case of a 2D flat-panel detector the scattering vector $\vec{Q}$ has to be calculated from its projected version $\vec{Q}^*$. The scattering vector $\vec{Q}$ "translates" the incident wavevector $\vec{k}_i$ to the wavevector $\vec{k}_s$ of the wave scattered elastically at scattering angle 2θ , where $|\vec{k}_s| = k_s = k_i = |\vec{k}_i|$. The inset (adapted from ref. Guo15) sketches a slanted view on the geometry illustrating the relation of sample, beams and diffraction pattern.

Since sample handling for levitation and the necessary cooling rates call for millimetre-sized samples the probe needs to be able to penetrate balls of corresponding diameters. This immediately excludes the use of electron diffraction since even with energies in the MeV range electrons can only penetrate samples with diameters $< 1 \mu\text{m}$ [Akk78, Aka06, Nun20], not to mention the levitation gas surrounding the sam-

ple. Furthermore, in contrast to neutrons and X-ray photons, electrons carry electric charge, i.e. electron diffraction would be excluded even in a reflection geometry due to distortion of the incident beam by the magnetic and electric fields used for EML and ESL as well as the charged levitating sample itself. Although millimetre-sized samples are unproblematic for neutrons to be penetrated it is the low achievable intensity and the necessary high acquisition times that exclude this type of radiation. Possible ways to mitigate these problems are discussed in Sec. 3.6. Thus the current state of technology only allows high-energy (synchrotron) X-rays to be used as structural probe to gain the wanted insights into metallic-glass forming alloys. With the term "high-energy" commonly used for energies $E_i > 60$ keV of the incident monochromatic X-ray beam [Ben12] all experiments listed in Tab. 2.1 fall into this category (for comparison the frequently used Cu- K_α radiation from a typical laboratory X-ray source has a wavelength $\lambda_i \approx 1.54$ Å corresponding to $E_i = 8.05$ keV). State-of-the-art sources of this kind of radiation are synchrotrons now available in different places around the globe. Only due to the high brilliance and high energy of synchrotron light sources it has been possible to reduce acquisition times by obtaining 2D-diffraction patterns with enough intensity per frame [Uri03, Koh16]. Details of X-ray generation in synchrotrons can be found elsewhere [Wil19]. Close to absorption edges of a specific given element its atomic form factor changes anomalously [Was02, Koh16]. Comparing scattering patterns using incident X-rays with energy close to such an absorption edge with those using energy away from it a substantial contrast can be found. Harnessing this effect the so-called anomalous X-ray scattering (AXS) technique provides element-selective information that can be used to disentangle partial structure factors [Ega03]. Different X-ray energies can so be considered as independent types of radiation. Although AXS has been widely used for amorphous materials (liquid and glass) at constant temperature [Mat94, Hos08, Koh14, Koh16, Kaw21] a temperature-dependent study of the pathway or parts thereof is missing so far. To achieve an accurate disentanglement experiments using different incident energies would need to be carried out at the same sample either simultaneously, which would be related to a very complex experimental setup that is not available to date, or in consecutive runs with all other parameters exactly reproduced. Another well-known element specific synchrotron X-ray method, EXAFS (extended X-ray absorption fine structure) [Cic20, Gru20], although fast enough [Buz16, Bor19], is limited by high absorption requiring very small sample thicknesses [Lee81, Gru20] and therefore suffers from similar problems as electron diffraction.

Total scattering diffraction patterns for synchrotron XRD are captured on two-dimensional (2D) flat-panel area detectors (custom build or purchased from commercial suppliers) that are capable of recording over a wide range of scattering angles θ or scattering vectors $\vec{Q}$ (modulus $Q = |\vec{Q}|$), respectively, simultaneously. This is possible since the used high energy E_i , i.e. small wavelength (Eq. (3.1)), "compresses" a wide Q -range into a cone (cf. Fig. 3.5) with small opening angle and enables the use of relatively compact setups [Ben12]. No angular scan, as in laboratory XRD setups, is necessary. In recent years X-ray free-electron lasers (XFEL) had their advent. The pulsed nature of their high-density X-rays will allow monitoring of very fast structural changes [Por10,Zal19]. So far XFELs have not been used to in-situ monitor vitrification but were for instance able to disclose LLCs in chalcogenide-based glasses [Zal19].

A challenge is the successive loss of information along the experimental chain. During the diffraction experiment the three-dimensional structure is reduced to information on a 2D detector and later reduced even more by azimuthal averaging to a one-dimensional function, the structure factor $S(Q)$. A partial reconstruction of the lost information would be possible by using different types of radiation which is difficult as described above. To learn more about the evolving element-specific local environments and chemical short-range order (CSRO) along the pathway other methods like computer simulations can be utilised. A relatively simple method is Reverse Monte-Carlo (RMC) refinement in which the position of the atoms in a simulation are varied until the structure factor coincides with the measured one [Gre01]. From this final configuration partial structure factors and all other information about local arrangement of the atoms like bond lengths and bond angles can be derived. The major drawback of this method is the massive overdeterminacy, i.e. a huge number of local configurations (three-dimensional) yield virtually identical structure factors (one-dimensional). Another computational method, Molecular Dynamics (MD) simulation, seeks to determine the structure based on solving the equations of motion for all atoms in a sample using interatomic potentials [Nos84, Pli95]. If these potentials are derived from first-principle quantum-mechanical calculations like density functional theory (DFT) the method is called ab-initio MD (AIMD) [Kre93]. The results of MD simulations can be used as additional input to improve RMC simulations. Currently, AIMD is computationally too expensive to be performed with the temperature increment as state-of-the-art diffraction experiments, but even a bigger step width can provide valuable insights [Geo15]. DFT calculations can also be used to evaluate changes in bonding among atomic pairs along the pathway.

3.3 Elastic scattering and structure functions

Incident monochromatic X-rays with energy E_i possess a wavelength

$$\lambda_i = \frac{hc}{E_i} \quad (3.1)$$

which translates to the modulus of the incident wave vector

$$|\vec{k}_i| = k_i = \frac{2\pi}{\lambda_i} \quad , \quad (3.2)$$

where c is the speed of light in vacuum and h PLANCK's constant. Considering only elastic scattering the modulus $|\vec{k}_s| = k_s$ of the scattered wavevector is identical to that of the incident wavevector, i.e. $k_s = k_i$ or $|\vec{k}_s| = |\vec{k}_i|$ (Fig. 3.5). The momentum transferred to the sample during the scattering event is expressed by the so-called scattering vector

$$\vec{Q} = \vec{k}_s - \vec{k}_i \quad , \quad (3.3)$$

of which in case of the isotropic nature (inset of Fig. 3.5) of the amorphous material (liquid and glass) only the modulus $Q = |\vec{Q}|$ is of interest. Both vectors $\vec{k}_i$ and $\vec{k}_s$ are vectors in the so-called k -space (not Q -space) or *reciprocal space*. Instead of Q , in some publications q or K is used. The modulus of the scattering vector is related to the scattering angle 2θ (Fig. 3.5), which is often used for presenting the results of laboratory X-ray experiments, by

$$Q = \frac{4\pi}{\lambda_i} \sin \theta \quad . \quad (3.4)$$

The important quantity for structural analysis is $S(Q)$ the *total scattering structure function* where 'total scattering' refers to the fact that the measured intensity comprises scattering not only from the atomic structure but also inelastic scattering due to the thermal movement of the atoms, i.e. their dynamics [Ega03]. Ways of separating both exist by evaluating the so-called DEBYE-WALLER factor [Sin89]. For amorphous materials $S(Q)$ is usually referred to as *structure factor* which must not be confused with the crystallographic structure factor [Ega03]. For all of the studies reviewed here the FABER-ZIMAN formalism has been used [Fab65, Ega03].

Although $S(Q)$ can already be used to analyse certain aspects of the structure, e.g. in connection with global electronic influences [Hau92, Sti19] and thermal expansion [Yav05] more often information in *real space* (r -space) is desired which can be obtained by a FOURIER transform that yields the *reduced pair-distribution function*

$$G(r) = \frac{2}{\pi} \int_0^{Q_{\max}} Q[S(Q) - 1] \sin(Qr) dQ \quad . \quad (3.5)$$

$G(r)$ can be interpreted as the distribution of probability of finding the centre of another atom at distance r from an arbitrarily chosen atom (at $r = 0$) and can directly provide an insight into the typical shell structure of amorphous materials. If ρ_0 , the material's (average) particle number density, is known further structure functions can be derived from $G(r)$ like the *pair-distribution function*

$$g(r) = \frac{G(r)}{4\pi\rho_0 r} + 1 \quad (3.6)$$

and the *pair density function* $\rho(r) = \rho_0 g(r)$. Both describe the shell structure as deviation from the mean density (of a structureless gas of the same mean density) to higher *as well as* to lower values. All these real-space functions give information on how the neighbourhood of an atom in the sample looks like on average. The *coordination number*

$$N_C = \int_{r_1}^{r_2} R(r) dr \quad , \quad (3.7)$$

provides the number of atomic centres located between two concentric spheres with radii r_1 and r_2 , where r_1 and r_2 usually delimit a nearest-neighbour (NN) shell. The function $R(r)$ in Eq. (3.7) is called *radial distribution function* (RDF) and can be calculated from $g(r)$ or $\rho(r)$, respectively, by

$$R(r) = 4\pi r^2 \rho_0 g(r) \quad . \quad (3.8)$$

Knowledge of the number density ρ_0 , necessary to determine $g(r)$, $\rho(r)$, $R(r)$ and N_C , can be obtained by measuring the macroscopic mass density or, ideally, from the scattering data directly (the initial slope of $G(r)$ is proportional to ρ_0). However, the latter is prone to uncertainties along the chain of structure analysis. To determine the

density macroscopically the temperature-dependent volume of the sample needs to be known along the pathway which, as already mentioned above, can be achieved by using cameras and appropriate lighting [Ish01, Li11, Wei13]. Unfortunately, especially for CNL this method is less attractive as parts of the sample are hidden by the nozzle. It is therefore important to gain as much structural information from $S(Q)$ and $G(r)$ as the structure functions that do not depend on the knowledge of ρ_0 .

3.4 Data acquisition and reduction

Temperature-dependent measurements upon cooling result in a huge amount of data depending on the temporal as well as spatial resolution of the detector. From the scattered intensity captured as diffraction pattern on the area detectors (Figs. 3.4 and inset of 3.5) to the structure functions in real space many steps are necessary which are carried out using several specialised software packages. Some of them are specific to a particular setup (mainly at early steps in the tool-chain of data-analysis) or common for a facility, beamline or a particular research group. Others, like those to perform the FOURIER transform, can be used interchangeably.

The raw-data is influenced by several factors not intrinsic to the measured material. These are related to the X-ray source, the sample environment, as well as the detector and need to be corrected for [Ega03, Ben12]. Routines for these corrections are usually included in the according software packages.

Diffraction patterns of amorphous materials are characterised by diffuse concentric rings (halos). Using e.g. DAWN [Bas15, Fil17] or FIT2D [Ham96] the diffraction patterns are azimuthally integrated to obtain the integrated diffraction intensities $I(Q)$. With subsequent normalisation to the X-ray atomic form factor and conversion to electron units per atom (generalised KROGH-MOE-NORMAN method [Kro56, Nor57]) the total structure factors $S(Q)$ can be calculated. Dedicated software for this step is e.g. GudrunX [Sop11] or PDFgetX3 [Juh13] which also FOURIER transform $S(Q)$ to the reduced pair-distribution function $G(r)$ as outlined above. While ideally $Q_{\max}$ in Eq. (3.5) is infinite, in practice it is necessary to choose a finite value, usually as high as possible, depending on the raw data. Improper choice can introduce artifacts in form of additional oscillations in $G(r)$ ("termination ripples") what can be somewhat mitigated by the use of modification functions during FOURIER transform [Sop12]. PDFgetX3 has been developed as a rapid and highly automatable software which can readily process hundreds of X-ray diffraction patterns within a few seconds [Juh13]

and is thus especially useful for the high number of temperature-dependent diffraction patterns taken along the pathway. In the end a variety of plotting programs can be used to visualise e.g. the temperature-dependent structure functions $S(Q, T)$, $G(r, T)$, $R(r, T)$.

For the mentioned RMC calculations also a variety of software packages are available with RMCProfile [Tuc07] and RMC++ [Ger07] being the most common. MD simulations are most commonly carried out based on the LAMMPS code [Pli95]. For DFT calculations the SIESTA code [San97, San99, Sol02] is often used which employs the standard KOHN-SHAM self-consistent scheme in local density approximation (LDA).

3.5 Data analysis

The two main results that can be obtained (more or less) directly from the in-situ measurements are the cooling curves $T(t)$ and (after the corrections outlined in Sec. 3.4) $S(Q)$, i.e. $S(Q, T)$ to be precise. All other structure functions are in turn derived from $S(Q, T)$. Although the main aspect of this thesis is the evolving structure, the cooling curves $T(t)$ themselves yield important results beyond indicating the sample temperature during cooling. From $T(t)$ the temperature rate $\dot{T}(t)$ can be calculated (upon cooling its values are negative; the absolute value is then called "cooling rate"). Upon free cooling, i.e. after deactivating all heating equipment, $\dot{T}(t)$ strongly changes (Fig. 3.6) and an exponentially decaying temperature is expected. Knowledge of $\dot{T}(t)$ is important in comparing different experiments and materials since effects like LLCs may be temperature-dependent (Sec. 2.2.2). Major deviations occur if the sample crystallises and recalescence occurs which leads to sharp temperature increase due to the release of latent heat of crystallisation. This behaviour is, of course, not desired as it prevents vitrification. Whether the glass transition can be observed by a small kink in $T(t)$ at T_g is not always clear although it has been reported [Wat10]. For an oxide-glass forming liquid a small kink in $T(t)$ related to a possible LLC has been reported [Hen07] as well as the visibility of decomposition of a Zr-based metallic glass [Kim96]. With the knowledge of the emissivity of the material and the STEFAN-BOLTZMANN law the temperature-dependent specific heat $c_p(T)$ of the alloy can be determined [Bus95, Sto16].

Deeper insights can be gained by closer scrutiny of the details of the structure functions. Since both in reciprocal as well as in real space these functions consist of a series of peaks (and troughs, i.e. "anti-peaks") it is fruitful to analyse those and

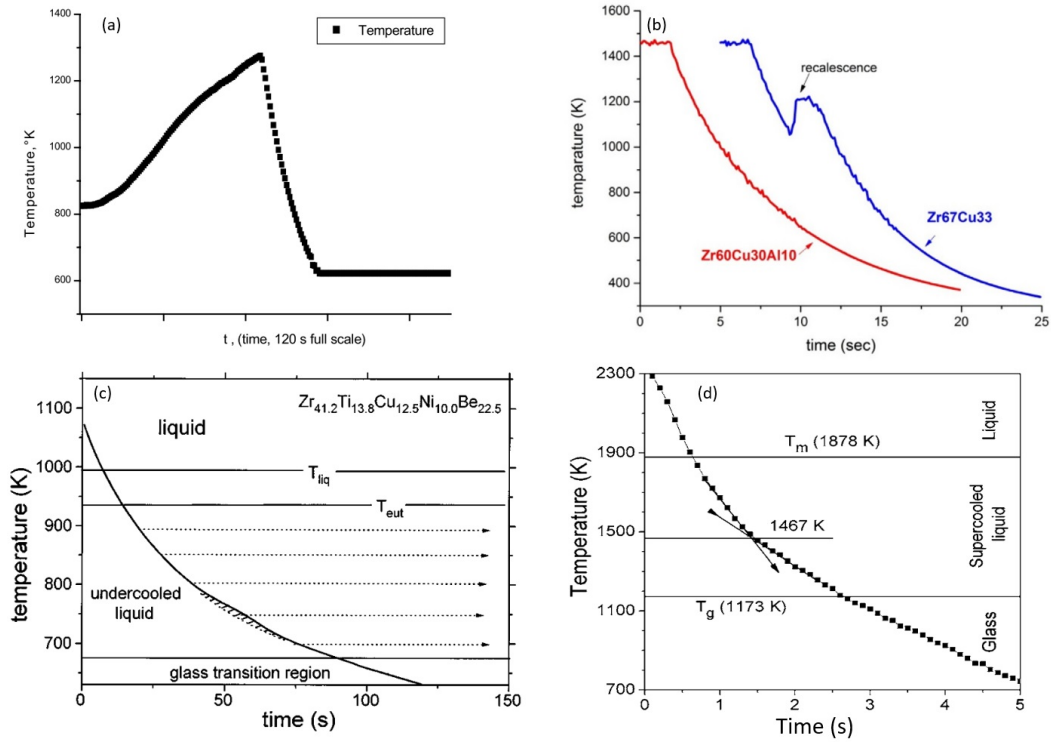


Figure 3.6: Examples of several $T(t)$ functions ("cooling curves") and proposed interpretations. (a) The first reported in-situ vitrification ($\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$) showing no recalescence that would point to crystallisation during free cooling after switching off the sample heating [Uri03]. (b) The comparison of $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ and $\text{Zr}_{67}\text{Cu}_{33}$ shows that in-situ vitrification of the latter alloy could not be achieved due to the intervention of crystallisation evidenced by the recalescence event at about 1050 K (this also shows the beneficial effect of Al on GFA) [Geo15]. (c) In $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10.0}\text{Be}_{22.5}$ a small recalescence event (hatched area) was attributed to a decomposition of the undercooled liquid with respect to Zr and Be [Kim96]. (d) A possible kink (determined using two tangents) in the cooling curve of CaAl_2O_4 interpreted as an increase in the degree of order related to a dynamical crossover temperature causing changes in thermodynamic properties as well [Hen07].

their temperature-dependence independently. Quantities like positions, widths or heights of peaks are commonly called *structural metrics* and be obtained by different methods as will be discussed further down. Great care must be taken when ascribing a physical meaning to a peak and according metrics. Furthermore, there is no unique and agreed-upon procedure for how the structure functions can be "dissected" into those peaks (halos for $S(Q)$ and NN shells for $G(r)$) nor where a peak begins/ends or if some sort of background needs to be subtracted [Lou11] (Fig. 3.7). However, the choice of background is subjective and may lack physical justification. One form of background is constructed by connecting the minima of the functions via straight lines [Lou11, Lou20]. This method misses important temperature-induced structural changes in the troughs between the peaks, i.e. it would cause a peak to increase in

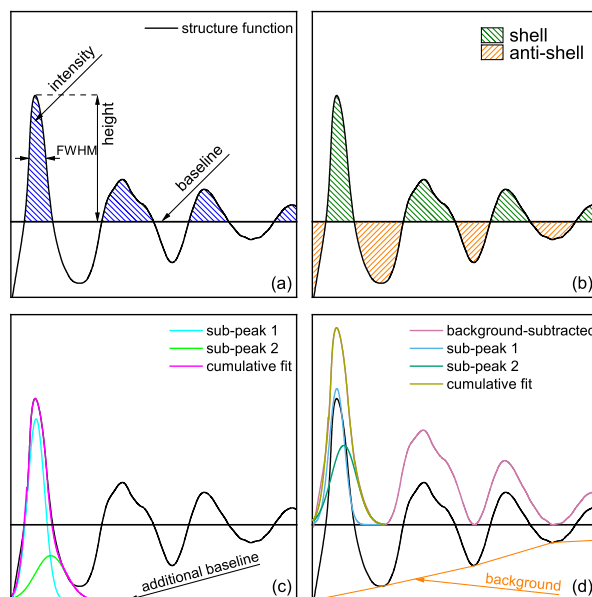


Figure 3.7: Possible ways of extracting peaks from a structure function (black) and their fitting: (a) using the parts above a baseline, implied by the average of a structure function, (horizontal black line) only (peaks not necessarily to be fitted), (b) using portions above and below that baseline (especially in real space called NN shell and anti-shell), (c) defining an additional baseline for a fit (shown exemplarily for the first peak fitted by two sub-peaks), (d) removing a background (orange, determined by a set of linear functions) before fitting. In a) the definitions of intensity, height and FWHM are highlighted.

height although actually the adjacent minima get deeper with decreasing temperature [Lou20]. Given that the structure functions oscillate about a line of constant y (e.g. $S(Q) = 1$; $G(r) = 0$; $g(r) = 1$) using the intersections of these function with that line can be used to demarcate the peaks (cf. also Ch. 5). Alternatively, the local minima within the troughs (or zeros after background subtraction) can be used (Fig. 3.7c,d). For results of simulations a less arbitrary way has been proposed in the case of $R(r)$ [Gre86, Rio20]. Different kinds of functions are commonly fitted to the individual peaks before they are subject to further analysis. Fits are performed for different reasons: (i) smoothing out noise from the experiment, where type of functions and number of curves fitted to one peak can be chosen arbitrarily (depending on time and computational power available), since no physical meaning is attached to the functions and the only aim is to reproduce the experimental curve as good as possible with scatter removed, (ii) showing that the peak consists of two (or more) features (by fitting of two or more curves) that e.g. may behave differently depending on temperature (e.g. first NN shell in ref. Geo15) or (iii) fitting of two or more curves, especially in r -space, that are supposed to directly relate to expected partial pair correlations or bond

lengths of elemental pairs in the alloy. The latter has to be done with great care and is often ill-fated when too many components are present. Even with less components, although tempting, sub-peaks not automatically relate to certain elemental pairs of the same number. The used fit functions depend on the authors and the purpose of the fit. Gaussian functions are frequently used [Lou11, Geo11, Geo15, Lou20], but also Lorentzian functions or combination/convolution of both in form of VOIGT or pseudo-VOIGT functions [Qu12, Eve14, Ryu20]), as well as spline functions [Mau13b, Wei13, Wei15, Sto16, Hec18]. Using different fit functions to obtain different parameters from a peak has been used as well [Wei13].

From the individual peaks or their fitted version several parameters or characteristics can then be derived and analysed as well as plotted as temperature-dependent structural metrics. The peak position may be considered the most straightforward, although the position of the maximum (i.e. the x -value belonging to the highest y value), the position of the centroid (centre of mass, i.e. first moment) or a quantity called R_{50} [Lou20] (the x -value for which 50% of the peak area is below as well as above) can be meant, where authors not always clearly indicate which definition they followed or if a baseline correction was carried out which can impede comparability of results. Subsequently, other metrics suffer from the same issue. For the width of a peak often the full width at half maximum (FWHM) Γ is used, but its second moment (i.e. variance) [Lan16] may deliver comparable information with less scatter (Ch. 7). Further commonly used metrics are height of the peak or area of the peak, where peak area, rather its height, is linked to its intensity. Also, the skewness or asymmetry of a peak can be analysed following different definitions, e.g. by comparing the left and right half-width [Din14a], the relative positions of the maximum and the centroid (Ch. 6) or by calculating its third moment. In general, metrics that involve an integration (centroid and other moments) are much more robust since they naturally include an averaging over many values. Frequently ratios of different metrics are discussed as well [Kel03, Lou11, Lou20, Ryu20]. Calculating and analysing the moments removes the subjectivity of choosing a specific fit function [Lan16, Don21] and in principle also moments beyond the third one can be used to discern possible temperature-dependent changes in behaviour (e.g. related to a possible LLC) along the pathway, although the physical meaning may not always be straightforward. The aforementioned quantities are sometimes taken only from sub-peaks or shoulders after applying fitting procedures [Lan16]. Although highlighting those temperature-dependent changes is usually the intention behind an author's

selection of a specific structural metric due to the constraints of the experiment one metric may have less noise than another and is therefore preferred [Wei13]. Calculating the relative Gaussian and Lorentzian proportion of a fitted VOIGT profile was proposed as another way of gaining further structural insights [Ryu20]. By using the intersections of the structure functions with their respective baselines to define peaks [Bed11, Wei13, Geo15, Hec18] and their analysis in terms of moment-related metrics without any fitting can be considered the least subjective processing. This procedure inspired the "shell/anti-shell" concept (Ch. 5) which showed to yield better defined metrics with less scatter. Generalised to include metrics in reciprocal space as well ("halo/anti-halo") this method could be referred to as "peak/anti-peak" concept with "anti-peak" being the troughs in the structure functions. One of the assets of the "shell/anti-shell" concept is its recognition that structure, especially in real-space, means deviations from the mean density to higher as well as to lower local density while not preferring the former over the latter. Additionally, the "shell/anti-shell" concept removes spurious increases in peak heights which are actually caused by deepening troughs and decreases the influence of subjectivity even further. Analysing the temperature dependence of the anti-peaks an additional set of metrics providing valuable information about the structural evolution along the pathway can be obtained.

3.6 Outlook

Although still a young field, in-situ monitoring of structural changes during undercooling of metallic melts, including liquid-liquid crossovers and vitrification itself, already yielded intriguing and important results. The main advantage of the structural measurements, opposed to e.g. viscosity measurements, is the possibility to gain detailed insights for the complete pathway of a liquid alloy to vitrification within a single experiment. Combined with simulations it could be shown that during undercooling clusters and their interconnection evolve being responsible for the viscous slowdown and LLCs. It is, however, still not clear what exactly determines the value of T_g , i.e. what condition has been met at this temperature, that the structure locks into place. ANDERSON's puzzle has still not been fully solved. However, it has to be considered that in-situ vitrification, after following the complete pathway, has only been reported for ten alloys so far (Tab. 2.1). More such measurements for much wider classes of glasses and according simulations are necessary. Further supporting studies, utilising new setups and methods, need to be carried out.

For X-ray investigations at synchrotrons and free-electron lasers it is mainly the desire for element-specific measurements, to obtain partial structure factors, that arises. At first sight it seems that AXS could be a relatively simple way to achieve this goal. However, the same experiment, i.e. following the pathway in the exact same manner, would need to be meticulously repeated several times with different wavelengths for the different elements in the sample. Alternatively, a setup for the *simultaneous* acquisition with different wavelengths, similar to what was recently proposed and demonstrated for other X-ray techniques [Bel13,Bel15,Mok15,Hrd16,Bru20,Cip21], would need to be devised. To monitor fast structural processes along the pathway or to increase temporal resolution in general the advent of XFELs will be immensely beneficial [Zal19] as small exposure times are compensated by the higher intensity to keep the SNR high. Together with faster detectors having better SNR and energy discrimination clearer identification of structural signatures of e.g. LLCs will be possible. Complementing the wide-angle measurements reviewed here, SAXS along the complete pathway, maybe even simultaneously [Bra03], would provide further and more direct insight into the different length scales that govern the structural changes during LLCs and vitrification. A further boost of studying the pathway in particular and the structure of (not only) glasses in general may be provided by the future prospect of a possible day-to-day use of compact X-ray sources [Jar06,Sch08,Cou18].

Since neutron sources and detectors, that allow for a time-resolution to cover the complete pathway as can be done with synchrotron radiation, are not to be expected anytime soon, let alone compact variants thereof, electrons as probe should be revisited. Recent advances have been made to use this method for the investigation of fast structural changes [Fei17,Nun20]. The use of electrons can be considered twofold. On the one hand, electron scattering provides additional information to disentangle the partial structure factors. Here the size of the facility is of minor relevance and accelerator-based setups would be acceptable [Wea15,Nun20]. On the other hand, as compact in-house total-scattering method e.g. in modified transmission electron microscopes (TEM) [Fei17] "replacing" synchrotrons. Since transmission electron diffraction in a TEM can only work properly with sample thicknesses up to ≈ 100 nm, levitating (and keeping the beam focussed onto) samples of this size is virtually excluded. Additionally, levitation is also excluded since the sample needs to be properly grounded and because the default configuration of TEMs uses vertical beams incompatible with levitation setups. Other reasons that prevent the use of levitation setups for electron diffraction have been mentioned above. Interestingly, vitrification of nm-sized metallic

samples *without* using containerless levitation has been achieved recently [Zho14]. However, such small sample sizes also lead to much higher cooling rates making it virtually impossible to record the complete pathway in a single run. As mitigation, a pump-probe-like experiment could be devised. Here, the sample would be heated up to a defined temperature $T_{\text{start}} > T_l$ where the pathway commences. Following the deactivation of the heating a single diffraction pattern would be recorded after a certain delay time at a temperature below T_{start} . After completing the pathway, the sample would be heated up to T_{start} again whereafter the next measurement is taken after a slightly longer delay time. In this way the complete pathway would not be probed in one run, but as a series of many of such cycles. As even the vitrification of nm-sized pure metals could be demonstrated [Zho14] such a technique is promising to work for most metallic-glass forming alloys. Appropriate samples could be prepared using FIB methods (focussed ion beam) and heated by pulses of electrical current [Zho14]. A possible deterioration of the sample during cycling in the pump-probe experiments, mainly by evaporation, may need to be taken into account. Progress in the development of direct electron-detectors [Har17, Mai17, Vec17, Mac19, Cha21] with high SNR could massively aid this method. However, electron diffraction alone would not allow for partial structure factors to be resolved. This issue could be mitigated by using a similar pump-probe setup for EXELFS (extended electron energy loss fine structure [Lea76, Sar96, Har19, Mac19]) as an energy-dispersive technique, analogous to EXAFS. These developments may turn electrons into a valuable tool to monitor the pathway and in-situ vitrification after all.

Being able to utilise environments with reduced gravity compared to ground-based experiments would facilitate levitation experiments. Even with continuing reduction in the sizes of radiation sources it is unlikely for high-resolution diffraction experiments to take place at parabola flights or aboard space stations. However, the prospect of constructing permanent habitats on Moon or Mars may nourish the hopes of levitation experiments in these reduced-gravity environments. This would also allow for the use of the lighter He as levitation gas leading to increased cooling rates due to its higher thermal conductivity enabling to follow the complete pathway for a wider range of metallic alloys.

As briefly mentioned above structural milestones along the pathway should be backed up by measurements of complementary properties. Ideally, those measurements would need to be carried out in the same setup or even parallel to the diffraction experiments. In any case those multi-messenger studies should be performed more fre-

quently. While some of those combined measurements have been reported as already mentioned (density [Par03, Muk04], thermal expansion, specific heat [Moh19, Moh20], electrical resistivity [Hoe19, Moh19], viscosity [Rhi99, Muk04, Par05], surface tension [Rhi99, Rhi01, Mil04, Par05]) further combinations are thinkable, even if not the complete pathway can be captured. Such a possible method could be nuclear magnetic resonance (NMR) spectroscopy. For oxide glasses NMR is used in CNL setups already [Poe94, Mas95]. In metals it is foremost the so-called KNIGHT shift that is measured by NMR [San11]. Although not in levitation experiments, for $\text{La}_{50}\text{Al}_{35}\text{Ni}_{15}$ it was shown that the KNIGHT shift can highlight signatures of a crossover above T_1 [Xu15] and for $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ above T_g [Li03]. Also, MD and RMC simulations carried out for as many temperatures along the pathway as possible and with small increments can give valuable insights. Here the ever-increasing power of modern computers will be an asset.

In-situ studies with varying cooling rates need to be performed more often. On the one hand since the cooling-rate dependence of LLCs needs to be investigated further. In this respect alloys that have been vitrified with ESL should also be investigated in a CNL setup. On the other hand, a sufficiently low cooling rate will lead to crystallisation. The analysis of the emerging crystal structures could help to learn more about SRO in the liquid and glass phase as well. A comparison with crystalline structures occurring during annealing of an already prepared glass may yield insights into the prerequisites for high GFA when its relation to a competition between crystalline structures is kept in mind [Rus18]. Only preliminary results exist to date [Geo13].

Additionally, independent of the particular type of experiment, the investigated temperature range should be extended on both ends of the pathway. For high temperatures this is necessary to examine how far the found non-linear behaviour of structural metrics continues and how common anomalies that point to LLCs above T_1 [Yu17, Su18] are. Going to temperatures way below T_g in situ after vitrification would be intriguing as well. To monitor possible further structural changes [Bia17, Bia17a] down to cryogenic temperatures reducing the temperature of the gas stream in a CNL setup could be supplemented by a cooled sample holder that "grabs" the already vitrified sample in situ, providing additional conductive cooling.

Finally, going the pathway in the opposite direction could be insightful as well, i.e. heating the glass rapidly enough to bypass crystallisation ending up at temperatures above T_1 . This "up-quenching" [Sch19] has been performed using ultrafast chip calorimetry, but not yet in combination with ultrafast structural investigations.

4 Global electronic influence on the structure of metallic glasses

The influence of global interactions between the static atomic structure and the valence electrons on structure formation in binary Al-(Ni,Cu,Zr), Zr-(Ni,Cu) and ternary Al-(Ni,Cu)-Zr metallic glasses is investigated over wide concentration ranges and discussed in terms of a HUME-ROTHERY-like theory by analysing and comparing data available in the literature. The results suggest that global interactions lead to an improvement of thermal stability and glass-forming ability. A complete understanding of structure formation in the considered alloys is assumed to be possible only by taking into account both local and global effects.

This chapter is based on the paper "**On the impact of global interactions on the structure of metallic glasses**" (doi:[10.1016/j.jallcom.2018.12.086](https://doi.org/10.1016/j.jallcom.2018.12.086)) authored by Martin E. STIEHLER, Mark R. JOLLY and Konstantinos GEORGARAKIS published 2019 in the *Journal of Alloys and Compounds* [Sti19].

4.1 Introduction

Metallic glasses are a promising class of materials for versatile future applications [Gre09, Kha18]. However, the small critical casting thicknesses still limit the dimension of parts engineered from these materials. Although Zr-based metallic glasses exhibit comparatively high casting thicknesses a comprehensive understanding of the conditions necessary for good glass-forming ability (GFA) is still missing. Most often only effects on the *local* level, i.e. due to clusters, chemical short range order (CSRO) or medium range order (MRO), are considered. On the other hand it is known that *global* interactions between the static atomic structure and the valence electrons, i.e. the electronic structure, play an important role during structure formation in liquid (l) and glassy (gl) systems [Hau92, Wan03, Hau05, Sod05, Sti07, Yu10, Jia12, Yua12, Wu16].

The influence of global effects was first recognised by HUME-ROTHERY in crystalline (c) solid-solutions by scaling their phase diagrams not versus composition but the mean valence $\bar{Z}$ (measured in electrons per atom, e/a) simply taking the usual valence of the components according to their position in the periodic table [Hum26]. It became obvious that these systems exhibit the same sequence of crystalline phases as function of $\bar{Z}$. An explanation of this correlation was given by Jones in terms of the dimensions

of the FERMI sphere and BRILLOUIN zones relative to each other [Jon37]. Since then the model was refined and put on the basis of state-of-the-art solid state theory [Met97, Miz17] as well as adapted to be applicable as guide in the search for new materials with promising applications and to understand phase stability in many different classes of materials [Oss91, Fen07, Sti07, Fen10, Miz14, Miz17, Miz18, Cal18, Deg18]. These include amorphous alloys to which the ideas were first transferred by Nagel and Tauc [Nag75] and later elaborated on by several authors [Hau92, Hau05, Sod05, Sti07, Yu10, Jia12, Yua12, Wu16].

In this global description instead of looking at single electrons and local bonds the subsystem of the valence electrons as a whole is considered and characterised by the FERMI sphere with the diameter

$$2k_F = 2\sqrt[3]{3\pi^2\bar{Z}\frac{1}{\bar{\Omega}_0}} \quad , \quad (4.1)$$

where $\bar{\Omega}_0$ is the mean atomic volume of the alloy [Ash76]. The energy of the highest occupied electronic states, at the edge of the FERMI sphere, is called FERMI energy E_F . The structure on the other hand is characterised by the BRILLOUIN zone in c-systems or pseudo-BRILLOUIN zone in gl-systems, respectively. The latter is always spherical and characterised by its diameter Q_1 which, in metallic systems, is identical with the position of the principal peak, i.e. the modulus of the according scattering vector, in the static structure factor $S(Q)$ [Hau92]. Due to (pseudo-)BRAGG scattering of valence electrons a rearrangement of electronic states to both higher and, more importantly, to lower energies is caused. This leads to the occurrence of gaps (c-systems) or pseudogaps, i.e. local minima, (gl-systems) bordered by maxima in the electronic density of states (DOS) [Hau04a, Hau07]. If optimally E_F lies close to the centre of the (pseudo)gap, only the states shifted to lower energies are occupied and the energy of the whole system is decreased, i.e. the system is more stable than without the (pseudo)gap. If in an alloy the composition is changed generally the mean valence and therefore E_F changes as well. Accordingly, E_F does not fall in the (pseudo)gap any more and the system loses its advantage. It is now favourable for the alloy to change its structure to re-achieve the advantage which explains HUME-ROTHERY's original observation [Jon37, Met97, Miz17]. Due to the lack of different phases gl-systems react on a change of $2k_F$ by an according change of Q_1 which has been shown experimentally in a large number of so-called "simple" gl-alloys with only s- and p-states present at E_F [Hau92]. The matching of $2k_F$ and Q_1 is referred to as *resonance* [Now99].

If the alloys contain transition metals (TM) the assumption that it is only the static structure that is adjusting to electronic constraints had to be dropped [Lan01]. Especially in the case of binary gl-Al-TM alloys it was argued that $2k_F$ can be influenced by hybridisation effects between Al-sp- and TM-d-states at E_F which can be described by an effective valence of Al or the TM [Lan01, Bar04, Tra05]. This flexibility of the electronic system provides a further degree of freedom for the system to achieve its most favourable state [Hau05, Sti07, Yua12, Wu17]. Furthermore, hybridisation has been demonstrated to cause effective valences already for pure TM [Pet77, Mor82, Wil83]. In this respect a valence of $Z = 1.5$ was found to be appropriate for the complete row of the 3d-TM, including Ca and Cu [Mor82]. For Zr, a 4d-TM, Z was assumed to lie between 1 and 2 [Pet77] and has been assessed successfully with, again, 1.5 in the context of amorphous alloys [Wan03]. Therefore, $Z = 1.5$ will be adopted for Ni, Cu and Zr for the remainder of this chapter.

The presence of TM-d-states at E_F , on the other hand, causes high values of the DOS at E_F , $N(E_F)$, which often impedes the easy identification of a pseudogap [Sod05]. In principal the measured $N(E_F)$ has to be compared to calculations without the pseudogap, $N_0(E_F)$, which can be done easily only for simple gl-alloys [Hau92]. However, other things being equal, even a small reduction of $N_0(E_F)$, i.e. a small energy gain, maybe decisive for the stabilisation of a specific structure of the alloy [Hau92, Sod05]. In general, DOS features like pseudogaps are the result of highly intertwined structural and electronic properties [Wei98, Tra05, Yua12]. A careful angular-momentum projected analysis of the DOS from experimental as well as theoretical considerations is inevitable. Experimentally photo-electron spectroscopy (PES) as well as inverse photo-electron spectroscopy (IPES) are necessary to obtain the exact shape of the DOS in the vicinity of E_F . If, for example, E_F is not located in the centre of the pseudogap and only PES results are considered, it may appear that E_F is mistakenly related to the aforementioned maximum below the pseudogap and not to the pseudogap itself leading to contradictory assumptions about the presence of resonance [Tia11, Ant14].

Complementary to the discussion of gl-systems in k -space there is also an indication of the resonance in r -space in form of the so-called spherical periodic order (SPO) [Hau92]. If the radii

$$r_n = \left(\frac{1}{4} + n \right) \cdot \frac{2\pi}{Q_1} \quad (n = 1, 2, 3, \dots) \quad (4.2)$$

of the coordination spheres around any chosen atom resonantly match with the wave-

length $\lambda_{\text{Fr}} = 2\pi/2k_{\text{F}}$ of the FRIEDEL oscillations of the effective pair potential a characteristic sequence of peaks in the pair correlation function according to

$$r_n = \left(\frac{1}{4} + n\right) \cdot \lambda_{\text{Fr}} \quad \text{with } n = 1, 2, 3, \dots \quad (4.3)$$

can be observed as a fingerprint of the resonance [Hau92]. In that situation an gl-system is especially stable since the atoms are located in the minima of the effective pair potential [Bec78, Obe79, Hau92, Kro95]. Alternatively, the SPO can be understood as the result of a self-organisation between the atoms and the valence electrons during structure formation to adjust the interatomic distances for an optimised pseudo-BRAGG scattering in order to enhance the pseudogap [Hau04a, Hau07]. It has to be noted that the SPO, in its current form, does not distinguish between the different species in an alloy and hence cannot explain the occurrence of the individual partial pair correlation functions. In this regard, the SPO is a purely topological but nevertheless powerful description of the interplay of order and energetic stabilisation in the system under consideration.

In the present study the impact of global effects on structure formation in gl-Al-(Ni,Cu,Zr), gl-Zr-(Ni,Cu) and its implications for the ternary systems gl-Zr-(Ni,Cu)-Al is investigated. This is done by comparing the positions of the peak centres Q_1 of the principal peak in the respective structure factors $S(Q)$ with $2k_{\text{F}}$ calculated using appropriate assumptions for the valences Z of the elements involved as outlined above as well as elaborated in more detail in the following sections. In the case of the binary gl-Zr-(Ni,Cu) alloys correlations with further properties are explored in order to substantiate the suggested global influences, i.e. the presence of resonance. All experimental data discussed is taken from the literature.

element	r_{at} (nm)	Ω_0 (Å ³)	$\Delta H_{A-\text{Zr}}^{\text{mix}}$ (kJ/mol)
Al	0.141	16.61	-44
Ni	0.126	10.94	-49
Cu	0.126	11.78	-23
Zr	0.158	23.28	–

Table 4.1: Data of the chemical elements considered in the present study: atomic radius (r_{at}) [Mir10], atomic volume (Ω_0) (calculated from mass density [Smi04] and atomic mass [Win21]) and enthalpy of mixing with Zr ($\Delta H_{A-\text{Zr}}^{\text{mix}}$) using the MIEDEMA model [Tak05].

4.2 Binary alloys

The ternary systems Zr-(Ni,Cu)-Al are bordered by the binary systems Al-(Ni,Cu), Al-Zr and Zr-(Ni,Cu). Therefore, the discussion will commence with the latter four systems. Table 4.1 lists for the chemical elements involved in this study data relevant for the subsequent discussion (atomic radius r_{at} , atomic volume Ω_0 , enthalpy of mixing with Zr $\Delta H_{\text{A-Zr}}^{\text{mix}}$). Tables 4.2 and 4.3 list, for the alloys under discussion, the method of production, their thicknesses (where appropriate), the physical quantities considered, the symbols used in Figs. 4.1 and 4.2 as well as the respective reference to the literature. Open, half-open and closed symbols are used for thin film samples, mechanically alloyed samples and melt-spun/bulk samples, respectively.

4.2.1 Binary gl-Al-(Ni,Cu,Zr) alloys

Figure 4.1 shows the positions Q_1 of the principal peaks in $S(Q)$ for binary gl-Al-(Ni,Cu,Zr) alloys. The lines in Fig. 4.1 represent calculations of $2k_F$ using Eq. (4.1). For these calculations the knowledge of the mean atomic volumes $\bar{\Omega}_0$ are necessary. Due to the absence of experimental values $\bar{\Omega}_0$ were calculated as an concentration-weighted average of the values of the pure crystalline elements (Tab. 4.1) under the assumption that the values in the gl-state are close those of the c-state and stay constant during alloying. Especially for Al-Ni it is known that the latter assumption, at least in the c-case, is not fulfilled over the complete concentration range and reduced values, i.e. higher packing densities, were observed [Yav98, Geo10]. For $\bar{Z}$ in Eq. (4.1) different assumptions were used as discussed in the following. While, as explained in the introduction, for all the TM $Z_{\text{TM}} = 1.5$ was assumed for Al different values were taken into consideration: using $Z_{\text{Al}} = 3$, as is to be expected from the position of Al in the periodic table, Eq. (4.1) delivers values of $2k_F$, denoted by $2k_F(3|1.5)$ (red dash-dotted lines in Fig. 4.1), that can in no case describe the measured Q_1 . It has been proposed that Al can exhibit an effective valence of 2 owing to the aforementioned hybridisation effects in gl-Al-TM alloys [Gil16] ($2k_F(2|1.5)$, blue dashed lines in Fig. 4.1). This provides indeed a reasonable assumption for gl-Al-(Ni,Cu). For gl-Al-Zr, especially for low Zr-content, however, $Z_{\text{Al}} = 1.5$, like for the TM, is more appropriate ($2k_F(1.5)$, green solid line Fig. 4.1c). For higher Zr-content a deviation towards even lower values of Z_{Al} seems to take place as illustrated by the black dotted curve in Fig. 4.1c which is calculated assuming $Z_{\text{Al}} = 1.3$, i.e. $2k_F(1.3|1.5)$. Altogether, it appears that depending on the TM, especially if it as an early or a late TM, the alloys exhibit

mat.	prep.	thick.	quantity	fig.	sym.	ref.
Al-Ni	f.e.	≈ 30 nm	Q_1	4.1a	$\circ$	[Bar03]
Al-Ni	f.e.	≈ 30 nm	Q_1	4.1b	$\square$	[Dai08]
Al-Cu	f.e.	≈ 30 nm	Q_1	4.1c	$\circ$	[Lam80]
Al-Zr	b.m.	–	Q_1	4.1c	$\blacklozenge$	[Fec90]
Al-Zr	s.d.	N/A	Q_1	4.1c	$\circ$	[Yos91]
Al-Zr	s.d.	N/A	Q_1	4.1c	$\triangle$	[Ho94]
Al-Zr	b.m.	–	Q_1	4.1c	$\blacklozenge$	[Ma95]
Al-Zr	b.m.	–	Q_1	4.1c	$\bullet$	[She98]
Al-Zr	b.b.	–	Q_1	4.1c	$\bullet$	[She99]
Al-Zr	b.m.	–	Q_1	4.1c	$\bullet$	[Jur03]
Al-Zr	s.d.	≈ 2 μ m	Q_1	4.1c,4.4	$\triangleleft$	[Wel15]
Al-Zr	s.d.	≈ 2 μ m	Q_1	4.1c,4.4	∇	[Wel16]

Table 4.2: Preparation method (f.e.: *flash evaporation* [Har48], m.s.: *melt spinning*, b.m.: *ball milling*, d.c.: results are obtained from a *data collection*, a.m.: *arc-melting* (i.e. arc-melted samples used directly), i.c.: *injection casting*) and thickness (where appropriate) of the binary alloys considered in this study together with the physical quantities used, the figures in which they are plotted, the respective symbols (open (thin films), half open (mechanical alloying), closed (preparation from the melt and bulk samples)) used in the figures and the literature reference.

different structural behaviour, reflected in an unusual variability of Z_{Al} . This, with special attention being paid to the behaviour for $x \lesssim 20$, shall be addressed in more detail in a future publication by additionally considering further gl-Al-TM-systems. From the considerations above an interval $1.3 \leq Z_{\text{Al}} \leq 2$ can be assumed which has to be taken into account when the role of Al in multinary alloys has to be evaluated.

The red triangles in Fig. 4.1 point to estimated values of Q_1 for the pure components in their hypothetical gl-state assuming that the nearest-neighbour distance r_1 (Eq. (4.2) with $n = 1$) is determined by their respective atomic radius r_{at} (Tab. 4.1), i.e. $r_1 = 2r_{\text{at}}$, which gives

$$Q_{1,\text{at}} = \left(\frac{1}{4} + 1 \right) \cdot \frac{2\pi}{r_1} = \frac{5}{4} \cdot \frac{2\pi}{r_1} = \frac{5}{4} \cdot \frac{2\pi}{2r_{\text{at}}} = \frac{5}{4} \cdot \frac{\pi}{r_{\text{at}}} \quad . \quad (4.4)$$

Regarding an extrapolation of the experimental results for Q_1 shown in Fig. 4.1 this indeed seems to be a good assumption for pure Cu, Ni and Zr. For Al, however, only in the case of gl-Al-Zr a good agreement can be found, highlighting again the possible variable behaviour of Al depending on the alloying element. It is interesting to note that $Q_{1,\text{at}}$ for Al, Ni, Cu and Zr is always close to their respective $2k_{\text{F}}(1.5)$ (Fig. 4.1).

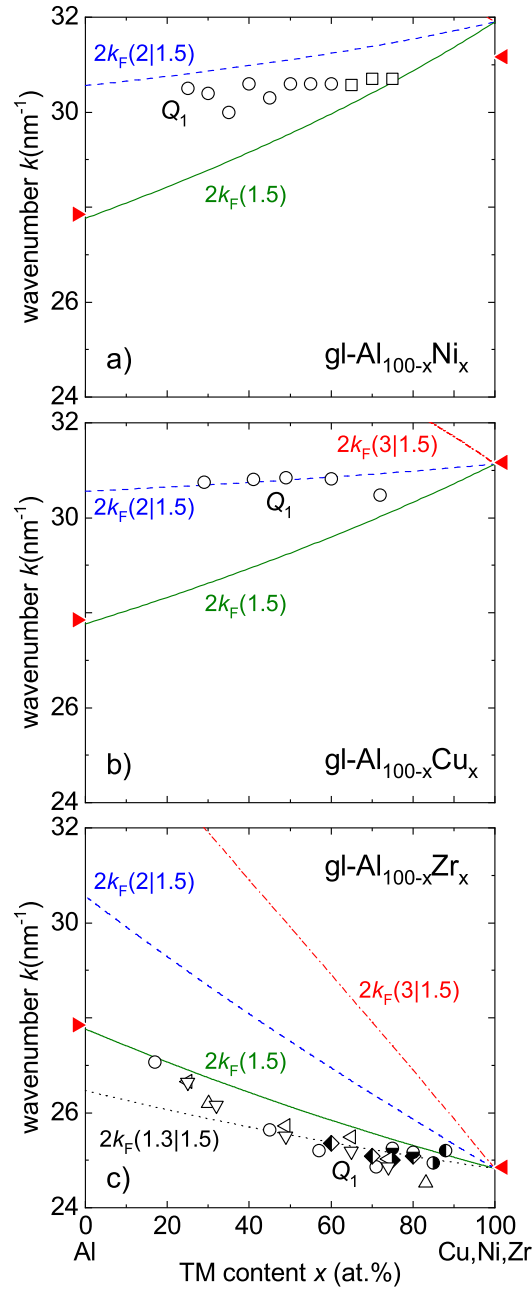


Figure 4.1: Positions of the principal peak Q_1 in $S(Q)$ of **a)** binary gl-Al-Ni, **b)** binary gl-Al-Cu and **c)** binary gl-Al-Zr alloys versus the concentration x of the respective TM element. Table 4.2 serves as legend for the symbols. The solid lines represent $2k_F$ calculated using Eq. (4.1) for different valences as denoted at the curves. The red triangles indicate $Q_{1,\text{at}}$ for the pure elements estimated from the atomic radii r_{at} via Eq. (4.4).

4.2.2 Binary gl-Zr-(Ni,Cu) alloys

In this section the relation between $2k_F$ and Q_1 for gl-Zr-(Ni,Cu) alloys and its reflection in several other properties of these alloys will be discussed (Fig. 4.2). Again, a valence of 1.5 for Zr as well as Ni and Cu is used, i.e. the mean valence is assumed to stay constant at 1.5 over the complete concentration range. The change of $2k_F$ therefore only depends on the change of the mean atomic volume Ω_0 which is again calculated as concentration-weighted average (solid black lines in Fig. 4.2a,b) over the values for the pure elements (Tab. 4.1). Compared with experimental results this seems to be a very good approximation over the complete known concentration range for gl-Zr-Cu (Fig. 4.2b) and is seen as an indication for ideal-solution behaviour [Bak05, Geo09, Ris15]. For gl-Zr-Ni, however, a deviation to smaller volumes, i.e. higher packing densities, in the range $40 \leq x_{\text{Ni}} \leq 80$ can be seen (dash-dotted black line in Fig. 4.2a). This behaviour has been observed before and was ascribed to strong local chemical interactions as hinted by the high negative $\Delta H_{\text{Ni-Zr}}^{\text{mix}}$ (Tab. 4.1) [Eck06, Geo10].

The calculated $2k_F$ are plotted in Fig. 4.2c,d over the complete concentration range using the atomic volumes according to the ideal-solution behaviour (solid green lines). For gl-Zr-Ni additionally the deviation from ideal-solution behaviour is taken into account which results in an increase of $2k_F$ especially for high Ni-content (dash-dotted green line in Fig. 4.2c). The close proximity of $Q_{1,\text{at}}$ (red triangles in Fig. 4.2c,d) calculated via Eq. (4.4) and $2k_F(1.5)$ for the pure elements is already an indication that global and local effects might act hand in hand. For both systems the measured Q_1 are close to $2k_F(1.5)$ also over the complete concentration ranges but $Q_1 < 2k_F(1.5)$ for $x_{\text{Ni}} < 55$ and $x_{\text{Cu}} < 50$, respectively (Fig. 4.2c,d).

While for gl-Zr-Ni a distinct S-shaped dependence of Q_1 versus x_{Ni} is obvious this behaviour is much less pronounced or virtually absent for gl-Zr-Cu. It can be seen that both systems behave very similar again up to around $x \approx 55$. For a better comparison the composition dependence of Q_1 for the respective other system is drawn as thick grey lines in Fig. 4.2c,d. In gl-Zr-Cu for $x_{\text{Cu}} \gtrsim 50$ up to virtually the highest measured x_{Cu} an almost perfect agreement of Q_1 and $2k_F(1.5)$ becomes obvious. For gl-Zr-Ni this agreement (dash-dotted green line) can only be found in the range $55 \lesssim x_{\text{Ni}} \lesssim 70$.

The good agreement of Q_1 and $2k_F(1.5)$, especially that Q_1 follows the “hump” in $2k_F$ for gl-Zr-Ni, can be regarded as strong indication for the influence of a global resonance as outlined in the introduction. The concentration ranges with perfect agreement, i.e. $Q_1 = 2k_F$, are highlighted by vertical dashed lines in Fig. 4.2c,d as well as in the remainder of Fig. 4.2.

That Q_1 and $2k_F(1.5)$ do not coincide over the complete concentration range suggests that further effects are active. Those can be seen in constraints on the local scale that have to be fulfilled as well. It can be assumed that none of the effects alone is able to explain the structural behaviour completely. Only if both local and global needs are satisfied the most favourable structure can emerge. Global (resonance) and local effects (CSRO) might support each other or are even mutually dependent on each other to achieve the most favourable situation for the alloy. It might furthermore be argued that an E_F not optimally located in the center of a pseudogap can be counterbalanced by local effects, e.g. local covalent bonding, i.e. strong local chemical interactions. The system can then be in a favourable state even if Q_1 and $2k_F$ do not coincide, as is observed in gl-Zr-(Ni,Cu) for $x_{\text{Ni}} \lesssim 55$ and $x_{\text{Cu}} \lesssim 50$, respectively (Fig. 4.2c,d). Altogether this helps to understand the good GFA in gl-Zr-(Ni,Cu) which, particularly for gl-Zr-Cu, was found unexpectedly less dependent on factors like the occurrence of eutectics or intermetallic phases [Ino04, Tan04, Wan04, Xu04, Wan18]. A deeper analysis of the intricate interplay between local and global effects might also be able to explain finer details like the oscillating GFA observed in gl-Zr-Cu for $48 \leq x_{\text{Cu}} \leq 69$ [Li08]. Below $x_{\text{Ni}} \approx 55$ and $x_{\text{Cu}} \approx 50$ global effects seem to be less important since for both systems $Q_1 < 2k_F$. Furthermore, Q_1 behaves virtually identical for both systems (cf. grey lines in Fig. 4.2c,d) although the slope of $2k_F(1.5)$ for gl-Zr-Ni is different than that for gl-Zr-Cu. In this concentration region Q_1 and $2k_F$ seem to be decoupled. The achievement of resonance accomplishes a smaller energy gain than optimising the local constraints, i.e. local effects are improved at the expense of those on the global scale. Additionally, it would be interesting to see how Q_1 approaches the respective $Q_{1,\text{at}}$ for the pure elements in their hypothetical gl-state for which the dashed red lines in Fig. 4.2c,d may serve as a prediction.

For a further discussion the knowledge of experimentally obtained DOS spectra over a wide concentration range with small steps in $x_{\text{Ni,Cu}}$ would be necessary to monitor composition dependent changes in detail. Currently available PES or IPES results cover only a few compositions [Ama78, Oel79, Ama80, Ste80, Fal81, Yan15, Hos18]. Theoretical investigations, on the other hand, cover a somewhat wider composition region [Tia11, Ant14], but their interpretation is controversial, ranging from a “lack of DOS minimum at the FERMI level” [Ant14] to “always a pseudogap in the density of state at the FERMI level” [Tia11] for virtually the same Cu-content. It is, however, possible to discuss at least the DOS at the FERMI level, $N(E_F)$, over a relatively wide concentration range. Those values can indirectly be obtained by measurements of the

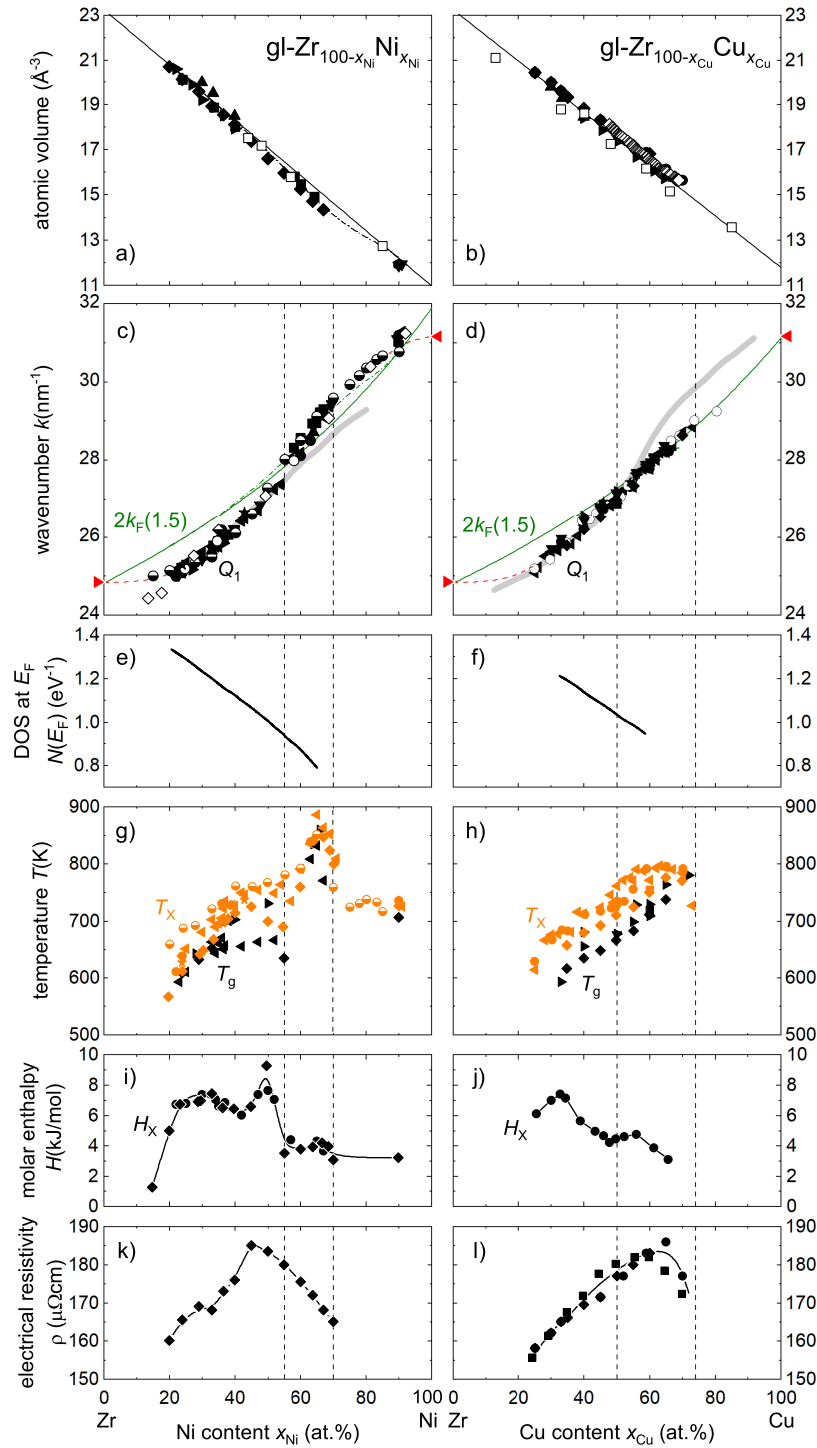


Figure 4.2: Comparison of gl-Zr-Ni (left) and gl-Zr-Cu (right) alloys. Table 4.3 serves as legend for the symbols. From top to bottom: **a,b**) atomic volume Ω_0 ; **c,d**) position Q_1 of the first maximum in $S(Q)$; **e,f**) density of states at the FERMI level $N(E_F)$; **g,h**) glass transition temperature T_g (black) and crystallisation temperature T_x (orange); **i,j**) enthalpy of crystallisation H_x ; **k,l**) electrical resistivity ρ versus the concentration $x_{\text{Ni,Cu}}$ of the alloying element (Ni,Cu). The additional lines mean in a,b) assumption of constant atomic volumes Ω_0 during alloying (solid black) and fit to the deviation from this behaviour (dash-dotted black); c,d) $2k_F$ calculated with Eq. (4.1) using $\bar{Z} = 1.5$ (solid green) and taking into account the decreased atomic volume (dash-dotted green) as well as the estimated continuation towards the pure elements (dashed red), the average composition dependence of Q_1 for the respective other system (thick solid grey); i,j,k,l) guides for the eye. The vertical dashed lines in c,d,e,f,g,h,i,j,k,l) limit the concentration regions where $Q_1 = 2k_F$ is fulfilled. The red triangles in c,d) indicate $Q_{1,\text{at}}$ of the elements estimated using Eq. (4.4).

mat.	prep.	thick.	quantity	fig.	sym.	ref.
Ni-Zr	m.s.	N/A	Q_1, T_X	4.2c,g	●	[Bus79]
Ni-Zr	m.s.	30 μm	Ω_0, Q_1	4.2a,c	◆	[Che81]
Ni-Zr	m.s.	20–50 μm	Ω_0, Q_1	4.2a,c	■	[Don81]
Ni-Zr	m.s.	$\approx 20 \mu\text{m}$	Ω_0, Q_1	4.2a	◆	[Alt83]
Ni-Zr	m.s.	20–30 μm	T_g, T_X, H_X, ρ	4.2g,i,k	◆	[Alt83a]
Ni-Zr	m.s.	25–35 μm	Ω_0, Q_1	4.2a,c	▶	[Kar83]
Ni-Zr	m.s.	N/A	Q_1, T_g, T_X	4.2c,g	◀	[Bus84]
Ni-Zr	m.s.	N/A	H_X	4.2i	●	[Hen84]
Ni-Zr	m.s.	N/A	Q_1	4.2c	◊	[Pri88]
Ni-Zr	b.m.	–	Q_1	4.2c	▼	[Miz90]
Ni-Zr	b.m.	–	Q_1, T_X	4.2c,g	⊖	[Har93]
Ni-Zr	d.c.	–	$N(E_F)$	4.2e	\	[Bak95]
Ni-Zr	d.c.	–	T_g	4.2g	▶	[Jia96]
Ni-Zr	m.s.	N/A	Ω_0	4.2a	▲	[Fuk06]
Ni-Zr	m.s.	N/A	Q_1	4.2c	▲	[Geo10]
Ni-Zr	s.d.	800 nm	Q_1	4.2c	○	[Ghi14]
Ni-Zr	a.m.	$\approx 2.5\text{mm}$	Q_1, T_X	4.2c,g	★	[Joh14]
Ni-Zr	s.d.	500 nm	Q_1	4.2c	◊	[Tur14]
Ni-Zr	s.d.	4–6 μm	Ω_0	4.2a	□	[Apr17]
Cu-Zr	m.s.	$\approx 20 \mu\text{m}$	Ω_0, T_X, H_X, ρ	4.2b,h,j,l	●	[Alt82]
Cu-Zr	m.s.	$\approx 20 \mu\text{m}$	Ω_0, ρ	4.2b,l	◆	[Alt83]
Cu-Zr	m.s.	N/A	Q_1	4.2d	●	[Cal83]
Cu-Zr	m.s.	N/A	Q_1, T_X	4.2d,h	◀	[Bus84]
Cu-Zr	m.s.	N/A	ρ	4.2l	■	[Pav85]
Cu-Zr	c.a.	2 μm	Q_1	4.2d	○	[Min88]
Cu-Zr	d.c.	–	$N(E_F)$	4.2f	\	[Bak95]
Cu-Zr	d.c.	–	T_g	4.2h	▶	[Jia96]
Cu-Zr	m.s.	N/A	Ω_0	4.2b	▲	[Fuk06]
Cu-Zr	m.s.	25 μm	Ω_0, T_g, T_X	4.2b,h	■	[Mat07]
Cu-Zr	s.d.	$\approx 128 \text{ nm}$	Ω_0	4.2b	□	[Li08]
Cu-Zr	m.s.	25 μm	Q_1, T_g, T_X	4.2d,h	◆	[Mat08]
Cu-Zr	i.c.	2 mm	T_g, T_X	4.2h	▼	[Bas09]
Cu-Zr	m.s.	N/A	Ω_0, Q_1	4.2b,d	▶	[Ma09]
Cu-Zr	m.s.	$\approx 2 \text{ mm}$	Q_1	4.2d	▼	[Men10]
Cu-Zr	m.s.	N/A	Q_1	4.2d	▲	[Kal11]
Cu-Zr	a.m.	$\approx 2.5 \text{ mm}$	Q_1	4.2d	★	[Mau13b]
Cu-Zr	s.d.	4–6 μm	Ω_0	4.2b	□	[Apr17]

Table 4.3: Preparation method (f.e.: flash evaporation [Har48], m.s.: melt spinning, b.m.: ball milling, d.c.: results are obtained from a data collection, a.m.: arc-melting (i.e. arc-melted samples used directly), i.c.: injection casting) and thickness (where appropriate) of the binary alloys considered in this study together with the physical quantities used, the figures in which they are plotted, the respective symbols (open (thin films), half open (mechanical alloying), closed (preparation from the melt and bulk samples)) used in the figures and the literature reference.

magnetic susceptibility, low temperature specific heat and superconducting properties [Alt83, Bak95, Bab18]. Such results are shown in Fig. 4.2e,f [Bak95]. For both systems a monotonic an almost linear decrease of $N(E_F)$ with decreasing difference between Q_1 and $2k_F$ is visible whereby for gl-Zr-Ni the modulus of the slope even increases in the region where $Q_1 = 2k_F$. This indeed hints the energetic advantage as expected from a system under resonance. Future measurements have to show how $N(E_F)$ behaves for higher $x_{\text{Ni,Cu}}$.

To verify whether the agreement $Q_1 = 2k_F$ is indeed reflected in a higher thermal stability of the gl-phase Fig. 4.2g,h shows the crystallisation temperatures T_X (orange) of the alloys and furthermore the glass transition temperatures T_g (black). Figure 4.2i,j shows H_X , the molar enthalpy of crystallisation. In the concentration region where $Q_1 = 2k_F$ for gl-Zr-Ni a peak in T_X accompanied by a considerable drop of H_X is obvious. At the same time T_g also shows a maximum. A similar behaviour can be observed in gl-Zr-Cu. This provides further evidence for the influence of global stabilisation effects as expected for systems under resonance.

Since electronic transport properties are inherently dependent on the electronic structure at E_F they can give further information on the resonance. Therefore, in the last row of Fig. 4.2 the electric resistivity ρ of gl-Zr-(Ni,Cu) versus $x_{\text{Ni,Cu}}$ is shown. For gl-systems Faber-Ziman-like theories are often used to directly connect $S(Q)$ with ρ [Fab65, Eva71, Ros87]. Thereafter high ρ are expected if the resonance condition $Q_1 = 2k_F$ is fulfilled. While for gl-Zr-Cu this indeed seems to be the case (Fig. 4.2l) the maximal ρ for gl-Zr-Ni occurs a few at.% below which reflects the more complicated behaviour when d-states at E_F are involved (e.g. Mott s-d-scattering [Eva71, Mot72, How88]). In addition to the properties presented in Fig. 4.2 it is known that gl-Zr-Cu exhibits extrema for further material parameters in the concentration region around $x_{\text{Cu}} = 65$ for instance a minimum of the plastic strain and maxima of YOUNG's modulus and yield strength [Par07].

To get an impression of the resonance effects in r -space Fig. 4.3 shows the structure factors $S(Q)$ (left) and pair correlation functions $g(r)$ (right) of gl-Zr-Cu for $x_{\text{Cu}} = 33, 50, 60$. The green vertical bars at the curves indicate in Fig. 4.3a $2k_F(1.5)$ and in Fig. 4.3b the shell distances according to the SPO (Eq. (4.3)). A good agreement both in k - and r -space can be seen. In r -space, however, there are structural features, like the split first peak, that cannot be explained by the SPO in its current form. A possible way of including such effects of chemical order in a refined future form is provided by the

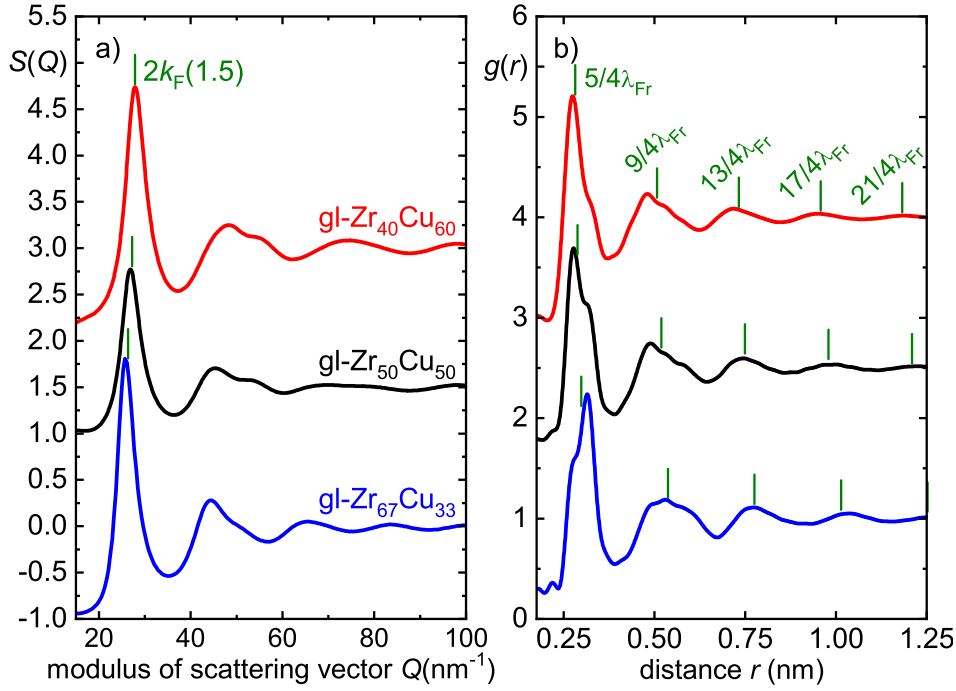


Figure 4.3: **a)** structure factors $S(Q)$ and **b)** pair correlation functions $g(r)$ of three gl-Zr-Cu alloys [Geo09]. The curves are shifted along the y-axes for better clarity. The green vertical bars indicate in **a)** the positions of $2k_F(1.5)$ (Eq. (4.1)) and in **b)** the radii of the coordination shells according to the SPO (Eq. (4.3)) calculated using $\tilde{Z} = 1.5$.

scattering interpretation of the SPO as outlined in the introduction, taking into account the different scattering properties of the individual species for the valence electrons. Moreover, it is known from binary and ternary gl-Al-TM alloys that act as precursors for quasicrystals that they show an additional sequence in $g(r)$ which is correlated with the Golden ratio $\tau \approx 1.618$ indicating icosahedral order [Hau02, Bar15]. A more detailed analysis for gl-Zr-Cu alloys, especially in the composition region where $Q_1 = 2k_F$ is fulfilled, has to show whether this is also the case here, since icosahedral order plays a major role in this system as well [Che11, Din17]. At least in molecular-dynamics simulations it was found that in this very composition region the icosahedron is the dominant short-range structure [Par07, Din14].

4.3 Ternary alloys

It is well-known that the addition of Al to gl-Zr-(Ni,Cu) improves their GFA greatly which was discussed mainly, again, on a local basis taking into account the high negative values of $\Delta H_{Al-B}^{\text{mix}}$ (Tab. 4.1) causing deviations from the ideal-solution behaviour and leading to an increased CSRO [Ino90, Xin96, Ant09, Geo09, Geo10, Kab13, Geo15].

Strong covalent-like directional bonding of Al with the other species in the alloy as a result of hybridisation was identified as an important driving force in shortening interatomic distances which results in an enhanced cohesion of clusters [Lek09, Geo15]. Global effects, on the other hand, can be discussed here as well in the same manner as done for the binary systems in the previous sections if straight lines in the ternary phase diagrams are chosen.

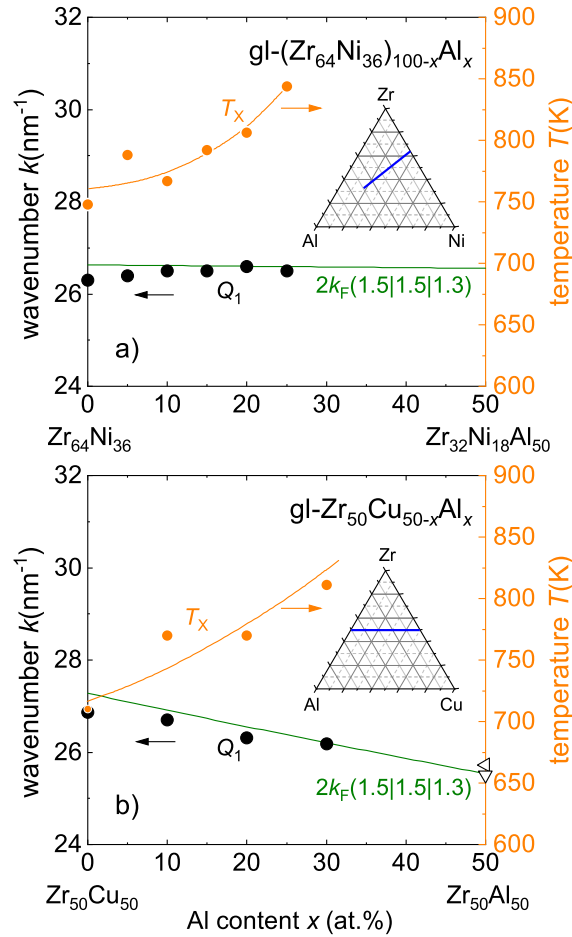


Figure 4.4: Positions of the principal peak Q_1 in $S(Q)$ of the ternary alloys **a)** $gl-(Zr_{64}Ni_{36})_{100-x}Al_x$ [Bha90] and **b)** $gl-Zr_{50}Cu_{50-x}Al_x$ [Geo09] (for $x = 50$ data for $gl-Al_{51}Zr_{49}$ from [Wel15, Wel16] is used). The solid green lines represent $2k_F(1.5|1.5|1.3)$ calculated using Eq. (4.1) with the given valences for Zr, (Ni,Cu) and Al. The insets may serve as an orientation as to where the respective alloys are located in the ternary phase diagrams (blue lines). The orange points show T_x (right y-axes) [Bha90, Geo09]. The orange lines are guides for the eye.

Here only one of such lines each for the ternary systems $gl-Zr-Ni-Al$ and $gl-Zr-Cu-Al$, respectively, will briefly be discussed. Figure 4.4 shows Q_1 for $gl-(Zr_{64}Ni_{36})_{100-x}Al_x$ (for $x = 0, 5, 10, 15, 20, 25$ from [Bha90]) and $gl-Zr_{50}Cu_{50-x}Al_x$ (for $x = 0, 10, 20, 30$ from [Geo09], for $x = 50$ data for $gl-Al_{51}Zr_{49}$ from [Wel15, Wel16] is used). Using

Eq. (4.1) the green solid lines in Fig. 4.4 showing $2k_F(1.5|1.5|1.3)$, i.e. assuming $Z = 1.5$ for Zr, Ni, Cu and $Z = 1.3$ for Al, were calculated. The latter assumption is based on the results from Sec. 4.2.1 for high Zr-content but has to be validated by more thorough studies in the future.

For both systems a good agreement $Q_1 \approx 2k_F$ can be found. With increasing Al-content the distance between Q_1 and $2k_F$ decreases in both cases which seems to be correlated with an increase of the crystallisation temperatures T_x (orange points and right y-axes in Fig. 4.4) indicating, again, the presence of resonance. To further investigate the influence of global effects on the multinary systems and its correlation with other properties, a lot more experimental data has to be acquired. Especially the systematic study of the influence of Al-addition to gl-Zr-(Ni,Cu) in the region of their highest stability, i.e. around 60 at.% (Ni,Cu), would be desirable. It is, finally, worth noting that a pseudogap at E_F was found experimentally for one of the most important bulk metallic glasses, gl-Zr₅₅Ni₅Cu₃₀Al₁₀ [Ino96], and was surmised to aid its large GFA [Sod05].

4.4 Conclusions

The effect of global interactions on glass forming ability of binary Zr-Ni and Zr-Cu metallic glasses has been studied. For this the positions of the principal maximum Q_1 in the static structure factors $S(Q)$ have been investigated in terms of their relation to the diameter of the FERMI sphere $2k_F$. A good agreement is found by taking into account a mean valence of $\bar{Z} = 1.5$ over the complete concentration ranges. Furthermore $2k_F$ is close to a structure that is to be expected from local packing constraints due to the atomic radii of the components which can provide an explanation of the good glass forming ability over wide concentration regions in these systems. The structure can be considered as the result of a mutual arrangement of global and local effects. Correlations of the atomic structure, formed under these circumstances, with other properties of the alloys are pointed out. The spherical periodic order can explain the average positions of the maxima in the pair correlation function very well but has to be refined in the future to be able to account for the details due to the partial pair correlations. In order to get a more complete picture of the electronic structure a systematic synchrotron-based photo-electron spectroscopic study over wide concentration ranges supplemented by according inverse photo-electron spectroscopy has to be undertaken. Only the combination of PES and IPES can successfully reveal minima and trends in

the DOS at E_F depending on the composition. Further valuable insights may arise from studies on gl-Zr-(Fe,Co) and gl-(Hf,Ti)-(Fe,Co,Ni,Cu). Especially for gl-(Hf,Ti)-(Ni,Cu) similar behaviour can be expected as hinted by previous studies [Bak95, Ris15, Bab18].

Using the insights obtained for the binary alloys as a basis trends in the structure of multinary systems can be understood, as shown exemplarily for gl-Zr-(Ni,Cu)-Al. A more detailed comprehension, however, is currently hampered by the uncertainty in the valence of Al. Further studies have to clarify what determines this quantity.

5 The effect of Ni or Co additions on the structure of $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ bulk metallic glass

The effect of substituting Cu by elemental additions of Ni or Co on the atomic structure of the $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ ternary bulk metallic glass (BMG) is studied using high-energy synchrotron radiation X-ray diffraction. Analysis of the structural features in reciprocal and real space using the structure factors $S(Q)$ and pair distribution functions (PDF) point to an increase in the structural disorder for the Ni- or Co-bearing quaternary alloys. This is consistent with the "confusion principle" since upon alloying the initially nearly identical atomic sizes of Cu, Ni and Co diversify due to local electronic interactions. In real space, the disordering is manifested by a reduced deviation from the average particle density visible in the nearest-neighbour (NN) atomic shell structure over the complete short- and medium-range order region. A novel concept, the NN "anti-shell", is suggested to complement the concept of NN atomic shell and simplify the description of structural disorder in amorphous materials. Despite their similar atomic size, enthalpies of mixing with the main alloy elements and apparent disordering of the structure, the additions of Ni or Co have different effects on the glass-forming ability (GFA) and thermal stability of the ternary "mother" alloy. In particular, the addition of Ni notably increases GFA and thermal stability of the BMG, whereas addition of Co does not show a similar effect. Possible reasons for this discrepancy are discussed.

This chapter is based on the paper "**The effect of Ni or Co additions on the structure of $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ bulk metallic glass revealed by high-energy synchrotron radiation**" ([doi:10.1016/j.mtcomm.2022.103531](https://doi.org/10.1016/j.mtcomm.2022.103531)) authored by Martin E. STIEHLER, Nikolaos T. PANAGIOTOPOULOS, Dean S. KEEBLE, Yurii P. IVANOV, Melita MENELAOU, Mark R. JOLLY, A. Lindsay GREER and Konstantinos GEORGARAKIS published in *Materials Today Communications*.

5.1 Introduction

Due to their amorphous structure, bulk metallic glasses (BMGs) exhibit interesting engineering properties typically superior to those of their conventional crystalline counterparts [Kha18, Gre09, You17, Sun16, Pan20]. However, glass formation in metallic alloys is still not well understood. A variety of parameters and rules have been considered for the prediction and enhancement of their GFA. Amongst them are

GREER's "confusion principle" suggesting that a mixture of many elements with a high diversity especially in the atomic radii could lead to dense packing in the liquid state favouring glass formation over crystallisation upon rapid solidification [Gre93a, Gre95] and INOUE's three empirical rules [Ino00]. The latter state that enhanced GFA can often be found (i) in alloys with more than three components, (ii) when the three main components exhibit significantly different atomic sizes (differences $\gtrsim 12\%$) and (iii) when enthalpies of mixing ΔH_{mix} between the three main components are negative. In a sense, the first and second of INOUE's rules specify different routes that can be taken to effectively "confuse" the liquid alloy's structure to avoid crystallisation by increasing the diversity in the properties among the components present, particularly their different sizes [Gre95]. Further factors that influence GFA are, inter alia, the crystal-liquid interfacial free energy [Gan18, Rus18, Kel04], the diffusivity of the components [Tur74, Gre93] as well as the alloy's proximity to eutectic compositions [Tur69, Rus18] or triple points [Bha07, Rus18] in their phase diagrams. The existence of eutectics and triple points themselves can be considered to arise from a kind of "structural confusion" due to competing orderings (e.g. different crystalline phases) [Rus18, Yav05a, Geo13]. Comparably, the dissimilarity of short (SRO) and medium range order (MRO) of the undercooled liquid phase and competing crystalline phases are another source of "confusion" that may be beneficial for GFA [Rus18, Gan19]. However, a rigorous way of quantifying "confusion" and disorder from a structural point of view is missing so far, and exceptions to virtually all of the aforementioned rules – towards lower as well as higher GFA – exist [Kab13, Tan04, Xia06, Ega12, Wan18, Wan04]. Ultimately, the necessary prerequisites for high GFA have to be explained by the interplay of the electrons and atoms in a material. Those electronic interactions can be discussed in a local [Lek09] as well as a global view [Hau92, Sti19, Yua20].

Using high-energy X-ray diffraction (XRD) and PDF analysis the effect of Al addition on SRO and MRO of the amorphous structure in Zr-Cu-Al BMGs in relation to their GFA and other properties has previously been shown [Geo09, Ant11, Geo15]. While the structure of binary Zr-Cu metallic glasses can be approximated by models equivalent to an ideal solution-like behaviour [Mat08], addition of Al strongly modifies the atomic structure leading to the formation of Zr-Al nearest neighbour populations far in excess of the random statistics of an ideal solution model [Geo09]. In this respect, the structure of the hypoeutectic ternary alloy $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ has recently been studied by different techniques [Ant11, Geo15]. Using high-energy synchrotron radiation combined with a containerless levitation technique the structural changes in this alloy were

continuously probed during in-situ vitrification, starting from the high-temperature liquid down to the amorphous solid. The findings suggested that the addition of Al introduces strong covalent-like bonding resulting in stronger cohesion and increased population of local polyhedral atomic clusters, i.e. enhancing their stability through local electronic interactions associated with bond shortening [Che09] which in turn is responsible for sluggish kinetics in the undercooled liquid favouring vitrification.

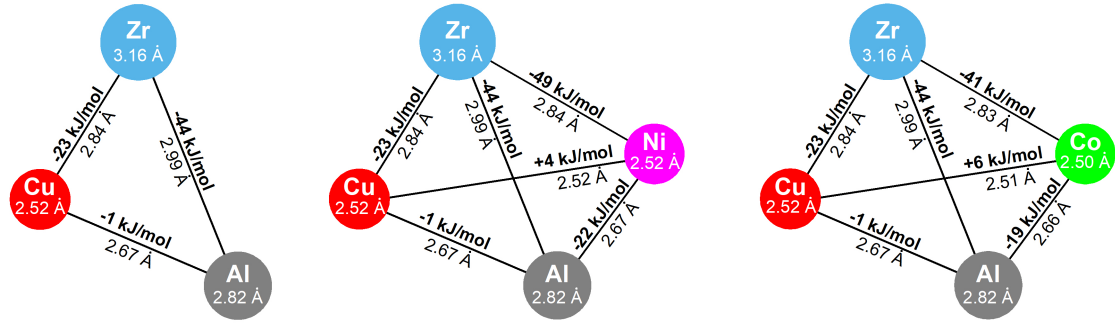


Figure 5.1: Enthalpies of mixing ΔH_{mix} (**bold**) according to MIEDEMA's model [Tak05] and interatomic distances d_{at} [Mir10] for all pairs of elements in the three alloys under consideration. The interatomic distance for pairs of the same element equals the atomic diameter of this element [Mir10] and is noted at each element. The numerical values can also be found in Tab. 5.2.

Additions of Ni are known to significantly increase GFA and thermal stability of Zr-Cu-Al alloys achieving values of d_c of up to 30 mm [Ino96, Yok07, Son09]. Additions of Co, on the other hand, have a smaller effect on GFA with maximum reported d_c values for the Zr-Cu-Co-Al system of 10 mm [Han17]. At the first glance, the increase in the number of components going from the ternary Zr-Cu-Al to the quaternary Zr-Cu-TM-Al (with TM being either Ni or Co) systems could be made responsible for the increased GFA due to an increase of diversity and confusion in the alloys. Interestingly, however, the atomic sizes of Cu, Ni and Co are so close to each other (Fig. 5.1, Tab. 5.2) that identical bond lengths d_{at} with Zr and Al have to be assumed [Mir04]. This would (neglecting further effects like the proximity to eutectic compositions) remove the second and to some extent also the first route of increasing confusion according to INOUE's rules and no change of GFA should take place. INOUE's third empirical rule, however, could still provide the possibility of an enhanced GFA since the addition of Ni or Co introduces elemental pairs with considerably higher negative values of ΔH_{mix} compared to those in the ternary alloy (Fig. 5.1, Tab. 5.2, bold). Related to that, another source of diversity may arise from the different electron configuration of Ni or Co compared to that of Cu. While, at least for the free atoms, all 3d states of Cu are

filled, Ni and Co possess one and two unoccupied 3d states, respectively. Based on this, changes of the chemical bonding network of $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ with addition of Ni or Co can be expected.

In the present work the atomic structure of the ternary alloy $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ as well as the quaternary alloys $\text{Zr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ and $\text{Zr}_{60}\text{Cu}_{20}\text{Co}_{10}\text{Al}_{10}$ were studied using high energy synchrotron radiation X-ray diffraction. Despite the very similar properties of Cu, Ni and Co, characteristic structural changes induced by the addition of Ni or Co to $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ could be identified. The associated effects on GFA and thermal stability of the glassy alloys are discussed.

5.2 Materials and methods

Samples of three alloys with nominal compositions (in at.%) $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$, $\text{Zr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ and $\text{Zr}_{60}\text{Cu}_{20}\text{Co}_{10}\text{Al}_{10}$ were prepared by arc-melting from high-purity raw materials (Zr: 99.5%, Co: 99.9%, Ni: 99.9%, Cu: 99.9%, Al: 99.9%) under Ar atmosphere. The ingots were flipped and re-melted four times as well as electromagnetically stirred during each step. Subsequent suction-casting of the ingots into a water-cooled Cu-mould was employed to obtain cylindrical samples 1 mm in diameter.

High-energy X-ray diffraction experiments in transmission mode were carried out at beamline I15-1 of the Diamond Light Source using an incident monochromatic beam with a wavelength of $\lambda_i = 0.161669 \text{ \AA}$ ($E_i = 76.69 \text{ keV}$). A Perkin Elmer XRD 4343 CT flat-panel detector was used for the acquisition of diffraction data up to a maximum momentum transfer of $38.86 \text{ \AA}^{-1}$. LaB_6 was used to calibrate the scattering geometry. A beam spot size of $10 \times 700 \mu\text{m}^2$ and an acquisition time of 600 s per sample was used. This enables the collection of diffraction data with sufficient statistics for very high signal-to-noise ratio and reliable PDFs. The diffraction images, after necessary corrections for polarisation, dark current and air (background) scattering, were azimuthally integrated using the DAWN software [Bas15, Fil17]. From the so-obtained integrated diffraction intensities $I(Q)$ the total structure factors $S(Q)$ were calculated using the GudrunX software [Sop11] following corrections for absorption, fluorescence, Compton scattering, background contribution as well as normalisation to the X-ray atomic form factor and conversion to electron units per atom with the generalised KROGH-MOE-NORMAN method [Kro56, Nor57]. GudrunX was also used

to Fourier transform $S(Q)$ [Ega03] to the reduced pair-distribution function

$$G(r) = \frac{2}{\pi} \int_0^{Q_{\max}} Q[S(Q) - 1] \sin(Qr) dQ = 4\pi r [\rho(r) - \rho_0] \quad (5.1)$$

to obtain structural information in real space, where r is the radial distance from a centre atom, ρ_0 the average particle number density and $\rho(r)$ represents the local atomic pair density (atomic pair density function) [Ega03]. While ideally $Q_{\max}$ in Eq. (5.1) is infinite, in practice it is necessary to choose a finite value as high as possible, depending on the raw data.

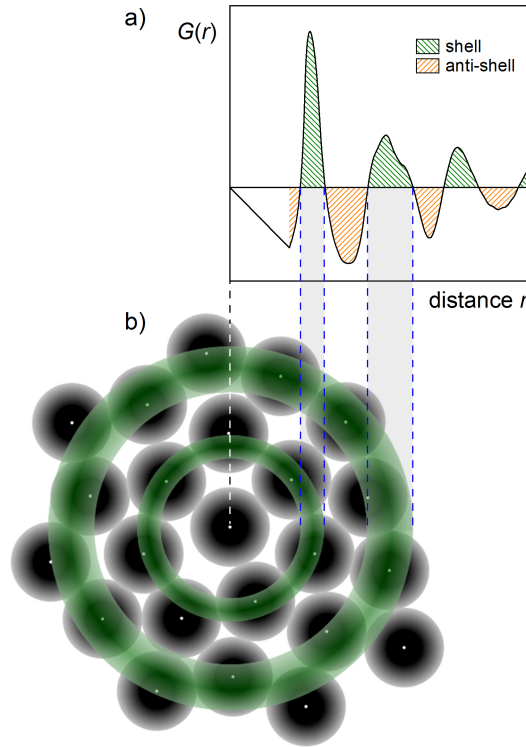


Figure 5.2: Schematic representation of the reduced pair distribution function $G(r)$ to illustrate the definition of NN shells and anti-shells **(a)** and its relation to the atomic arrangement in a two-dimensional monatomic model glass **(b)**. The centres of the atoms in **(b)** are marked by white dots. The areas of the atoms shaded in grey symbolise the softness of the interatomic potential.

Figure 5.2 shows a schematic $G(r)$ where the distinct broad peaks are associated with the NN shells. More specifically, in the present study, an NN shell will be defined as the r -range where $G(r) > 0$ (areas hatched green in Fig. 5.2a), i.e. where the local densities $\rho(r)$ are higher (excess local density) than the average density ρ_0 . To facilitate the discussion of structural disorder the novel concept of NN "anti-shells" is introduced

here for the r -ranges with $G(r) < 0$, i.e. the r -ranges between the NN shells where the local densities $\rho(r)$ are lower (deficient local density) than the average density ρ_0 (areas hatched orange in Fig. 5.2a). The reduction of local deviations from the average density is associated with an increase of disorder [Dmo10, Ton15, Ton18], i.e. the less "contrast" between shells and anti-shells exists the higher the degree of disorder is. Furthermore, the shell/anti-shell concept allows for a less subjective and more reliable way of determining structural metrics (e.g. area, height or centre of mass of a peak) by using a reference inherently associated to the structure function itself (e.g. $G(r) = 0$ in case of the reduced pair distribution function) without the need for any background subtraction or fitting procedure.

Differential scanning calorimetry (DSC) was employed to obtain characteristic temperatures and to evaluate the thermal stability of the glassy alloys. A TA Instruments Q2000 DSC was used to measure the glass-transition temperatures T_g and the crystallisation temperatures T_x . Alloy samples with masses of about 10 mg were encased in Al pans with lids. During a first heating run the samples were heated up to 823 K, i.e. well above T_x . The furnace was kept under a constant flow (50 ml/min) of N_2 . After cooling down to room temperature, the same protocol was used on the crystallised samples to obtain the baselines. A TA Instruments Q600 DSC/TGA was used to identify the liquidus temperatures T_l . Samples with masses of about 9 mg were placed in Al_2O_3 pans without lids. During heating, the furnace was purged with Ar at a constant flow of 100 ml/min. All heating runs were performed at a heating rate of 0.667 K/s.

5.3 Results

Figure 5.3a shows the structure factors $S(Q)$ for $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$, $\text{Zr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ and $\text{Zr}_{60}\text{Cu}_{20}\text{Co}_{10}\text{Al}_{10}$ up to $18 \text{ \AA}^{-1}$. The three alloys exhibit very similar structure factors with diffuse peaks typical for amorphous alloys and decaying intensity with increasing Q . No Bragg peaks could be observed up to the maximal Q of $38.86 \text{ \AA}^{-1}$. The amorphous nature of the samples could also be verified by transmission electron microscopy (TEM; Sec. 5.6.5).

For the remainder of this chapter these diffuse peaks in reciprocal space will be referred to as halos which are numbered as shown in Figure 5.3a. Starting from the features of $S(Q)$ for the ternary $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ alloy the subtle differences induced by the addition of Ni and Co, respectively, are discussed. The first halo, which bears information mainly from the MRO in real space [Car75, Ryu20], is very distinct and

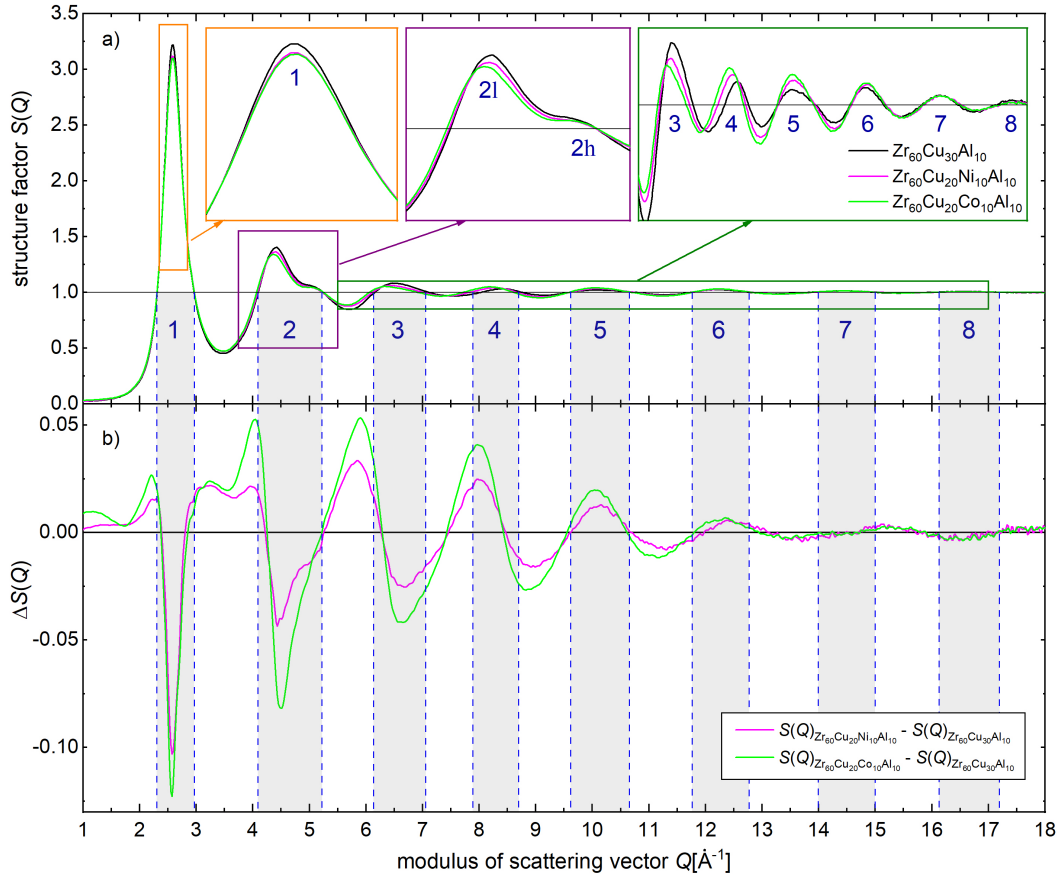


Figure 5.3: **a)** Structure factors $S(Q)$ up to $18 \text{ \AA}^{-1}$ of all three alloys together with several enlarged views for the first eight halos (as numbered) and **b)** the difference functions $\Delta S(Q)$ with respect to $S(Q)$ of $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$. The vertical dotted lines and the shaded areas highlight the Q -ranges of the halos.

almost symmetrical. Interestingly, the addition of Ni or Co leads to a decrease of its intensity while its position ($Q_1 = 2.59 \text{ \AA}^{-1}$) and width remain virtually unchanged (Figure 5.3a). Taking into account the very similar X-ray form factors of Cu, Ni and Co this observation may be related to an increase in the structural disorder caused by Ni or Co addition, without changing the principal structure considerably. While the changes in going from the ternary to the quaternary alloys are distinct, the difference between the two quaternary alloys are comparably small. The second halo shows a structure consisting of (at least) two features that are frequently observed in metallic glasses [Che11]. These two features, denoted as 2l (at the *low*- Q side) and 2h (at the *high*- Q side) are not separated by a local minimum, i.e. feature 2h remains a shoulder for all three alloys leaving halo 2 with a skewness towards higher Q . The split of the second halo has previously been discussed in connection with icosahedral SRO which is assumed to be the prevailing motif in Zr-based BMGs and critical for their

high GFA [Tan03, Sac84, Kel03, Ma15]. Experimentally, as well as by simulations, icosahedral order has been shown to dominate SRO in $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ [Geo15]. It is interesting to note that the intensity of sub-halo 2h stays virtually unaffected whereas the intensity of 2l changes (decreases) markedly (Figure 5.3). In other Zr-bearing metallic glasses an increasing intensity of the low- Q feature was related to increasing next-NN ordering [Dai18], indicating again an increasing disorder by alloying with Ni or Co in the present case.

The trend of decreasing intensity of $S(Q)$ with Ni or Co addition can be observed up to the third halo (Fig. 5.3a). For the higher-order halos (right inset of Figure 5.3a) this sequence is reversed, with the intensity of halos 4 to 6 for the Ni- and Co-bearing alloys becoming higher than those of $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$. This and some other peculiarities of $S(Q)$ for higher Q (like changes of skewness or a non-monotonic change of the depth of consecutive troughs) indicate the possible presence of beats [Cra68, Ble78, Zac03] in $S(Q)$ caused by Ni or Co addition which are discussed further in the Supplementary section 5.6.2. Considering again the very similar X-ray form factors of Cu, Ni and Co as well as their virtually identical atomic diameters (Fig. 5.1, Tab. 5.2) the differences in the $S(Q)$ point to differences in the structure of the three alloys which must be attributed to properties emerging from interactions between the added elements (Ni or Co) and the elements of the base ternary alloy (Zr, Cu, Al). To further elucidate the effect of the substitution of Cu by Ni or Co, $S(Q)$ for the ternary alloy was subtracted from those for the quaternary alloys and the so-obtained functions $\Delta S(Q)$ are plotted in Fig. 5.3b. Differences in intensity can be observed over the complete Q -range suggesting that structural changes due to the substitution arise within SRO as well as MRO.

Figure 5.4 shows the reduced pair-distribution functions $G(r)$ for the three alloys obtained by Fourier transforming the respective $S(Q)$ up to $Q_{\text{max}} = 25 \text{ \AA}^{-1}$ (Eq. (5.1)). Again, a similar overall behaviour of the three alloys is visible with distinct broad peaks corresponding to the NN shells.

Following the shell/anti-shell concept introduced in Section 5.2 the r -ranges of the shells ($G(r) > 0$) are shaded and marked with dashed vertical lines in Fig. 5.4. Although these ranges can be considered equal for the three alloys, a general overall trend can be clearly observed: Ni or Co addition leads to a decrease of the intensity of $G(r)$ for the NN shells accompanied by an increase of $G(r)$ within the anti-shells, effectively reducing deviations from the average density and thus indicating a more disordered structure.

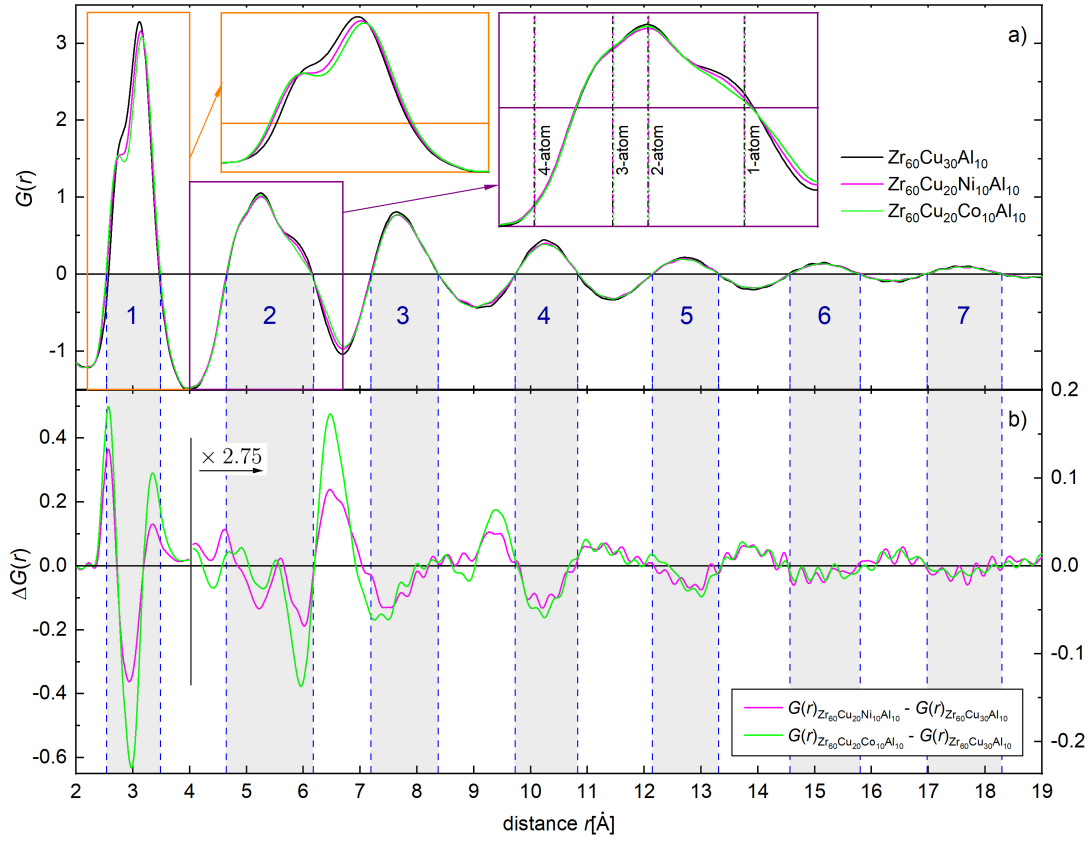


Figure 5.4: **a)** The reduced pair distribution functions $G(r)$ for all three alloys together with enlarged views for the first and second NN shell. The dotted vertical lines and shaded areas highlight the regions of the NN shells (as numbered). Vertical lines in the inset for the second NN shell mark expected distances if interconnected coordination polyhedra sharing 1-, 2-, 3- and 4-atoms, respectively, are assumed. **b)** Differences $\Delta G(r)$ in the reduced PDF induced by alloying (the y-axis has been scaled by a factor of 2.75 from $r = 4 \text{ \AA}$ onwards for clarity, cf. right y-axis). The "ripples" at high r are an artifact from the cut-off at finite $Q_{\max}$ during FOURIER transform [Sop12].

The most obvious differences between the $G(r)$ for the three alloys (Fig. 5.4) can be observed in the first two NN shells (Fig. 5.4a). All three alloys show a split first NN shell similar to what has been previously observed in some Zr-based metallic glasses [Ste87, Geo09, Geo10, Hua11, Geo15]. The split increases from a shoulder in the ternary alloy via a saddle point in the Ni-bearing to a minimum in the Co-bearing alloy.

The second $G(r)$ peak, corresponding to the second NN shell, is asymmetric and possesses shoulders at the low- as well as the high- r side. Especially the shoulder at about $5.9 \text{ \AA}$ weakens upon alloying. While the peak associated with the third NN shell is also asymmetric with a slight skewness towards higher r , all peaks related to higher NN shells are virtually symmetric, almost independent of the particular alloy and $G(r)$ resembles a damped sinusoidal oscillation in this r -region. Underlying reasons for the

possible existence of two regions with different order mechanisms (i.e. NN shells 1,2,3 compared to NN shells 4 and above) are discussed in the Supplementary section 5.6.4 in relation to local and global electronic interactions [Hau92, Sti19, Yua20].

For further clarification, $\Delta G(r)$ functions corresponding to the difference between the $G(r)$ of the quaternary alloys and that of the ternary base alloy were calculated (Fig. 5.4b). The negative values of $\Delta G(r)$ clearly indicate that the intensity of $G(r)$ within the regions of the NN shells decreases for the Ni- and Co-bearing alloys, whereas positive values of $\Delta G(r)$ occur mainly in the anti-shell regions corresponding to the increase of the $G(r)$ there. This corroborates the observation of a redistribution of atoms from the shells to the anti-shells reducing deviations from the average density, which can be interpreted as an increase of disorder in the short-to-medium-range order due to Ni or Co addition. The effect seems to be slightly bigger for the Co- than for the Ni-bearing alloy.

5.4 Discussion

The results in reciprocal (Fig. 5.3) as well as in real space (Fig. 5.4) suggest a small but unambiguous difference in the atomic structure of $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ following the addition of Ni or Co consistent with an increase in structural disorder. This direct comparison of different alloys is possible only because of the similar properties of Cu, Ni and Co, especially their initially almost identical sizes (Fig. 5.1, Tab. 5.2). Keeping this in mind, a partial substitution of Cu by Ni or Co should not have any effect apart from INOUE's first empirical rule. However, a simple increase in the number of components cannot be effective towards an increase of disorder or GFA as long as the components are not connected with an increase of diversity in their physical properties.

For a more detailed discussion in the present case it is instructive to start with a consideration of the first NN shell. The increase of its characteristic split as well as its width at the base (i.e. at $G(r) = 0$) compared to $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ (Fig. 5.5 and left inset of Fig. 5.4a) is mainly due to a shift of the low- r portion towards lower r . From the FABER-ZIMAN weighting factors [Fab65]

$$W_{ij} = (2 - \delta_{ij}) \frac{c_i c_j f_i f_j}{\left(\sum_i c_i f_i \right)^2}, \quad (5.2)$$

of the elemental pairs i - j that are visualised as vertical bars (placed at interatomic

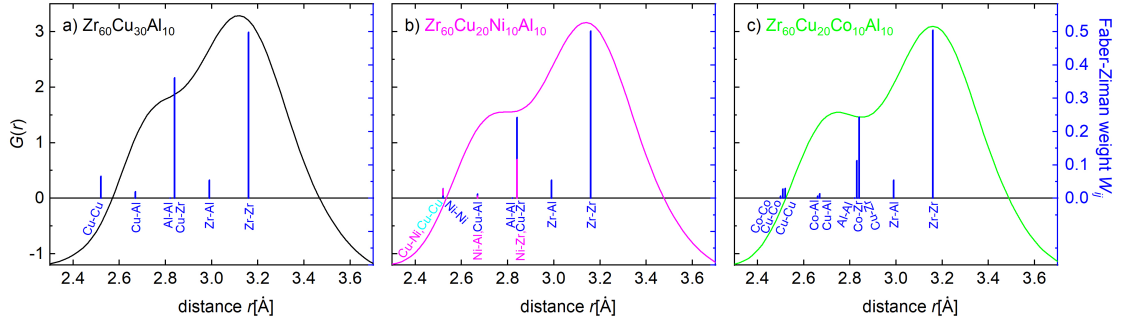


Figure 5.5: $G(r)$ of the first NN shell for the three alloys together with the FABER-ZIMAN weighting factors W_{ij} (right y-axis) for the individual elemental pairs (blue bars; in case of pairs located at the same distance magenta or cyan bars in front of blue bars; the numerical values of W_{ij} can be found in Tab. 5.2) calculated using Eq. (5.2) and positioned at the interatomic distances d_{at} according to Fig. 5.1 (Tab. 5.2).

distances from Fig. 5.1, height proportional to W_{ij}) in Fig. 5.5, as well as the probability [Jel14, Ton16]

$$\begin{aligned}
 P_{ij} &= (2 - \delta_{ij})c_i c_j \\
 &= W_{ij} \frac{\left(\sum_i c_i f_i \right)^2}{f_i f_j}
 \end{aligned} \tag{5.3}$$

of occurrence of these pairs, it can be assumed that the low- r feature is dominated by Cu-Zr as well as additional Ni-Zr or Co-Zr elemental pairs for the quaternary alloys (c_i , c_j are the atomic concentrations of the elements i and j , f_i , f_j their atomic form factors neglecting the Q -dependence and δ_{ij} the KRONECKER delta; the numerical values of W_{ij} and P_{ij} can be found in Tab. 5.2). The shift of the low- r feature towards lower r therefore suggests a shortening of the Ni-Zr and Co-Zr distances compared to those expected from Fig. 5.1 (Tab. 5.2), which can be connected to the high negative ΔH_{mix} of Ni-Zr and Co-Zr compared to that of Cu-Zr (Fig. 5.1, Tab. 5.2) [Ant09, Geo09, Geo10, Kab13]. Further differences between Cu and Ni or Co relate to details of the interatomic potentials associated with different bonding behaviour due to the different electron configurations of Cu, Ni and Co. Bonding in the alloys with Ni or Co is expected to be more directional due to the participation of anisotropic d-states as opposed to the isotropic s-dominated bonding with Cu [Wan18a]. Hence, it is electronic interactions that effectively change the initially almost identical sizes of Cu, Ni and Co, leading to an increase of the diversity in this property. Since this change cannot take place in

these elements alone but becomes manifested only due to interactions with the other species (most importantly Zr) in the alloys this can be considered as *emergent diversity* (in effective atomic sizes). INOUE's third rule [Ino00] is utilised to increase confusion according to the second (and effectively also the first) route to enhance confusion.

Extending the discussion to substitution-induced changes in the second NN shell shows most prominently a reduction of the shoulder on the high- r side of the according peak (Fig. 5.4a). Computer simulations related distances in the second NN shell to the interconnection of coordination polyhedra sharing different number of atoms [Ben72, Din15]. According to these simulations, atoms in the second NN shell can be found at distances $2r_1$, $\sqrt{3}r_1$, $\sqrt{\frac{8}{3}}r_1$ or $\sqrt{2}r_1$ if their coordination polyhedra share 1, 2, 3 or 4 atoms with coordination polyhedra of atoms located at $r = 0$ Å, respectively, where r_1 is the position of the centroid of the first peak in $G(r)$. These characteristic distances are marked with vertical lines in the inset for the second NN shell in Fig. 5.4a. Accordingly, the observed changes in the present case point foremost to a reduction in 1-atom interconnections which are not compensated by an increase in other interconnection schemes. Instead, it seems that the reduction is accompanied by an increase in the number of atoms in the adjacent anti-shell (inset of Fig. 5.4a). Thus, the observed changes for the second NN shell again corroborate the disordering induced by Ni or Co addition, with Co having the bigger effect.

Although every atom in the alloy is at the centre of "its own SRO" and the described local effects should therefore be reflected in the high- r region of $G(r)$ as well, its many-body nature may lead to additional emergent effects [Ryu20, Ega20, And72]. The local effects can be regarded to average out for higher distances, and are replaced by a coarse-grained description of the structure [Ryu20]. In the same manner, local electronic effects may become replaced by global electronic interactions [Hau92, Sti19, Hau05]. Shells 4 and above show a common pattern in $\Delta G(r)$, i.e. an almost symmetrical redistribution of pair density to lower as well as higher r , with $\Delta G(r) < 0$ exclusively within the shells and $\Delta G(r) > 0$ exclusively for the anti-shell regions (Fig. 5.4b). To gain more insight into this behaviour, Fig. 5.6 shows the absolute values of the reduced pair distribution functions $|G(r)|$ for all three alloys in a semi-logarithmic plot highlighting the nearly exponential decay of the density oscillations with increasing distance r . This decay can be characterised by a structural coherence length ξ_s according to $G(r) \propto \exp\left(-\frac{r}{\xi_s}\right)$ [Ryu20]. Overall, the addition of Ni or Co leads to a slight reduction of ξ_s (cf. broken lines in Fig. 5.6). In Fig. 5.9 (Supplementary section 5.6.3) it is demonstrated that two $G(r)$, differing slightly only in their coherence lengths, lead to a $\Delta G(r)$ very similar

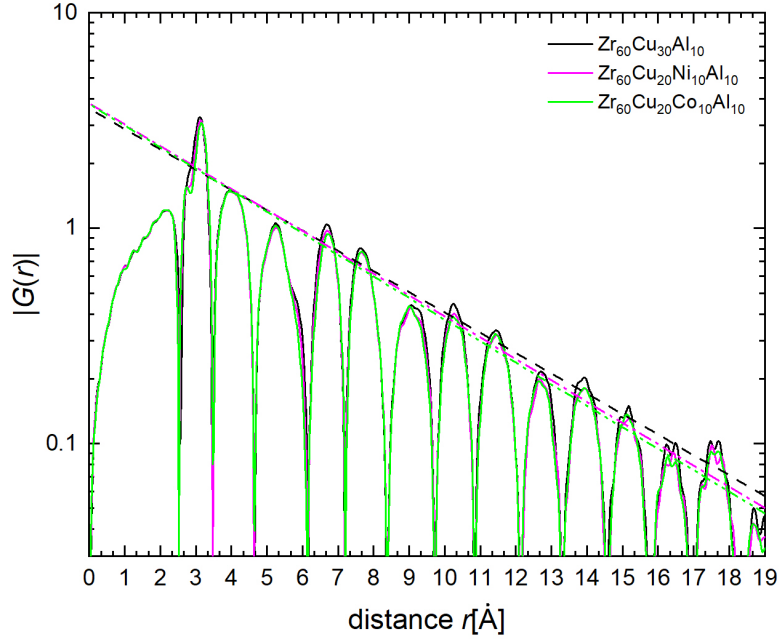


Figure 5.6: The absolute values of the reduced pair distribution functions for all three alloys in a semi-logarithmic plot. The broken lines are linear guides for the eye. Their slopes correspond to the structural coherence lengths ξ_s .

to that observed in Fig. 5.4b for NN shells 4 and beyond. This suggests that disorder in the form of a reduced deviation from the average particle density, as outlined above, is equivalent to a reduction in long-range density correlations, i.e. the redistribution of atoms from the shells to the anti-shells is reflected in a reduced coherence length ξ_s . Recently it was shown that ξ_s is nearly proportional to the height of the first peak in the structure factor $S(Q_1)$ of many metallic glass-forming alloys [Ryu19], which is in accordance with the alloying-induced reduction in $S(Q_1)$ observed in the present case (left inset of Fig. 5.3a).

To decide whether the increase in structural disorder leads to a stabilisation of the glassy state, the GFA for all three alloys needs to be assessed. Although the critical casting diameter d_c is often used as measure for GFA other parameters such as the reduced glass transition temperature $T_{rg} = \frac{T_g}{T_1}$ and the undercooled liquid region $\Delta T_X = T_X - T_g$ are also frequently used as (less strong) comparative indicators for GFA within the same family of alloys.

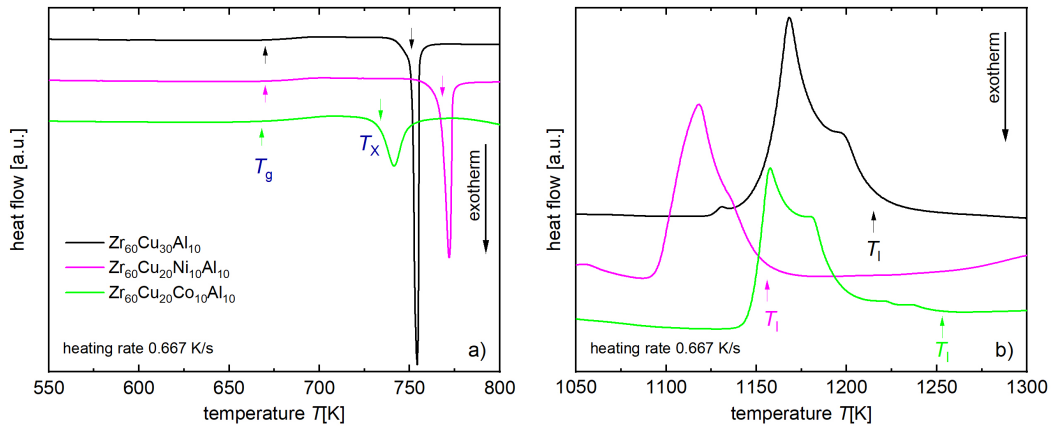


Figure 5.7: DSC traces for the three alloys for different temperature ranges. The arrows indicate in a) the glass transition temperature T_g and the crystallisation temperature T_X and in b) the liquidus temperature T_l . The curves are shifted along the y-axis for clarity.

Figure 5.7 shows the DSC traces for the temperature ranges relevant to obtain these characteristic temperatures in the present case. The values measured here are listed in Tab. 5.1 together with additional values from the literature. T_g remains practically the same for the three alloys. However, the addition of Ni increases T_X (thus increasing the thermal stability of the glassy phase) and reduces T_l , shifting T_{rg} slightly closer to 2/3, the value considered optimal [Tur69]. In addition, d_c was previously shown to increase to 20 mm for the Ni-bearing alloy [Son09] compared to 8 mm of the ternary alloy [Zha10]. On the other hand, the Co-bearing alloy exhibits lower thermal stability as shown by the lower T_X and lower T_{rg} pointing to lower GFA. However, judging from Fig. 5.3a, Fig. 5.4b and Fig. 5.6, the increase of disorder is stronger for the Co- than for the Ni-bearing alloy. Moreover, if the local chemical interactions leading to the bond shortening (and thus the increased split in the first NN shell (Fig. 5.4 and Fig. 5.5) were considered as the only factor responsible for more sluggish kinetics during vitrification, the Co-bearing alloy should exhibit an increase in GFA exceeding that of the Ni-bearing one. The beneficial effect of bond shortening for GFA has been pointed out already decades ago [Tur74, Gre93]. However, since the shortening of the Zr-Co distance seems to be slightly stronger than that of the Zr-Ni distance, it appears that in the present case other factors affecting GFA, that are influenced by Ni or Co addition as well, outweigh the impact of bond shortening or the increase of disorder. Elemental pairs with positive ΔH_{mix} (in the present case Cu-Ni and Cu-Co, cf. Fig. 5.1 and Tab. 5.2) introduce repulsive interactions and could weaken the atomic bonding in the alloy causing an increase of free volume or even phase separation on

the nanometre scale [Par12]. This, in turn, could cause a reduction of GFA which would be expected to be bigger for the Co-bearing alloy ($\Delta H_{\text{mix}}^{\text{Cu-Co}} = +6$ kJ/mol) as compared to the Ni-bearing alloy ($\Delta H_{\text{mix}}^{\text{Cu-Ni}} = +4$ kJ/mol), supporting the present results. Phase separation in glassy $\text{Zr}_{60}\text{Cu}_{20}\text{Co}_{10}\text{Al}_{10}$, as result of annealing, observed by TEM has indeed been reported in the literature [Wan17a]. However, no phase separation could be observed by TEM investigations for the as-cast samples in the present case (Sec. 5.6.5). Thus, the reason for the reduced stability of the glass phase of $\text{Zr}_{60}\text{Cu}_{20}\text{Co}_{10}\text{Al}_{10}$ seems to be founded in intrinsic structural properties. An according factor could be related to possible differences in the icosahedral SRO of the alloys (split nature of halo 2), as was briefly mentioned above.

To assess GFA, it is always a combination of criteria and their mutual interference that has to be considered, thus leading to exceptions to the empirical rules as mentioned in Section 5.1. In a future more detailed study, calculations within the framework of density-functional theory (DFT), complementing those recently performed for the ternary alloy [Geo15], could provide a better understanding of the alloying-induced changes to the local electronic interactions that lead to the observed structural changes and their effect on GFA.

alloy	T_g [K]	T_X [K]	T_l [K]	T_{rg}	ΔT_X [K]	d_c [mm]	reference
$\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$	670	751	1215	0.55	81	–	this work
	677	753	–	–	76	–	[Ino98]
	663	755	1207	0.55	92	8	[Zha10]
	671	–	1207	0.56	–	–	[Geo15]
$\text{Zr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$	670	768	1156	0.58	98	–	this work
	666	768	1153	0.58	102	20	[Son09]
	674	–	–	–	–	–	[Ket18]
$\text{Zr}_{60}\text{Cu}_{20}\text{Co}_{10}\text{Al}_{10}$	668	734	1253	0.53	66	–	this work
	676	–	–	–	–	–	[Ket18]

Table 5.1: Glass-transition T_g , crystallisation T_X and liquidus T_l temperatures as well as the reduced glass-transition temperature $T_{rg} = T_g/T_l$, the undercooled liquid region $\Delta T_X = T_X - T_g$ and the critical diameter d_c for the alloys under consideration. The present results are supplemented by literature values (references given in the table). T_{rg} and ΔT_X were calculated here from the shown (literature) values.

5.5 Conclusions

Insights into the effect of the addition of Ni or Co on the atomic structure of $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ bulk metallic glass were gained using high-energy synchrotron radiation X-ray diffraction. The additions cause an increase of disorder of the amorphous structure. This becomes manifest in the short- and medium-range order by an overall decrease in the amplitude of the oscillations in the reduced pair-distribution function $G(r)$ and the reduction of the structural coherence length ξ_s . Both are related to a redistribution of atoms from the nearest-neighbour shells towards the anti-shells. The novel concept of anti-shells introduced here provides a fruitful basis to facilitate the description of disordering in amorphous alloys. Disorder is connected to increased confusion resulting from an increased diversity of atomic species and their different sizes under introduction of a further component. Electronic interactions can cause an increase of diversity of atomic sizes leading to an emergent increase of confusion. Adding further elements might at the same time impact other factors leading to an overall decrease in glass-forming ability. Increasing structural disorder does not necessarily imply increasing glass-forming ability. Alloying to achieve an increased glass-forming ability has to be performed wisely and relying on one criterion alone is ill-fated. Nevertheless, further routes to "confusion enhancement" need to be explored and more quantitative measures of confusion are sought.

5.6 Supplementary Material

5.6.1 Alloying-induced structural changes in an animated view

The movie under cord.cranfield.ac.uk/account/projects/121164/articles/16432695 shows the alloying-induced structural changes in $S(Q)$ and $G(r)$ in an animated way highlighting the Q - and r -regions affected by Ni- or Co-addition.

5.6.2 Bond shortening in real space – Beats in reciprocal space

The close scrutiny of the alloying-induced changes in $S(Q)$ at high Q suggests the presence of a signature of the shortening of the Ni-Zr or Co-Zr bonds, respectively. In Fig. 5.3a it can be seen that halos 2 and 3 exhibit a skewness towards higher Q . While the skewness of the 4th halo is towards lower Q that for the 5th halo points towards higher Q again (all higher halos can be considered symmetrical within the experimental

resolution). Additionally, for the quaternary alloys the trough of $S(Q)$ between the 4th and 5th halo is deeper than the previous and subsequent one. Furthermore, in contrast to all other halos, the maxima and minima for the three alloys are not located at the same Q for the 3rd and 4th halo (Fig. 5.3). All these properties leave the Q -range from the 3rd to the 5th halo with a peculiar overall shape. Moreover, for $Q \gtrsim 4 \text{ \AA}^{-1}$ $\Delta S(Q)$ is similar to a (damped) sinusoidal oscillation which is *incommensurate* with the oscillations in $S(Q)$ (cf. vertical lines in Fig. 5.3a,b). These features resemble the effect of two oscillations of similar wavelength being superimposed to cause a beat [Cra68]. Such a behaviour was predicted to occur in amorphous alloys under certain conditions [Ble78, Zac03] and might especially be visible in the present case due to the high resolution of the experimental data.

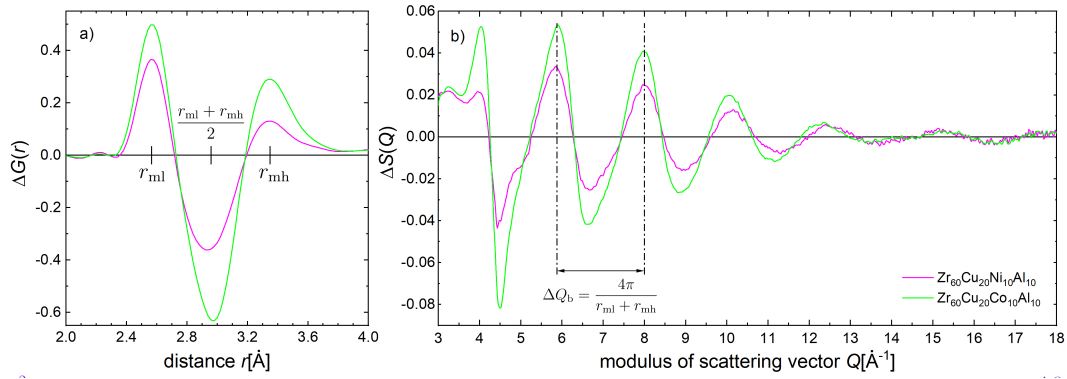


Figure 5.8: **a)** Enlarged view of $\Delta G(r)$ for the 1st NN shell for $\text{Zr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ and $\text{Zr}_{60}\text{Cu}_{20}\text{Co}_{10}\text{Al}_{10}$ where r_{ml} and r_{mh} denote the positions of the two peaks visible (almost the same position for both alloys). Also marked is the average position $(r_{\text{ml}} + r_{\text{mh}})/2$ of both peaks. **b)** Enlarged view of $\Delta S(Q)$ with the dash-dotted vertical lines highlighting the oscillation period $\Delta Q_b = 4\pi / (r_{\text{ml}} + r_{\text{mh}})$, i.e. $2\pi / \Delta Q_b = (r_{\text{ml}} + r_{\text{mh}})/2$.

For a further investigation of this assumption and the origin of these oscillations Fig. 5.8a shows an enlarged view of $\Delta G(r)$ for the 1st nearest neighbour (NN) shell. The positions of the two pronounced and relatively sharp maxima occurring in that range are denoted by r_{ml} and r_{mh} (Fig. 5.8a). In reciprocal space two oscillations related to $\sim \sin(Q \cdot r_{\text{ml}})$ and $\sim \sin(Q \cdot r_{\text{mh}})$ can then be expected (damping neglected for reasons of simplicity) which will give rise to a beat [Cra68] according to $\sim \sin(Q \cdot (r_{\text{ml}} + r_{\text{mh}})/2)$ enveloped by $\sim \cos(Q \cdot |r_{\text{ml}} - r_{\text{mh}}|/2)$. The oscillation found in $\Delta S(Q)$ (Fig. 5.8b) indeed exhibits the period $\Delta Q_b = 2\pi / ((r_{\text{ml}} + r_{\text{mh}})/2) = 4\pi / (r_{\text{ml}} + r_{\text{mh}})$ and therefore directly reflects *in reciprocal space* structural changes associated with the addition of Ni or Co in the *short-range order* (SRO) *in real space*. All the peculiarities in the shape of $S(Q)$ described above may then be attributed to the addition of the beat to

$S(Q)$ of $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$. The occurrence of a "peculiarly shaped" $S(Q)$ at high Q , possibly related to beats, may therefore act as an indicator for structural changes in the SRO induced by alloying. This emphasizes that structural features of the SRO are encoded in the higher Q -range [Car75] and illustrates the duality between real and reciprocal space exemplified by the present alloys: a simple shape of $S(Q)$ for the 1st halo, that is almost independent of composition, relates to a simple shape of the medium-range order (MRO) of $G(r)$ being almost composition-independent as well; an intricate shape of $G(r)$ for the 1st NN shell relates to an intricate structure of $S(Q)$ at higher Q . Furthermore, this analysis highlights the importance of high-resolution diffraction data and a Fourier transform up to high Q to yield reliable and detailed structural information.

5.6.3 Structural coherence length and density redistribution

In order to analyse the alloying-induced changes visible in the MRO in more detail it is instructive to recall that the reduced pair distribution functions $G(r)$ can be written as

$$G(r) = G_0(r) \exp\left(-\frac{r}{\xi_s}\right) , \quad (5.4)$$

where $G_0(r)$ is the reduced pair distribution function of a proposed hypothetical "ideal-glass" state possessing long-ranged (non-decaying) density correlations and ξ_s the structural coherence length [Ryu19,Ryu20]. This description is especially applicable for the MRO where coarse-grained density correlations become more and more dominant over local chemical effects (e.g. different bonding behaviours) [Ega20]. To investigate the influence of a varying ξ_s $G(r)$ of $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ (black curve in Fig. 5.9) is divided by $\exp\left(-\frac{r}{4.58 \text{ \AA}}\right)$, i.e. assuming $\xi_s = 4.58 \text{ \AA}$ (cf. Fig. 5.6), what yields $G_0(r)$ as shown in the inset of Fig. 5.9. Multiplying this $G_0(r)$ by $\exp\left(-\frac{r}{4.38 \text{ \AA}}\right)$, i.e. using the slightly smaller coherence length $\xi_s = 4.38 \text{ \AA}$ corresponding to the quaternary alloys (cf. Fig. 5.6), yields a $G(r)$ shown as orange curve in Fig. 5.9. Calculating the difference $\Delta G(r)_{\xi_s} = G(r, \xi_s = 4.38 \text{ \AA}) - G(r, \xi_s = 4.58 \text{ \AA})$ yields the blue curve in Fig. 5.9 (magnified by a factor 4 for better visibility).

Comparing this with the difference function due to Ni addition (magenta curve in Fig. 5.9 and Fig. 5.4b) shows a very good agreement for the 4th NN shell and beyond. This shows that the alloying induced changes to the MRO (an almost symmetrical redistribution of pair density to lower as well as higher r with $\Delta G(r) < 0$ exclusively

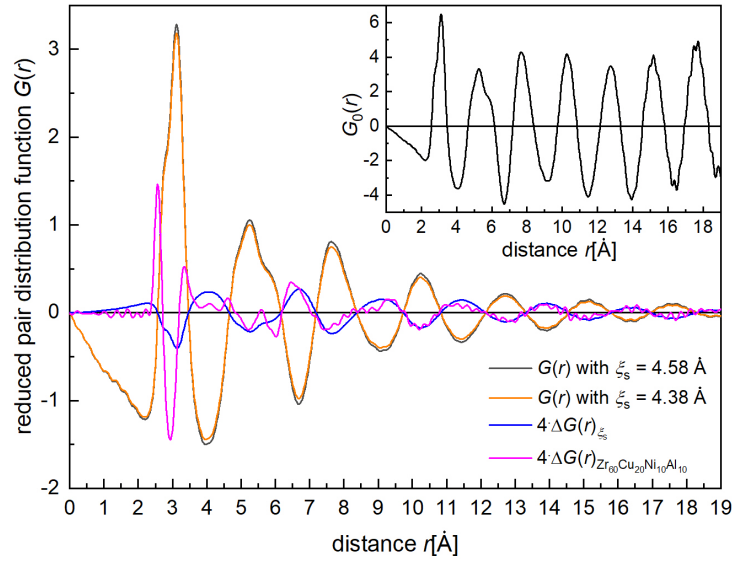


Figure 5.9: Experimentally derived reduced pair distribution function $G(r)$ of $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ (black solid line) possessing a structural coherence length ξ_s of around 4.58 Å (see also Fig. 5.6). The inset shows $G_0(r)$ derived from $G(r) = G_0(r) \exp(-r/4.58 \text{ Å})$ by dividing by $\exp(-r/4.58 \text{ Å})$. The orange line shows a $G(r)$ derived from $G_0(r)$ by multiplying with $\exp(-r/4.38 \text{ Å})$ corresponding to a slightly smaller structural coherence length $\xi_s = 4.38 \text{ Å}$ close to that found for $\text{Zr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ and $\text{Zr}_{60}\text{Cu}_{20}\text{Co}_{10}\text{Al}_{10}$. The blue curve shows $\Delta G(r)_{\xi_s} = G(r, \xi_s = 4.58 \text{ Å}) - G(r, \xi_s = 4.38 \text{ Å})$ and the magenta curve the experimentally obtained changes introduced by alloying with Ni (Fig. 5.4b). The latter two curves are magnified by a factor 4 for better visibility.

within the shells and $\Delta G(r) > 0$ exclusively for the anti-shell regions as shown in Fig. 5.4b) can be mapped onto a reduction of the structural coherence length ξ_s . However, the alloying-induced changes in the SRO, especially for the 1st NN shell, deviate drastically from those introduced by a changed ξ_s alone showing the dominant influence of local interactions at those small distances. This supports the notion, that a demarcation between two structural regions dominated by different ordering effects is located between the rd and 4th NN shell as hinted above.

5.6.4 The influence of global electronic interactions

The reduced pair-distribution functions $G(r)$ for all three alloys $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$, $\text{Zr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ and $\text{Zr}_{60}\text{Cu}_{20}\text{Co}_{10}\text{Al}_{10}$ are almost identical for the 4th and higher NN shells and the shape of the according peaks is almost symmetric there (Figs. 5.4a and 5.8). Since for these high values of r local properties like distances between atomic pairs and clusters are more and more averaged out in favour of a more coarse-grained perspective, a description in terms of local effects needs to be replaced by a discussion of the structure in terms of global effects [Hau92, Hau05, Sti19].

In many metallic (and semiconducting) amorphous systems it could be shown that the positions of the NN shells in $G(r)$ can be described by the spherical *periodic* order (SPO) according to

$$r_n = \left(\frac{1}{4} + n\right) \frac{2\pi}{Q_1} \quad (n = 1, 2, 3, \dots) \quad , \quad (5.5)$$

with n the number of the NN shell and the position Q_1 of the 1st halo in $S(Q)$ [Hau92]. This sequence of distances is assumed to originate from the influence of global resonances on structure formation [Hau92, Sti19]. In contrast to local electronic interactions between atomic pairs, the interacting entities considered for global effects are the entirety of all valence electrons involved (described by the FERMI sphere with diameter $2k_F$) as one subsystem and the atomic structure (described by the pseudo BRILLOUIN-zone with diameter Q_1) as another. The aim of a mutual adjustment of both subsystems is to achieve the "resonance condition" $2k_F = Q_1$, constituting the energetically most favourable state of the alloy in terms of the band-structure energy [Nag75, Haf87, Hau92, Now99, Sti07]. The sequence of distances described by Eq. (5.5) is assumed to originate from the FRIEDEL oscillations (with wavelength $2\pi/2k_F$) in the pair potential $\Phi(r)$ that govern especially the high- r part of $\Phi(r)$ [Hei70, Haf87], i.e. the distances related to the MRO.

The shell distances according to Eq. (5.5), using the measured $Q_1 = 2.59 \text{ \AA}^{-1}$ which is identical for all three alloys in the present case, are marked by small vertical lines in Fig. 5.10. A good agreement, especially for high distances (NN shell 4 and beyond), with the centroids of the NN shells (Fig. 5.10, vertical arrows) is obvious. This good agreement indicates the presence of global effects in the alloys studied here and at the same time corroborates the relationship [Car75] between the 1st halo in reciprocal space and the MRO in real space. Based on the resonance condition $2k_F = Q_1$ it could be conjectured that the diameter of the FERMI sphere $2k_F$ is the same for all three alloys. A high flexibility of the electronic subsystem was found in transition-metal (TM) bearing alloys with Al, mainly caused by TM-d-Al-p hybridisation effects [Tra05, Sti07, Sti19]. This may allow the electronic subsystem, i.e. $2k_F$, to adapt to better suit structural constraints of the SRO as well (e.g. related to distances of atomic pairs or sizes of clusters) in order to achieve an energetically more favourable state. As a result, considering the distances according to Eq. (5.5) and $Q_1 = 2k_F$, SRO and MRO would be coupled. This coupling may be seen by the positions of the centroids of the NN shells at low distances that can also be described by Eq. (5.5) reasonably well. However, a more

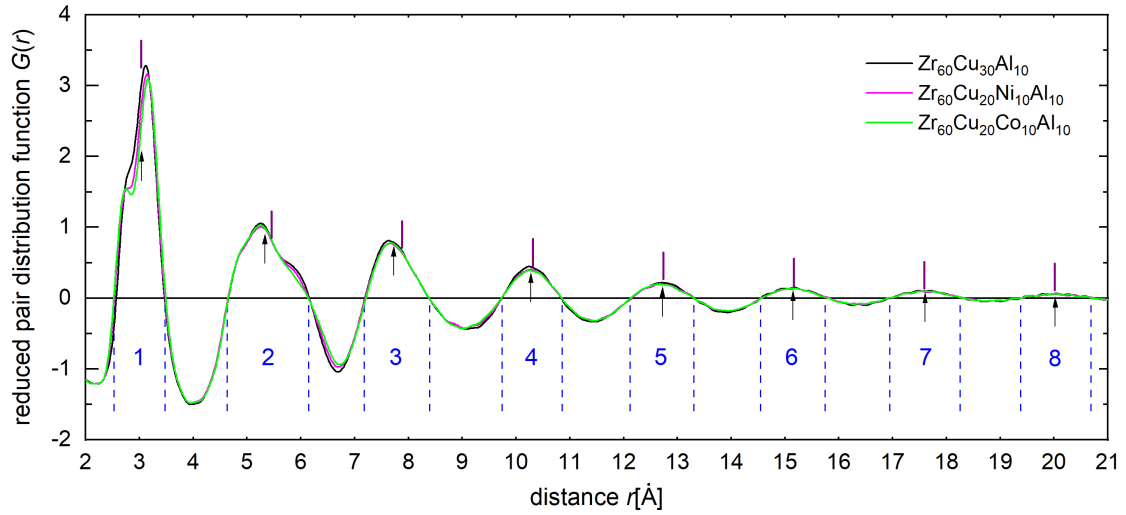


Figure 5.10: The reduced pair distribution functions $G(r)$ for the three alloys. The vertical bars indicate the positions of the SPO according to Eq. (5.5) and the arrows the positions of the centroids of the NN shells for $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ (those of the other two alloys are virtually at the same positions and are omitted for clarity).

detailed explanation of the "fine structure" (especially for the 1st NN shell) and the differences between the three alloys goes beyond the global description in its current form [Sti19]. Satisfying both the local and the global requirements may constitute the basis for another source of confusion. That the agreement of the positions of the centroids of the NN shells with the distances according to the global effects (Eq. (5.5)) is best for the 4th NN shell and beyond (Fig. 5.10) corroborates again the possible demarcation of two regions influenced by different (electronic) ordering effects located between the 3rd and 4th NN shell. A future more detailed study including a wider variety of (metallic) glasses is needed to determine the generality of this observation.

5.6.5 Electron-microscopic results

A FEI Titan G2 60–300 aberration-corrected transmission electron microscope (TEM) equipped with a high-brightness field-emission gun and a Gatan US1000 CCD camera was used to obtain high-resolution images as additional means to prove the amorphous nature of the three samples (Fig. 5.11). Additionally, high-angle annular dark-field (HAADF) imaging and energy-dispersive X-ray (EDX) spectroscopy was carried out to provide evidence for the homogeneous distribution of the alloying elements in the samples (Fig. 5.12).

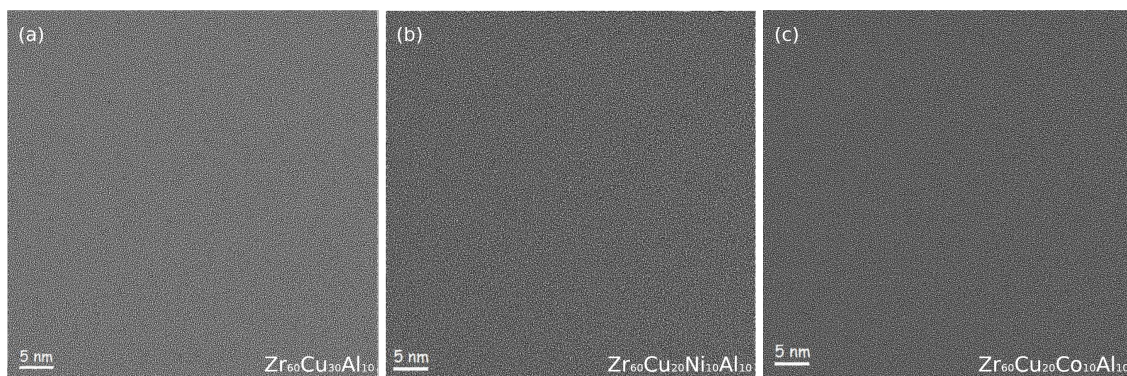


Figure 5.11: Transmission electron micrographs for the three samples corroborating their homogeneously amorphous structure.

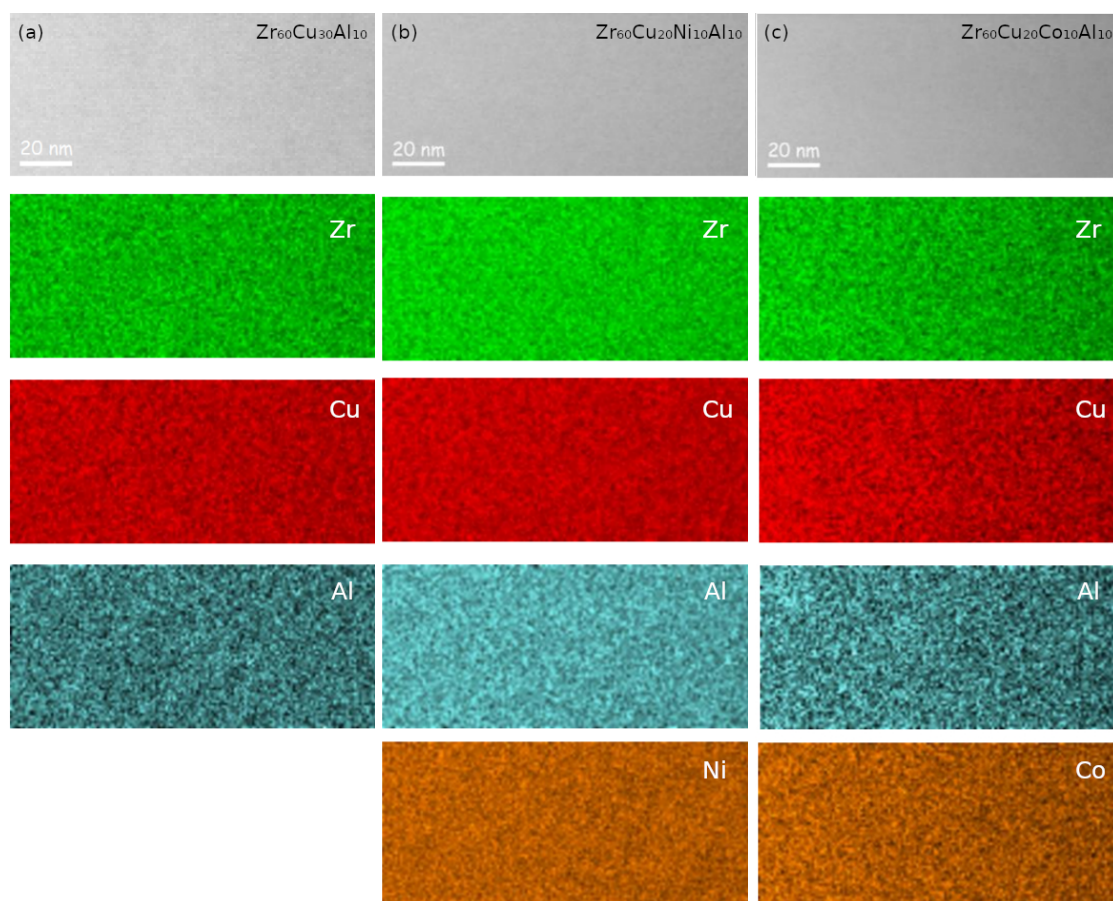


Figure 5.12: HAADF images (top) and EDX mappings for the elements in the three samples highlighting their homogeneity.

5.6.6 Properties of elemental pairs

Complementary to the data shown in Fig. 5.2 Tab. 5.2 lists for all relevant elemental pairs in the three alloys $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ (a), $\text{Zr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ (b) and $\text{Zr}_{60}\text{Cu}_{20}\text{Co}_{10}\text{Al}_{10}$ (c) the FABER-ZIMAN weights W_{ij} using Eq. (5.2) and the probability P_{ij} using Eq. (5.3).

	pair i - j	d_{at} [Å]	W_{ij}	P_{ij}	ΔH_{mix} [kJ/mol]
$\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$	Zr-Zr	3.16	0.498	0.36	0
	Cu-Zr	2.84	0.361	0.36	-23
	Cu-Cu	2.52	0.065	0.09	0
	Al-Zr	2.99	0.054	0.12	-44
	Al-Cu	2.67	0.02	0.06	-1
	Al-Al	2.82	0.001	0.01	0
$\text{Zr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$	Zr-Zr	3.16	0.501	0.36	0
	Cu-Zr	2.84	0.242	0.24	-23
	Cu-Cu	2.52	0.029	0.04	0
	Ni-Zr	2.84	0.117	0.12	-49
	Ni-Cu	2.52	0.028	0.04	+4
	Ni-Ni	2.52	0.007	0.01	0
	Al-Zr	2.99	0.054	0.12	-44
	Al-Cu	2.67	0.013	0.04	-1
	Al-Ni	2.67	0.006	0.02	-22
	Al-Al	2.82	0.001	0.01	0
$\text{Zr}_{60}\text{Cu}_{20}\text{Co}_{10}\text{Al}_{10}$	Zr-Zr	3.16	0.504	0.36	0
	Cu-Zr	2.84	0.244	0.24	-23
	Cu-Cu	2.52	0.029	0.04	0
	Co-Zr	2.83	0.113	0.12	-41
	Co-Cu	2.51	0.027	0.04	+6
	Co-Co	2.5	0.006	0.01	0
	Al-Zr	2.99	0.055	0.12	-44
	Al-Cu	2.67	0.013	0.04	-1
	Al-Co	2.66	0.006	0.02	-19
	Al-Al	2.82	0.001	0.01	0

Table 5.2: Interatomic distances d_{at} , enthalpies of mixing ΔH_{mix} , FABER-ZIMAN weights W_{ij} and probabilities for random contact P_{ij} for all atomic pairs in $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$, $\text{Zr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ and $\text{Zr}_{60}\text{Cu}_{20}\text{Co}_{10}\text{Al}_{10}$.

6 The pathway of $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$

A metallic glass is formed when a molten metallic alloy is cooled rapidly enough that crystallisation is avoided upon solidification. However, the way the atomic structure of the liquid converts to the structure of the glass is generally unknown, mainly because the acquisition of structural information in the undercooled liquid regime is most often hindered by the non-availability of sufficiently high cooling rates to avoid crystallisation. In the present study, using aerodynamic levitation, the Ni-free Ti-based alloy $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ was vitrified in-situ in a high-energy synchrotron X-ray beam while diffraction data was acquired during cooling from above the liquidus temperature T_l to well below the glass transition temperature T_g . The results indicate that the liquid's pathway to vitrification is divided into different non-crystalline regimes. The structural evolution below the melting temperature T_m deviates from that of the equilibrium liquid, pointing to a crossover in the evolution of the undercooled liquid's structure. The local order in the short (SRO) and medium range (MRO) increases rapidly as the undercooled liquid approaches T_g , below which the amorphous structure "freezes". The structural rearrangements in the undercooled liquid are found to be correlated with a rapid increase in viscosity of the metallic liquid upon cooling.

6.1 Introduction

Understanding the remarkable kinetic arrest in glass-forming liquids and the dramatic change in viscosity by 12 orders of magnitude between melting temperature T_m and glass transition temperature T_g is one of the most intriguing unresolved issues in materials research. Although the underlying microscopic origins remain unclear recent studies indicate a relation with the evolution of the atomic structure of the glass forming liquids [Lou11, Geo15, Mau14, Sto16]. Using ANGELL plots liquids can be categorised into strong or fragile [Ang88]. In a strong liquid viscosity (and relaxation time) exhibit ARRHENIUS-type behaviour as a function of temperature which implies a simple thermally activated behaviour for viscosity $\eta(T) = \eta_0 \exp\left(\frac{E_A}{k_B T}\right)$ where T is the temperature, η_0 a pre-exponential factor related to the viscosity at infinite temperature, k_B the BOLTZMANN constant and E_A an effective activation energy for viscous flow. Viscosity of a fragile liquid, however, exhibits a non-ARRHENIUS behaviour. The bigger the deviation from ARRHENIUS behaviour the more fragile the liquid is, with viscosity increasing rapidly as T_g is approached [Ito99]. In several

liquids, including water, silica, chalcogenides and glass-forming metals the evolution of viscosity with temperature suggests a crossover from a non-ARRHENIUS behaviour at high temperatures towards an ARRHENIUS type behaviour at lower temperatures (near T_g) known as fragile-to-strong transition (FST) [Sto16, Ito99, Sai01, Lad12, Ora15, Mal10, Web18]. A possible scenario is the existence of a phase transition in the liquid or the undercooled liquid state. However, experimental evidence for such a transition is scarce since the acquisition times of in-situ diffraction experiments for metallic liquids are typically bigger than the small quenching time of the undercooled melt between T_m and T_g necessary to achieve vitrification. Recent advances in containerless solidification methods such as electrostatic and aerodynamic levitation give new possibilities to study undercooled metallic liquids using synchrotron and neutron scattering techniques [Hen11, Mau11]. However, the acquisition of structural information in the whole temperature range from the liquid to the glassy state for metallic liquids still remains challenging since avoiding crystallisation during quenching requires cooling rates that are not easily achievable in in-situ diffraction experiments.

Because of their relatively simple structure, as compared to polymers and oxides, investigation of metallic undercooled liquids offer unique opportunities for improving the understanding of glass formation and glass transition. At the same time this aides the understanding of glassy metals and their processability in general since they possess an attractive combination of engineering properties such as high mechanical strength, high elastic strain, good corrosion resistance and excellent soft magnetic properties [Ino00, Gre09, Che11a, Gos18]. Furthermore, compared to their crystalline counterparts, metallic glasses exhibit lower YOUNG's, bulk and shear moduli reduced by about 10%, 6% and 30%, respectively [Gre09]. These characteristics make them attractive for a variety of applications including biomedical body implants, potentially diminishing the stress shielding effect that is often associated with conventional metallic implants [Cal13]. However, many of the bulk glass forming alloys contain toxic elements such as Be, Ni, V or Al [Cal13, Guo15a]. In this respect, Ti-based metallic glasses, free of toxic elements, are a particularly interesting class of alloys with high specific strength and good biocompatibility [Gos18, Cal13, Zhu07]. Among the Ni-free Ti-based metallic glasses $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ possesses the highest glass forming ability (GFA) with a critical diameter d_c higher than 10 mm [Zhu08]. Recent in-situ high-energy synchrotron diffraction experiments yielded results on the structural evolution of $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ metallic glass upon heating from room-temperature towards crystallisation including signs of a possible metallic glacial glass

phase [Zhe10, Kos20, She20]. Revealing the structural evolution during vitrification may offer new insights in the glass formation in Ti-based alloys leading to the design of biocompatible alloys with high bulk GFA and high functionality.

In this work aerodynamic levitation was used for in-situ probing the structure of $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ bulk glass forming alloy during undercooling and vitrification in a high-energy, high-flux synchrotron beam. The results indicate a rapid increase in structural evolution of the short (SRO) and medium range order (MRO) in the undercooled liquid, below T_m and above T_g , with the pathway of the liquid alloy to vitrification being divided into several distinct non-crystalline regimes.

6.2 Materials and methods

Spherical ingots about 2 mm in diameter of a quinary alloy with the nominal composition $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ (in at.%) were prepared by arc melting from high-purity raw materials (Ti: 99.9%, Zr: 99.8%, Cu: 99%, Pd: 99%, Sn: 99.8%) under Ar atmosphere. The ingots were remelted at least five times to ensure chemical homogeneity. The spheres of the alloy were then levitated by a high-purity Ar flow through an Al nozzle [Hen11] and melted using two CO_2 -laser beams. During the subsequent free cooling the alloy's structure was investigated in-situ by high-energy X-ray diffraction in transmission mode carried out at beamline ID-15 of the European Synchrotron Radiation Facility (ESRF) in the temperature range between 1473 K (well above $T_l = 1176$ K (Tab. 6.1)) and 487 K (well below the caloric glass transition temperature $T_g = 689$ K (Tab. 6.1)). The wavelength of the incident monochromatic beam was $\lambda_i = 0.1245$ Å ($E_i = 100$ keV). X-ray diffraction spectra were continuously recorded by a Perkin-Elmer two-dimensional flat-panel detector with a time resolution of 100 ms as function of the scattering vector $\vec{Q}$ (modulus $Q = |\vec{Q}|$ up to 25 Å⁻¹), where $Q = \frac{4\pi}{\lambda_i} \sin \theta$ and 2θ the diffraction angle. Two optical pyrometers were used to measure the temperature T . Values below 620 K were calculated assuming a continued exponential temperature drop (Fig. 6.1). The average cooling rate during vitrification was of the order of 80 K/s. The temperature calibration was verified using T_m and the crystallisation temperature T_x of the alloy (Tab. 6.1). The accuracy of the temperature values was estimated to be around ± 12 K above 900 K and better than ± 7 K below 900 K. The high achievable cooling rates set the present setup apart from other containerless levitation techniques like electromagnetic [Hol05] or electrostatic levitation [Mau11] used in similar studies (cf. Ch. 2). This allows for the in-situ vitrification of metallic melts, like

T_g [K]	T_X [K]	T_m [K]	T_l [K]	ΔT_X [K]	T_{rg}	reference
689	739	1126	1187	50	0.58	[Zhu08]
682	740	-	1164	58	0.59	[Cal12]
695	743	-	-	48	-	[Zhe10]
688	730	-	-	42	-	[Yam14]
689	738	1126	1176	50	-	average

Table 6.1: Thermophysical parameters of $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ acquired by calorimetric methods taken from literature (average values, the reduced glass-transition temperature $T_{rg} = T_g/T_l$ and undercooled liquid region $\Delta T_X = T_X - T_g$ were calculated from these).

$\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$, that have a comparably low GFA. Minor non-amorphous features of unknown origin been observed in a limited number of spectra below ≈ 950 K which were exempted from further analysis. For each temperature T the diffraction images were azimuthally integrated after corrections for polarisation and dark currents using the FIT2D software [Ham96] yielding the integrated diffraction intensities $I(Q, T)$. After corrections for sample absorption, fluorescence, COMPTON scattering, LAUE diffuse scattering, background contribution and normalisation to the atomic X-ray form factor the total structure factors $S(Q, T)$ were obtained with the help of the PDFgetX3 software package [Juh13]. For structural analysis in real space PDFgetX3 furthermore performs the FOURIER transformation [Ega03] of $S(Q, T)$ yielding the reduced pair distribution function

$$G(r) = \frac{2}{\pi} \int_0^{Q_{\max}} Q[S(Q) - 1] \sin(Qr) dQ \quad (6.1)$$

with an upper integration limit of $Q_{\max} = 15 \text{ \AA}^{-1}$ in the present case.

6.3 Results

Figure 6.1 shows the temperature-time profile $T(t)$ of the $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ sample during cooling. The absence of recalescence phenomena indicates that crystallisation was avoided during solidification leading to the formation of a metallic glass. Small temperature fluctuations are related to noise of the pyrometric measurements as well as to slight oscillations of the sample position and become more visible at lower temperatures when the cooling rate is reduced.

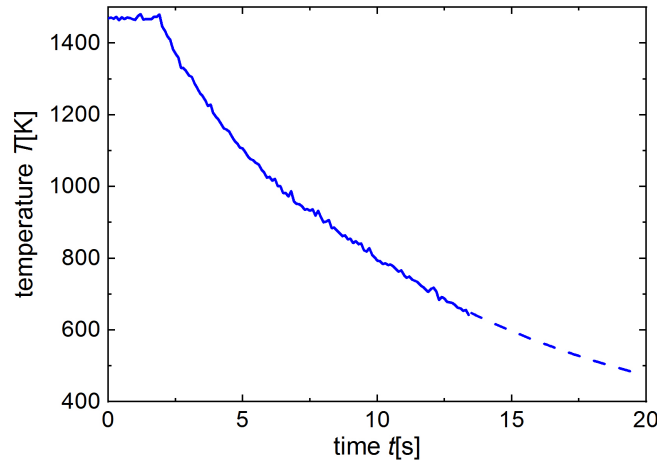


Figure 6.1: Temperature-time profile $T(t)$ of the $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ sample during free cooling in the aerodynamic levitation setup while in the synchrotron beam (the temperatures below 620 K (dashed) were calculated assuming exponential behaviour). The absence of recalescence indicates successful vitrification. Small temperature fluctuations are related to experimental uncertainties.

Figure 6.2 shows a set of X-ray diffraction spectra in the form of the structure factor $S(Q, T)$ recorded during in-situ vitrification. The structure factor $S(Q, T)$ is observed to evolve with decreasing temperature indicating a structural evolution during cooling that leads to a more ordered structure. In particular, the shift of the maximum $Q_1(T)$ of the first peak, corresponding to the first diffuse diffraction halo, to higher Q with decreasing temperature T is consistent with the macroscopic volume contraction during cooling [Yav05]. In addition, the increase of $S(Q_1(T), T)$ and the splitting of the second peak, corresponding to second diffuse diffraction halo, centred at around $5.2 \text{ \AA}^{-1}$ observed during cooling clearly indicate an increasingly ordered structure at lower temperatures. This splitting is a frequent observation in metallic glasses and was discussed in relation to the presence of certain cluster-types [Lee08]. It is interesting to note that is mainly the low- Q feature of the second halo that is changing during cooling while the shoulder at the high- Q side remains almost unchanged over the complete measured T -range indicating that the responsible structure is already present at high T in the equilibrium liquid. For a better visualisation of the structural changes in reciprocal space the reader is referred to Movie 1 of the Supplementary Material (Sec. 6.6.3).

In order to follow the structural evolution during cooling several structural metrics derived from the first peak in $S(Q, T)$ were analysed over the complete range of temperatures studied (Fig. 6.3). Figure 6.3a shows the position $Q_1(T)$ of the maximum (black open pentagons) as well as the positions of the centroids $Q_{1,c}(T)$ (green open pentagons).

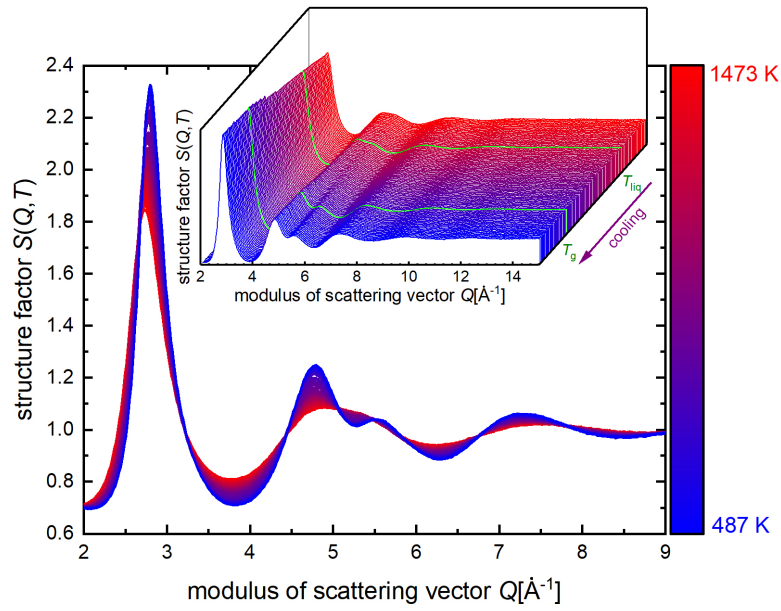


Figure 6.2: The evolution of the structure factor $S(Q, T)$ of $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ during free cooling from 1473 K to 487 K. The inset illustrates the evolution of $S(Q, T)$ with temperature in form of a 3D representation. See also Supplementary Movie 1 (Sec. 6.6.3).

The latter, also used for the analysis of other peaks throughout this study, provides the opportunity to treat split peaks as well as non-split peaks in the same way. Furthermore, the height $S(Q_1(T), T)$ (Fig. 6.3c) and the full width at half maximum (FWHM) $\Delta Q_1(T)$ (Fig. 6.3d) are shown. While the latter two quantities are directly derived from the experimental data (grey shaded area in inset of Fig. 6.3a) $Q_1(T)$ is obtained by fitting GAUSS functions. It can be seen that above T_l (in the equilibrium liquid) and below T_g (in the glassy state) $Q_1(T)$ follows quasi-linear relations with temperature. Quasi-linear relations of $Q_1(T)$ with temperature were previously described for several glass-forming alloys in their liquid and glassy states [Sto16,Zhe10,Yav05,Geo12,Bed11,Geo11,Mat03]. Interestingly, as $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ is cooled below T_m $Q_1(T)$ deflects from the linear trend observed for the equilibrium liquid state indicating that the structural ordering of the undercooled liquid does not follow that in the equilibrium liquid state. The deflection indicates an acceleration of structural ordering similar to the observations for $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ [Geo15]. Also similar to $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$, another deflection point can be observed upon further cooling near the caloric glass transition temperature T_g . Interestingly $Q_{1,c}(T)$ does not show a change in slope close to T_g while $Q_1(T)$ does. Using both quantities a measure of asymmetry of the first peak in $S(Q, T)$ can be defined according to $\Lambda(T) = \frac{Q_{1,c}(T) - Q_1(T)}{Q_1(T)}$. A pronounced kink in $\Lambda(T)$ at a temperature

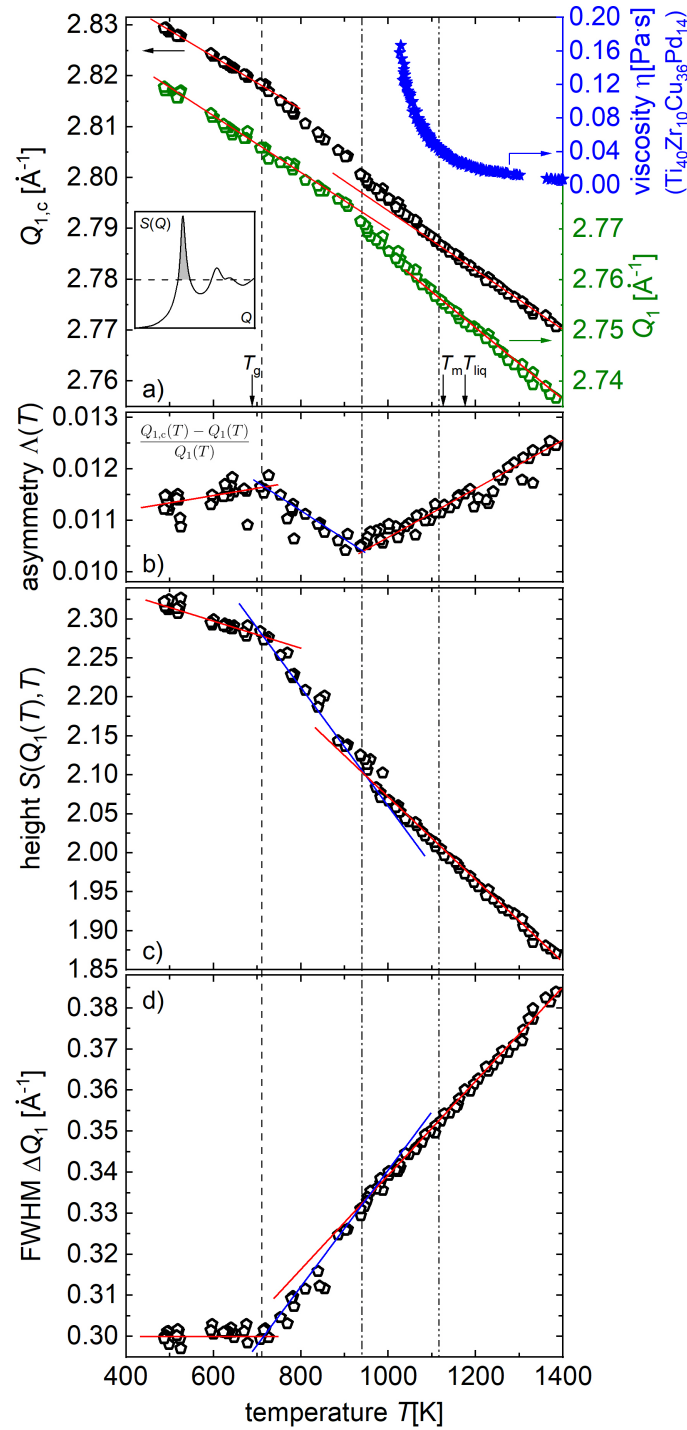


Figure 6.3: Structural metrics of $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ in reciprocal space during free cooling derived from the first peak (corresponding to the first halo) of the structure factor $S(Q, T)$ as shown in the inset of a). **a)** positions of the maximum $Q_1(T)$ (black pentagons) and the centroid $Q_{1,c}(T)$ (green pentagons) as well as literature data [Mau14] for the viscosity $\eta(T)$ of the very similar alloy $\text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{30}\text{Pd}_{20}$ ($T_g = 687$ K [Zhu07], $T_l = 1279$ K [Gan14]) (blue stars), **b)** the peak asymmetry $\Lambda(T)$, **c)** the height $S(Q_1(T), T)$ and **d)** the FWHM $\Delta Q_1(T)$. The vertical lines indicate temperatures where changes in the behaviour of the metrics occur. All other lines are guides for the eye. The arrows in a) indicate the average values of T_g , T_m and T_l of $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ given in Tab. 6.1.

$T_s \approx 940 \text{ K} \approx 1.36T_g$ between T_m and T_g is visible (Fig. 6.3b) suggesting a possible liquid-liquid crossover (LLC). The existence of T_s hints at three (high-temperature liquid (HTL) for $T \gtrsim T_s$; low-temperature liquid (LTL) for $T_s \gtrsim T \gtrsim T_g$; glass for $T_g \gtrsim T$) distinct non-crystalline structural regimes during vitrification which bears resemblance to ANGELL's three domains of interest for non-crystallising liquids [Ang08]. Interestingly, also the position of the centroid $Q_{1,c}(T)$, the height $S(Q_1(T), T)$ and $\Delta Q_1(T)$ exhibit a change of slope at T_s (Fig. 6.3a,c,d). The linear increase of $S(Q_1(T), T)$ together with the almost constant $\Delta Q_1(T)$ below T_g indicates that the T -dependent behaviour is now dominated by the DEBYE-WALLER factor only, i.e. structural changes have ceased to dominate and changes of the position of the centroid can mainly be attributed to normal thermal expansion only.

The reduced pair distribution function $G(r, T)$ (Fig. 6.4a and Supplementary Movie 2 under Sec. 6.6.3) evolves noticeably with decreasing T reflecting the changes towards vitrification as well. The first peak of $G(r, T)$, corresponding to the first nearest-neighbour (NN) shell, changes only very slightly in position, but increases in intensity and decreases in width indicating a narrower distribution of interatomic distances as well as a gradual increase in the number of atoms in the first NN shell. For the remainder of this chapter the term NN shell is used for regions with $G(r, T) > 0$ (Sec. 5). The NN shells are numbered consecutively ($n = 1, 2, 3, \dots$) with increasing distance from the central atom at $r = 0 \text{ \AA}$. The regions with $G(r, T) < 0$ (for $r > r_c$) are denoted as anti-shells (see inset of Fig. 6.4). The second NN shell also evolves and a shoulder gradually develops on the high- r side ($r_{2h} \approx 5.4 \text{ \AA}$) resulting in a partial splitting of the peak at lower temperatures. A split second NN shell is considered a characteristic difference between the glassy and the liquid state attributed to the enhancement of chemical and topological MRO [Vol97]. The NN shells with $n \geq 3$ shift to smaller interatomic distances r and increase in height during cooling. The presence of clearly distinguishable NN shells in $G(r, T)$ extends up to about $r \approx 18 \text{ \AA}$ at higher temperatures (liquid state), whereas at lower temperatures (glassy state) NN shells can clearly be observed up to $r \approx 25 \text{ \AA}$ (inset of Fig. 6.4a) indicating an extension of the MRO along the pathway from the liquid to the glassy state. This is consistent with the increasing coherence length $\frac{2\pi}{\Delta Q_1(T)}$ (c.f. decreasing $\Delta Q_1(T)$ during cooling in Fig. 6.3d). It is important to note that, in addition to the increasing height of $G(r, T)$ for the NN shells, the local minima of $G(r, T)$ (anti-shells) become more pronounced as well during cooling indicating a migration of atoms from anti-shells to shells. This migration has been linked to the cluster evolution during glass formation leading to a distinct increase of the local

ordering [Geo15]. The visibility of the evolution of $G(r, T)$ can be enhanced using $\Delta G(r, T) = G(r, T) - G(r, 1473 \text{ K})$ highlighting the changes in $G(r, T)$ compared to that of the highest measured temperature (Fig. 6.4b). The local maxima of $\Delta G(r, T)$ correspond to the increase of atomic population in the NN shells, whereas negative $\Delta G(r, T)$ correspond to the decrease of the number of atoms in the anti-shells. Especially the visibility of the increasingly split second NN shell in $G(r, T)$ (Fig. 6.4a) that develops during cooling is underlined by the two maxima at $r \approx 4.5 \text{ \AA}$ and $r \approx 5.5 \text{ \AA}$ in $\Delta G(r, T)$ (Fig. 6.4b). Furthermore, $\Delta G(r, T)$ emphasises that the evolution of $G(r, T)$

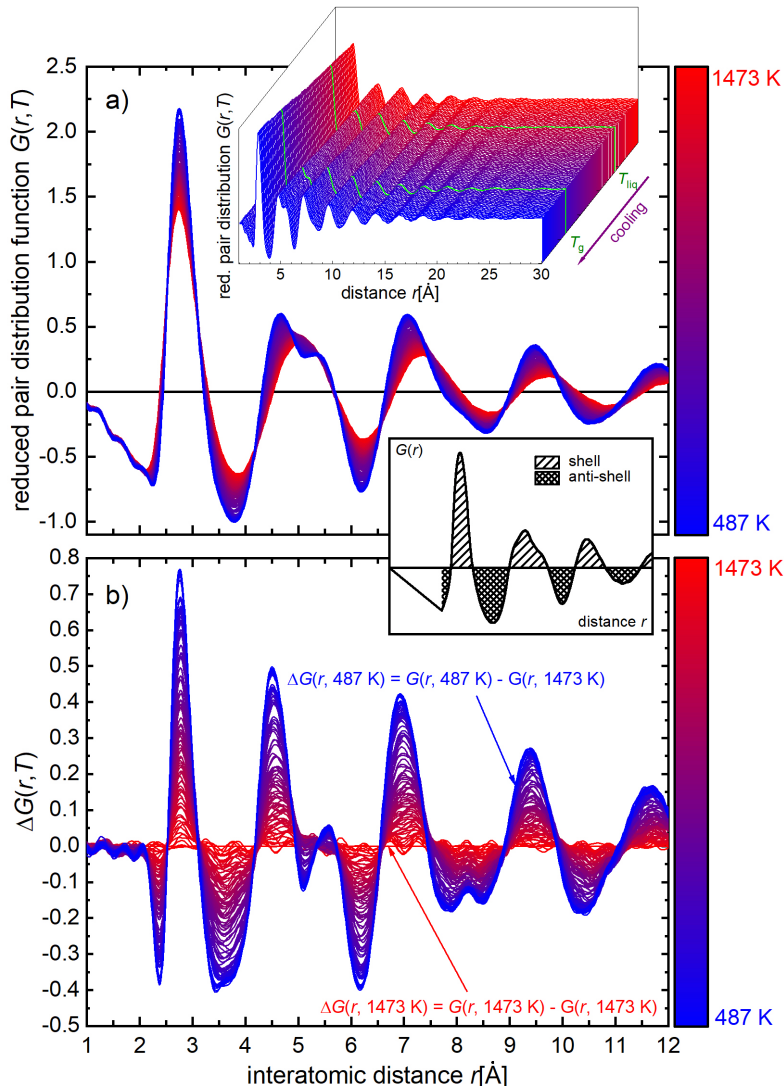


Figure 6.4: (a) The evolution of reduced pair distribution function $G(r, T)$ during cooling from 1473 K to 487 K (cf. also Supplementary Movie 2 under Sec. 6.6.3). (b) $\Delta G(r, T) = G(r, T) - G(r, 1473 \text{ K})$ functions showing the increasing difference between $G(r, T)$ at various temperatures during cooling and the one at 1473 K. Inset: $G(r, 478 \text{ K})$ to illustrate the shell/anti-shell concept (see text). See also Movie 2 in the Supplementary Material (Sec. 6.6.3).

with decreasing T extends up to high r indicating a significantly enhancement of SRO as well as MRO along the alloy's pathway to vitrification. Integrating $\Delta G(r, T)$ for $\Delta G(r, T) > 0$ (purple region in inset of Fig. 6.5d) yields the same value for each T (purple dots in Fig. 6.5d) as the absolute values of the integral of $\Delta G(r, T)$ for $\Delta G(r, T) < 0$ (green region in inset of Fig. 6.5d and green dots in Fig. 6.5d). This does not only corroborate the mentioned migration but also indicates an apparent acceleration of this effect in the undercooled region below T_m . The changes below T_g can be attributed to the DEBYE-WALLER factor. Figure 6.5a,b,c shows metrics derived for the first shell obtained in analogy to the first halo in reciprocal space. As in reciprocal space, in addition to the positions of the maximum $r_1(T)$ (black open dots in Fig. 6.5a) the positions $r_{1,c}(T)$ of the centroids (green open pentagons) are shown to characterise the NN shell distances. The use of centroids provides the possibility to obtain a measure for the position also for NN shells with high n where a proper fit is hampered by termination ripples. Both $r_1(T)$ and $r_{1,c}(T)$ show an apparent negative thermal expansion in the liquid and undercooled liquid regions which will be discussed further down. Below T_g , as expected, a positive thermal expansion can be observed. The height $G(r_1, T)$ and the FWHM $\Delta r_1(T)$ show a quasilinear behaviour over the complete T -range. The metrics for the first NN shell in real space presented in Fig. 6.5a-c do not reflect the changes in behaviour between T_l and T_g , i.e. deflection points near T_m or T_s , as clearly as in reciprocal space. This may partially be attributable to the bigger scatter of the data. On the other hand, the values for the integrated areas of $\Delta G(r, T)$ (Fig. 6.5d), representing the combined effect of all NN shells of a wide range of distances, reflect the accelerated ordering below T_m very well which resembles the behaviour known from $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ [Geo15].

6.4 Discussion

Various models have been proposed to describe the structure of metallic glasses since the 1960s, including BERNAL's dense random packing model of hard spheres [Ber60], GASKELL's stereochemically designed local structure units [Gas78] as well as the efficient space filling scheme of solute-centred clusters by MIRACLE [Mir04]. The influence of global interactions between the valence electrons and atoms of an alloy has also been shown to have an influence on structure formation in metallic glasses [Nag75, Hau92, Sti19, Don19]. It is now widely accepted that the main structural motif of metallic glasses are atomic clusters that give rise to SRO and MRO, but lack the

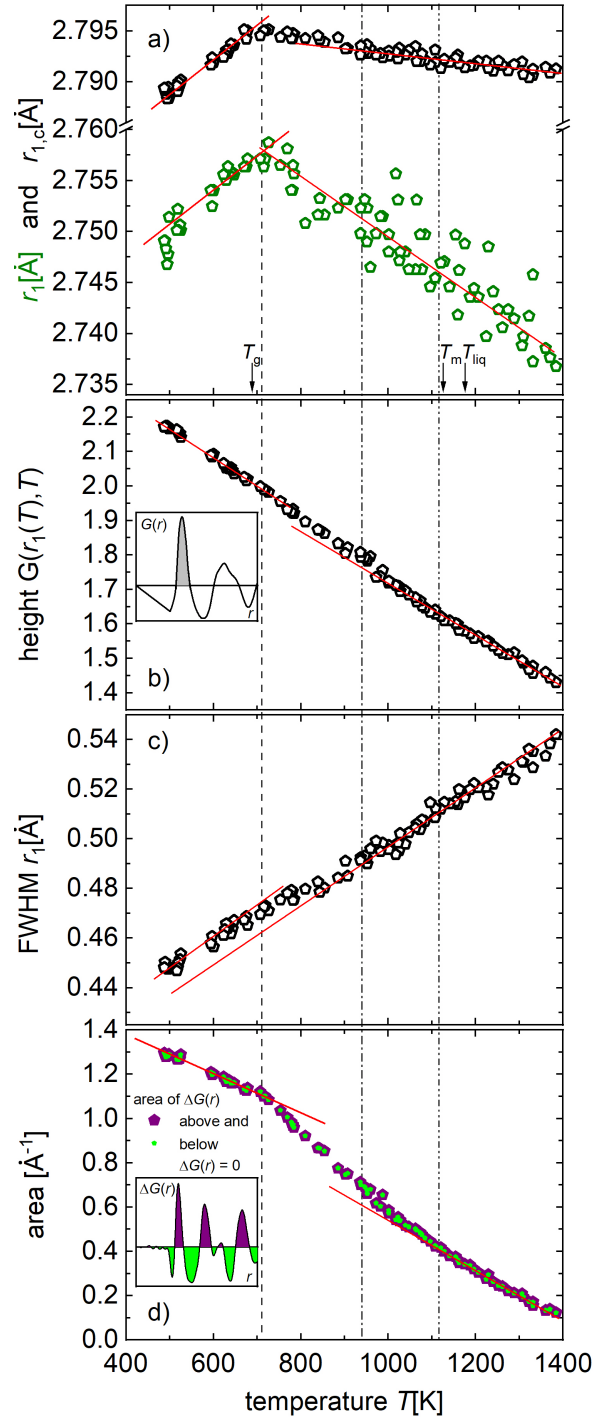


Figure 6.5: Structural metrics of $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ in real space during free cooling derived from the first peak (first NN shell, $n = 1$) of the reduced pair distribution $G(r, T)$ as shown in the inset of b). **a)** position of the maximum r_1 and the centroid $r_{1,c}(T)$, **b)** the peak height $G(r_{1,c}(T), T)$, **c)** its full width at half maximum (FWHM) and **d)** the integrated area of $\Delta G(r, T)$ below and above the baseline $\Delta G(r, T) = 0$. Lines and arrows as in Fig. 6.3.

long-range order of crystalline materials. For many glassy alloys, specific local structural motifs have been identified by simulations and experiments [She06, Geo09, Geo10], including the direct observation of interconnected atomic polyhedra by nano-beam electron diffraction [Hir13]. The local atomic packing order as well as topological arrangements of clusters are important features that enable not only the description of the structure of metallic glasses but also provide insights about structure-property relationships. The formation of various local atomic clusters is controlled by both atomic size ratio and chemical bonding. It is also widely accepted that local icosahedral and icosahedral-like order prevails in many metallic-glass forming alloys [Che08, Hir13, Ant11]. On the other hand, the local order in metallic liquids is less pronounced than in the glassy state as shown in Fig. 6.2 and Fig. 6.4. Although the prevailing type of polyhedra in the local atomic symmetry of Ti-based BMGs has not been unambiguously established yet, the formation of quasicrystals with icosahedral symmetry has been reported for some Ti-based alloys [Guo15a, Lee08, Kim04]. According to the hard-sphere packing model, it requires an atomic size ratio $R_{A/B} = r_A/r_B = 0.902$ (r_A and r_B being the radii of centre and first NN shell atoms, respectively) to form an ideal icosahedral cluster around a central atom [Mir03]. In the case of $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ $R_{\text{Ti}/\text{Cu}}$ and $R_{\text{Cu}/\text{Ti}}$ are 1.127 and 0.887, respectively [Mir10]. Thus, around Ti or Cu, which are the most abundant elements in this quinary alloy, icosahedral packing might not be favourable. However, especially the atomic size ratio $R_{\text{Ti}/\text{Zr}}$ (0.899) and to a somewhat lesser extent $R_{\text{Ti}/\text{Sn}}$ (0.916) [Mir10] are closer to the ideal value of 0.902 and therefore the additional elements Zr and Sn may facilitate the formation of local icosahedral like symmetry in the cooling liquid. This could also be the reason underlying the high GFA of Ti-Zr-Cu-Pd-Sn-alloys as compared to other Ti-based alloys. Nonetheless, this must be further explored in order to verify the developing local symmetry during cooling. The increase of the atomic populations in the NN shells with decreasing temperature as inferred from Fig. 6.4a and b could be the result of i) the rearrangement of atoms previously located in anti-shell regions (local minima in Fig. 6.4a) into atomic clusters with local symmetry as the temperature decreases, ii) the reorganisation of atomic clusters existing at higher temperatures into clusters with higher packing density at lower temperatures or iii) a combination of both mechanisms. Recent results from molecular dynamics simulations in Zr-based metallic glasses support the idea that the population of atomic clusters with icosahedral local symmetry increases with higher rates than other clusters as the liquid metal is cooled between T_l and T_g [Che08, Geo15]. With the exception of Cu-Sn (and Ti-Zr) all the atomic pairs of $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$

pair $i-j$	d_{at} [Å]	W_{ij}	P_{ij}	ΔH_{mix} [kJ/mol]
Ti-Ti	2.84	0.085	0.160	0
Cu-Ti	2.68	0.192	0.272	-9
Cu-Cu	2.52	0.107	0.116	0
Pd-Ti	2.84	0.125	0.112	-65
Pd-Cu	2.68	0.140	0.095	-14
Pd-Pd	2.84	0.046	0.020	0
Zr-Ti	3.00	0.078	0.080	0
Zr-Cu	2.84	0.087	0.068	-23
Zr-Pd	3.00	0.057	0.028	-91
Zr-Zr	3.16	0.018	0.010	0
Sn-Ti	2.97	0.019	0.016	-21
Sn-Cu	2.81	0.022	0.014	7
Sn-Pd	2.97	0.014	0.006	-34
Sn-Zr	3.13	0.009	0.004	-43
Sn-Sn	3.10	0.001	0.001	0

Table 6.2: Interatomic distances d_{at} , enthalpies of mixing ΔH_{mix} [Tak05] (according to MIEDEMA's model), FABER-ZIMAN weights W_{ij} and probabilities for random contact P_{ij} for all atomic pairs in $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$.

have negative heats of mixing (Tab. 6.2) which supports good GFA according to one of the main (empirical) criteria suggested by INOUE [Ino00]. In a simplistic approach, glass formation can be described as the rapid cooling of a liquid structure down to the glass transition temperature T_g below which it "freezes" to become an amorphous solid. However, below T_m , crystalline phases are thermodynamically favoured and a remarkable slowdown of the kinetics in the undercooled liquid is necessary in order to suppress crystal nucleation and growth during solidification. This kinetic arrest is manifested by a significant increase of viscosity in the undercooled liquid whose origins remain understood only poorly to the present day [Ito99, Ang00]. To relate the evolution of the atomic structure to the evolution of the viscosity Fig. 6.3a shows literature data [Mau14] for $\eta(T)$ of the very similar Ti-based alloy $\text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{30}\text{Pd}_{20}$ ($T_g = 687$ K [Zhu07] and $T_l = 1279$ K [Gan14]) as such data for $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ itself was not available. Interestingly, the deviation of $Q_1(T)$ from linear behaviour below T_m occurs in the same temperature range as a sharp increase in viscosity by 1.5 orders of magnitude takes place. This observation strongly supports the idea that the sharp increase of viscosity, the kinetic arrest as well as the structural changes in the

undercooled liquids may have the same origin [Lou11, Geo15, Mau14]. The deflection and change of slope observed in the structural metrics as function of T beginning just below T_m (Fig. 6.3a) point to a structural crossover in the undercooled liquid below which atomic rearrangements appear to be accelerated compared to the undercooled and equilibrium liquid at higher T . The underlying origins of this crossover in the behaviour of undercooled liquids have been discussed before in terms of a liquid-liquid transition [Lad12, Mal10, Tan10]. The experimental investigation of such a transition is often hindered by crystallisation in the undercooled liquids. The results presented here support the scenario of a structural crossover below T_m . However, anomalies like the change in slope of e.g. $Q_1(T)$ (Fig. 6.3a) with decreasing temperature without an abrupt change in $Q_1(T)$ point to a second order transition occurring below T_m and above T_g [Fon13, Geo15], rather than a first order transition as observed in other glass forming metallic liquids [Sto16]. The scenario of a structural crossover originating from a possible second order transition is also supported by recent observations in other glass forming metallic liquids in the Zr-Cu-Al and Pd-Cu-Ni-P alloy systems, respectively [Lou11, Geo15]. Recent results for Zr-based metallic glasses point to a marked cooling-rate dependence of the observability of such crossovers in structural metrics [Hec18, Jon19]. Distinct kinks, pointing to abrupt changes, become smeared-out with increasing cooling rates [Jon19]. The same high cooling rates necessary to achieve in-situ vitrification may therefore prevent a better visibility of the hinted structural crossovers. Molecular dynamics simulations of $\text{Cu}_{64}\text{Zr}_{36}$ point to the occurrence of a set of characteristic temperatures in metallic liquids [Sok16]. While at a temperature $T_A \approx 2T_g$ cooperativity commences due to interconnecting clusters a second characteristic temperature $T_D \approx 1.4T_g$ has been associated to the beginning of glassy dynamics with an abrupt drop of the diffusion coefficients of the components and the occurrence of macroscopically domains of connected clusters which then percolates the complete simulated volume towards T_g [Sok16]. In the present case, using the caloric glass transition temperature (Tab. 6.1), these estimations yield $T_D \approx 965$ K and $T_A \approx 1378$ K, respectively. While T_A is too close to the highest measured temperature of the present study in order to be able to determine a change in structural behaviour there T_D is very close to the characteristic temperature T_s discussed above. Although it has to be kept in mind that the cluster types in the present case may differ from those observed in the simulated sample from ref. Sok16 changes in structural behaviour at $T \approx 1 \dots 1.5T_g$ have recently been found experimentally in other alloys like $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ (Vitrelloy 1) [Wei13], $\text{Zr}_{57}\text{Nb}_5\text{Al}_{10}\text{Cu}_{15.4}\text{Ni}_{12.6}$ (Vitrelloy

106) [Lan16] or $\text{Zr}_{58.5}\text{Cu}_{15.6}\text{Ni}_{12.8}\text{Al}_{10.3}\text{Nb}_{2.8}$ (Vitreloy 106a) [Sto16]. A more general analysis of about 100 glass-forming liquids indicated that FSTs occur at $T \approx 1.36T_g$ [Zho15] in close agreement with T_g found here. Further analysis pointing to an FST at T_g is presented in Sec. 6.6.2 following a method described in the literature [Wei15, Sto16]. It is also interesting to note that a dynamical crossover in the same temperature range is predicted by the mode-coupling theory and shown to exist in a wide variety of glass-forming materials [Nov03, Oss06, Dre19]. As mentioned above an apparent negative

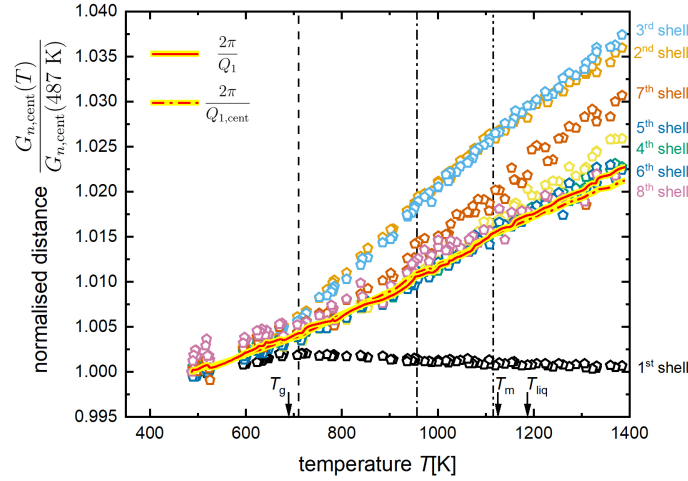


Figure 6.6: Positions of the centroids of the first 8 NN shells normalised to their respective values at $T = 487$ K. Additionally, again normalised to their respective values at $T = 487$ K, $2\pi/Q_1(T)$ (solid red line on yellow background) and $2\pi/Q_{1,c}(T)$ (dash-dotted red line on yellow background) are plotted for comparison. Other lines and arrows as in Fig. 6.3.

thermal expansion can be observed for the first NN shell above T_g . This phenomenon has been reported before in the literature and different possible explanations have been put forward [Lou13, Din14a, Din17, Gan18a]. Figure 6.6 shows the positions of the centroids up to the eighth NN shell ($n = 8$) normalised to the respective value at 487 K. The different behaviour of the first NN shell in comparison with all other NN shells can clearly be seen. Interestingly, for $n = 2$ and $n = 3$ the shell distances behave very similar to each other, but show a much stronger thermal expansion than for $n > 3$. Except for $n = 7$ all other NN shells behave virtually alike within the experimental uncertainty. The existence of two structural regions with a demarcation between $n = 3$ and $n = 4$ was proposed for glassy $\text{Zr}_{60}\text{Cu}_{20}(\text{Cu}, \text{Ni}, \text{Co})_{10}\text{Al}_{10}$ alloys (Sec. 5) where a possible explanation was given in terms of the influence of the electronic structure. The availability of T -dependent measurements in the present case enables a more detailed study of this behaviour. As for the different behaviour for $n = 7$ it is currently not clear whether this is a structural feature or merely an experimental artefact. Also

shown in Fig. 6.6 are $\frac{2\pi}{Q_1(T)}$ (solid red line on yellow background) and $\frac{2\pi}{Q_{1,c}(T)}$ (dash-dotted red line on yellow background), respectively. A good agreement for $n \geq 4$ (again with the exception of $n = 7$) is obvious. These observations corroborate the early conjecture by CARGILL [Car75] according to which the first maximum in $S(Q)$ represents the MRO (but not SRO) from a certain distance onwards [Car75, Ma09]. Since according to YAVARI et al. the macroscopic thermal expansion is correlated with $Q_1(T)$ [Yav05] the present results indicate that above T_g only the behaviour for relatively high distances of the MRO, but not that for smaller distances or even that for the SRO ($n = 1$), can be used to evaluate thermal expansion in real space. A similar behaviour was described for glassy $\text{Cu}_{65}\text{Zr}_{35}$ [Mat13] as well as liquid and glassy $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ [Mat03] where T -dependent changes of the distances of the individual NN shells were compared to the macroscopic thermal expansion obtained by dilatometry. Together with the present results this hints that the link between macroscopic thermal expansion and $Q_1(T)$ as suggested by YAVARI et al. [Yav05] also holds true for the undercooled liquid range. Furthermore, this provides the opportunity to separate structural changes from the thermal expansion in the liquid and undercooled liquid regimes. Below T_g no structural changes take place any more and all NN shells behave roughly in the same way showing mainly the effects of thermal expansion (Fig. 6.6) corroborating the findings in reciprocal space (Fig. 6.3), especially the constant FWHM of the first peak in $S(Q, T)$ below T_g (Fig. 6.3d). In general, it can be assumed that SRO and MRO are affected differently during cooling towards vitrification. Structural changes beyond a usual linear thermal expansion manifest themselves mainly in the first three NN shells which is why this region should not be used to describe thermal expansion of metallic glasses as discussed above. If the correlation between $Q_1(T)$ and the high- r part of $G(r)$ holds, changes in behaviour, e.g. at T_s , observed for the first halo in reciprocal space should also be visible in the real space shell distances for higher n . Furthermore, due to the possibility of different effects on different length scales, changes in behaviour of the temperature-dependent distances (and other metrics) can be expected at different characteristic temperatures (T_s , T_m). However, the scatter of the data prevents a more detailed analysis based on the present data. It is interesting to note that the positions of the maxima $r_n(T)$ as well as those of their centroids $r_{n,c}(T)$ for the peaks in $G(r, T)$ agree with each other for $n \geq 4$ (not shown) which seems to indicate that a transition from local to global mechanisms of structure formation of the real space structure has taken place between $n = 3$ and $n = 4$: the influence of the individual local properties of the elemental species (i.e. mainly their radii) has ceased to dominate

and is more and more replaced by a global statistical distribution irrespective of the particular element underlining the abovementioned reason for the demarcation put forward in Sec. 5. Indeed, Q_1 is also connected to a description of the structure of metallic glasses in terms of global interactions between atomic and electronic structure neglecting the differences between the individual species [Hau92, Sti19]. In this model the energetically optimal state for an alloy is reached when the "resonance condition" $Q_1 = 2k_F$ is fulfilled, i.e. the pseudo BRILLOUIN-zone (diameter Q_1) coincides with the FERMI-sphere (diameter $2k_F$) [Nag75, Hau92, Now99]. In this case a sequence of distances, known as spherical periodic order (SPO), for the consecutive NN shells from the central atom according to $r_n = \left(\frac{1}{4} + n\right) \frac{2\pi}{Q_1}$ [Hau92] is expected. This relation would suggest a parallel behaviour of *all* NN shells depending only on Q_1 , which, at least in the present case, is clearly contradicted by the results presented in Fig. 6.6. The global description, therefore, seems to be valid for the higher distances within the MRO only ($n \geq 4$) where the influence of local effects between the atoms is negligible as discussed above. In this respect a description of the real-space structure of metallic glasses based on global electronic interactions, especially by invoking the SPO, has to be reconsidered for small distances ($n \leq 3$). It is interesting to note that a mean valence $Z \approx 1.5$, which has been discussed for other metallic glasses as well [Sti19], seems to be an appropriate value to obtain a FERMI-sphere diameter $2k_F$ to be compatible with Q_1 or $Q_{1,c}$, respectively, observed in the present case (cf. Supplementary Section 6.6.1 for details of the according calculations). In a sense the measurement of the temperature-dependent shell distances $r_n(T)$, especially in the undercooled region, acts as a powerful tool to probe the correlations between the different regions in real (SRO and MRO, respectively) and reciprocal space (halo 1) and helps to clarify the role of global effects in metallic glasses: NN shells for $n \leq 3$ seem to be strongly influenced by local effects which are also responsible for the apparent negative thermal expansion, whereas for $n \geq 4$ NN shells reflect global effects and are compatible with an expected positive thermal expansion. Above T_g global electronic effects can influence the shape of the atomic arrangement in the MRO during undercooling. Below T_g , i.e. after structure formation has largely ceased, changes in shell distances take place foremost due to thermal expansion affecting all length scales almost identically. The different influence of global electronic effects on different length scales cannot be discerned easily any more possibly leading to the false impression that they are equally as important in the SRO as well.

6.5 Conclusions

The evolution of the structure of $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ metallic liquid during vitrification has been observed in-situ utilising high-energy synchrotron radiation and aerodynamic levitation. X-ray diffraction data have been recorded over a wide temperature range starting from above the liquidus temperature T_l down to well below the glass transition temperature T_g . The structural evolution has been analysed in terms of the temperature-dependent structure factor $S(Q, T)$ and reduced pair distribution function $G(r, T)$. The results indicate that the pathway of the $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ metallic liquid alloy to vitrification is divided into different non-crystalline structural regimes. Below the melting temperature T_m rapid structural changes occur by atoms migrating from anti-shell to shell regions leading to a strong enhancement of the short and medium range order as T_g is approached. The structural rearrangements in the undercooled liquid of $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ are found to be correlated with a rapid increase in viscosity and fragility. Indications for a fragile-to-strong transition in the undercooled liquid were found reciprocal as well as real space. The structural rearrangements also cause an apparent negative thermal expansion of the first nearest-neighbour shell in the undercooled liquid while in the glassy state a usual positive expansion occurs. The validity of a global description of the structure of metallic glasses, at least in the present alloy, is restricted to distances beyond the third nearest-neighbour shell. The evolution of the atomic structure of metallic liquids during vitrification may shed light on glass formation and on the structural origins of the sluggish long-range order kinetics that suppresses nucleation and growth of crystalline phases.

6.6 Supplementary Material

6.6.1 The mean valence

The positions of the NN shells for $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ in real space and their temperature dependence, respectively, indicate the influence of global resonances on structure formation for NN shells with $n \geq 4$ that can be described by the spherical periodic order according to $r_n = \left(\frac{1}{4} + n\right) \frac{2\pi}{Q_1}$ [Hau92]. For this the "resonance condition"

$$Q_{1,c} = 2k_F \tag{6.2}$$

needs to be fulfilled taking into account an appropriate FERMI sphere with diameter $2k_F$ that coincides with the pseudo BRILLOUIN-zone for which a diameter Q_1 or $Q_{1,c}$ can be assumed [Hau92, Nag75, Now99]. The FERMI-sphere diameter is calculated according to

$$2k_F = 2\sqrt[3]{3\pi^2\rho_0 Z} \quad , \quad (6.3)$$

where Z is the mean valence and ρ_0 the particle number density of the alloy [Ash76]. The valence Z necessary to fulfil the resonance condition can be calculated from the measured structural data by combining Eqs. 6.2 and 6.3. Since experimental values of ρ_0 were only available for room temperature (RT) (average value $\rho_0(\text{RT}) = 63.27 \text{ nm}^{-3}$ [Yam14, Zhe13]) $Q_{1(c)}(\text{RT})$ needs to be obtained. This was done by

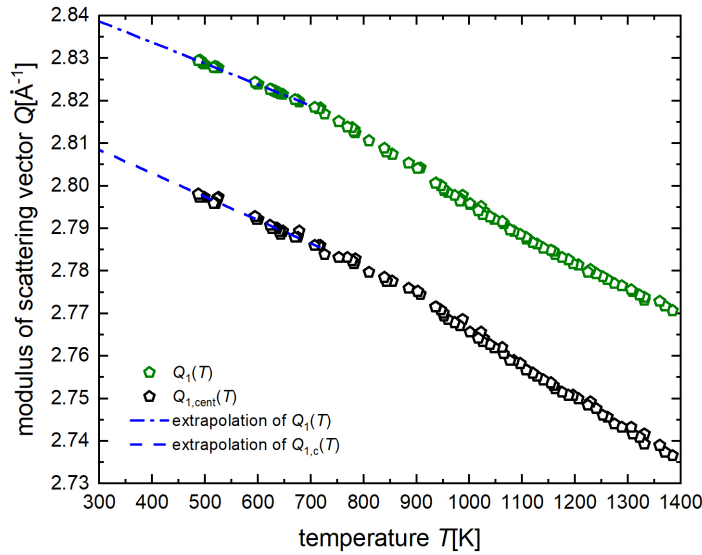


Figure 6.7: Positions $Q_1(T)$ (green pentagons) and $Q_{1,c}(T)$ (black pentagons) extrapolated below T_g linearly to RT ($T = 300 \text{ K}$) (blue dash-dotted/dashed lines).

extrapolating $Q_{1(c)}(T)$ below T_g linearly to RT ($T = 300 \text{ K}$) (blue dotted/dash-dotted lines in Fig. 6.7). Combining Eqs. 6.2 and 6.3 yields

$$Z = \frac{Q_{1,c}^3(\text{RT})}{24\pi^2\rho_0(\text{RT})} \quad (6.4)$$

from which the two valences ≈ 1.526 using $Q_{1,c}$ and ≈ 1.478 using Q_1 , respectively, can be calculated. Interestingly, the mean value, $Z \approx 1.5$, has been found to occur in

other BMGs as well [Gil16, Sti19]. For binary Cu-Zr and Ni-Zr metallic glasses a mean valence of 1.5 was shown to be a reasonable assumption considering that the valences of the elements Cu, Ni and Zr (and other transition metals likewise) can be assessed with 1.5 as well [Sti19]. Since $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ mainly consists of transition metals the same arguments as in ref. Sti19 (Ch. 4) can rationalise a similar mean valence also here. Only the minor alloying with Sn ($Z_{\text{Sn}} = 4$) should increase the average value slightly above 1.5. However, given that the individual valences are not necessarily constant but can depend on several factors the mean value of $Z \approx 1.5$ derived in the present case seems to be a reasonable estimation. Future investigations have to show whether $Z \approx 1.5$ occurs in further metallic glasses as well and if a temperature dependence exists. If the latter is the case, temperature-dependent values $\rho_0(T)$ would be necessary to calculate $2k_F(T)$ for a comparison with $Q_{1,c}(T)$ to calculate a possible $Z(T)$ using Eq. (6.4).

6.6.2 Structure and fragility

According to previous investigations of glass-forming metallic liquids it is possible to infer the fragility from structural data in real space along the pathway towards vitrification [Wei15, Sto16]. Thereafter only the evolution of the position of the fourth NN shell correlates with fragility suggesting the fragility is determined by the real-space structure on a length scale of about 3 to 4 atomic diameters [Wei15]. Starting from the volume

$$V_{4-3} = \frac{4}{3}\pi r_{4,c}^3 - \frac{4}{3}\pi r_{3,c}^3 = \frac{4}{3}\pi (r_{4,c}^3 - r_{3,c}^3) \quad (6.5)$$

"enclosed" between NN shells 4 and 3 its relative change during undercooling

$$\begin{aligned} \delta(T) &= \frac{\Delta V_{4-3}(T)}{V_{4-3}(T_g)} = \frac{V_{4-3}(T) - V_{4-3}(T_g)}{V_{4-3}(T_g)} = \frac{V_{4-3}(T)}{V_{4-3}(T_g)} - 1 \\ &= \frac{r_{4,c}^3(T) - r_{3,c}^3(T)}{r_{4,c}^3(T_g) - r_{3,c}^3(T_g)} - 1 \end{aligned} \quad (6.6)$$

can be defined [Wei15,Sto16]. When plotting $-\delta(T)$ versus the normalised reciprocal temperature $\frac{T_g}{T}$ its slope

$$m_{\text{str}} = -\frac{d\delta(T)}{d\left(\frac{T_g}{T}\right)} \quad (6.7)$$

can be considered a structural measure of fragility [Wei15,Sto16]. In turn m_{str} can be "translated" into fragility [Boh93] using [Wei15]

$$m = \frac{m_{\text{str}} + 0.124}{2.95 \cdot 10^{-3}} \quad (6.8)$$

and, furthermore, into the fragility parameter D of the VOGEL-FULCHER-TAMANN equation using [Boh93]

$$D = \frac{590}{m - 16} \quad (6.9)$$

Plotting $-\delta(T)$ for $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ over $\frac{T_g}{T}$ yields indeed a change of behaviour at

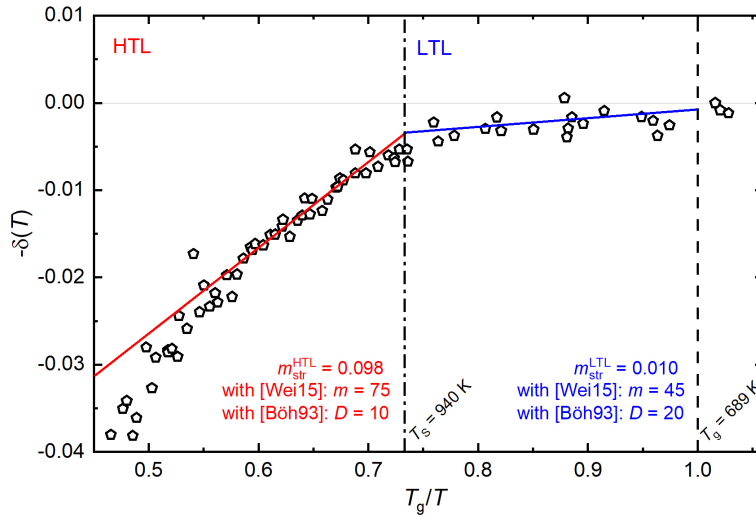


Figure 6.8: The T -dependence of the volume dilation δ of $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ and its relation to (structural) fragility. The parameters shown are derived from the slopes of the linear functions for the high-temperature (red) and low-temperature (blue) liquid.

the previously determined characteristic temperature $T_s = 1.36T_g$ also in this metric (Fig. 6.8) related to a change in fragility. According to this analysis a (fragile) HTL with a fragility of $m_{\text{HTL}} = 75$ transforms into an (stronger) LTL with the lower fragility $m_{\text{HTL}} = 45$ indicating that the possible LLC at T_s may indeed be related to an FST.

6.6.3 The pathway of $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ animated

Movie 1 under cord.cranfield.ac.uk/account/projects/121164/articles/16432536 and Movie 2 under cord.cranfield.ac.uk/account/projects/121164/articles/16432581 show the temperature-dependent structural changes of $S(Q)$ and $G(r)$ along the pathway for $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ in an animated way. The structure functions are coloured in red for $T > T_l$, in blue for $T_l > T > T_g$ and in green for $T_g > T$.

7 The pathways of Zr- and Ti-based metallic alloys – A comparison

A comparative study of the atomic structure of three metallic alloys, $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$, $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ and $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$, monitored in-situ along their pathways from the high-temperature equilibrium liquid, during undercooling, through their vitrification and in the subsequent glassy state was conducted. Quasi-containerless aerodynamic levitation and laser-heating in combination with high-energy synchrotron radiation was used to perform the necessary in-situ diffraction experiments. Structural data was analysed in reciprocal space by means of several metrics derived from the structure factor $S(Q)$ as well as by those derived from the reduced pair distribution function $G(r)$ in real space. While an overall very similar behaviour of $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$, $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ and $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ was found several characteristic differences could be unveiled. Strong indications for a liquid-liquid crossover are prominent in $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ only. Possible universal structural features of metallic-glass forming liquids are discussed.

7.1 Introduction

Upon fast enough cooling the amorphous structure of a metallic liquid can be retained during solidification. The result of this vitrification is called a metallic glass. Vitrification as well as the process in the opposite direction are called glass transition. Comparing the liquid and the glass phase at the microscopic level only very subtle changes of the atomic structure are detectable. In contrast, a huge change in macroscopic properties like viscosity $\eta(T)$ during cooling and vitrification take place. The latter increases by several orders of magnitude during cooling from above the liquidus temperature T_l to the glass transition temperature T_g . It is this discrepancy that causes the glass transition to be still poorly understood even after extensive research spanning more than six decades. To understand the relations between the macroscopic and microscopic changes during vitrification a continuous monitoring of the according quantities is necessary. However, due to necessary high cooling rates the experiments need to be performed equally as fast. Suitable experimental setups to monitor the changes at the atomic scale using diffraction techniques became available only recently. As discussed in Ch. 2, from several levitation techniques available only electrostatic levitation (ESL) and aerodynamic levitation, the latter usually in the form of conical

nozzle levitation (CNL), is used for the study of metallic glasses. From the palette of structural probes (i.e. mainly electron, neutron and X-ray diffraction) only X-ray diffraction (XRD) is currently able to provide the necessary speed, intensity and resolution for monitoring the structural changes in the systems under investigation (Ch. 2).

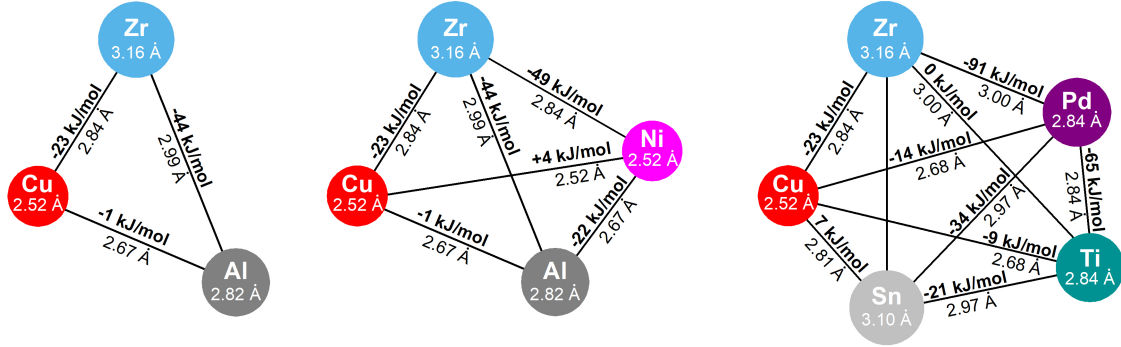


Figure 7.1: Enthalpies of mixing ΔH_{mix} (**bold**) according to MIEDEMA's model [Tak05] and interatomic distances d_{at} [Mir10] for all pairs of elements in Zr₆₀Cu₃₀Al₁₀, Zr₅₅Cu₃₀Ni₅Al₁₀ and Ti₄₀Cu₃₄Pd₁₄Zr₁₀Sn₂. The interatomic distance for pairs of the same element equals the atomic diameter of this element [Mir10] and is noted at each element. The diameter of the dots for each element is proportional to d_{at} . The numerical values can also be found in Tab. 7.2.

In the present chapter, a ternary, quaternary and quinary metallic-glass forming alloy whose structures have been monitored in-situ during rapid cooling by high-energy synchrotron radiation in the same levitation setup (CNL) will be compared. Several aspects of Zr₆₀Cu₃₀Al₁₀, Zr₅₅Cu₃₀Ni₅Al₁₀ and Ti₄₀Cu₃₄Pd₁₄Zr₁₀Sn₂ have already been published (cf. refs. Geo15, Lou20 and Ch. 6). The purpose of the present chapter is the analysis of the evolving atomic structure along the complete pathway from the high-temperature equilibrium liquid, during undercooling, through vitrification and in the subsequent glassy state of the three alloys in an identical way to identify possible universal behaviour, but also differences between the alloys that may point to the origin of their different glass-forming abilities (GFA). This includes the possible existence of liquid-liquid crossovers (LLCs) along the pathway in the undercooled liquid regime.

At first glance, amongst the three alloys, Ti₄₀Cu₃₄Pd₁₄Zr₁₀Sn₂ promises to possess the highest GFA as it exhibits the highest diversity in the properties of its components and therefore appears to be most "confused" [Gre93a, Gre95] (Ch. 5). In particular, considering INOUE's empirical rules [Ino00], this alloy does not only have the highest number of components but also the pairs with the highest negative enthalpies of mixing and the biggest atomic size differences of the constituent elements (Fig. 7.1, Tab. 7.2).

Nevertheless, it is $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ that has the highest measured GFA in terms of the critical casting diameter d_c (Tab. 7.1). The reason for this discrepancy must therefore be founded in other properties possibly related to specific structural differences. For deeper insights, a multitude of structural metrics in reciprocal as well as in real space will be analysed and compared.

7.2 Materials and methods

Only a short outline of sample preparation and experimental arrangements will be given here. Details can be found in refs. Geo15, Lou20, references therein as well as in Chapters 2 and 6.

Spherical ingots of about 2 mm in diameter were prepared by arc-melting of the elements (purity 99.9 at.% or better) in a Ti-gettered Ar atmosphere. The ingots were remelted at least 5 times to achieve chemical homogeneity. In-situ high-energy synchrotron X-ray scattering at beamline ID-15 of the European Synchrotron Radiation Facility (ESRF) with an incident wavelength $\lambda_i = 0.124 \text{ \AA}$ ($E_i = 100 \text{ keV}$) in a transmission geometry with a two-dimensional flat-panel detector (1 frame per 100 ms) was employed. Using a stream of Ar from a conical nozzle, the samples were aerodynamically levitated during the experiment. Following heating to temperatures well above T_l using CO_2 lasers, the samples were allowed to cool freely after switching off the lasers which leads to non-constant cooling rates over the investigated temperature range (Fig. 7.2). Temperatures were recorded with optical pyrometers. Below 620 K temperatures were calculated using an exponential decay function fitted to the measured values above 620 K. The changing cooling rates also cause a non-constant uncertainty ΔT of the temperature determination (Fig. 7.2).

After several steps of processing the raw diffraction data (cf. refs. Geo15, Lou20 and references therein; Ch. 2) the total structure factor $S(Q)$ is obtained, where $Q = |\vec{Q}|$ is the modulus of the scattering vector ($\hbar Q$ is the absolute value of the momentum transfer during the scattering event with $\hbar$ the reduced PLANCK constant). This simplification is possible due to the isotropic nature of the expected amorphous structure of the alloys under consideration. The structure factor for an amorphous material oscillates around $S(Q) = 1$ and shows diffuse peaks only. These peaks, especially the Q -regions where $S(Q) > 1$, will be called *halos* further on. From these regions structural metrics (heights; positions of maxima: centres of mass; areas, i.e. intensities) will be obtained and their T -dependence discussed.

Structural data in *real space* is obtained by a FOURIER transform [Ega03] which yields the *reduced pair-distribution function*

$$\begin{aligned}
 G(r) &= \frac{2}{\pi} \int_0^{Q_{\max}} Q[S(Q) - 1] \sin(Qr) dQ \\
 &= 4\pi r [\rho(r) - \rho_0] \\
 &= 4\pi r \rho_0 [g(r) - 1].
 \end{aligned} \tag{7.1}$$

where r is the distance from a centre atom at $r = 0$ Å and ρ_0 the average particle number density. $\rho(r) = \rho_0 g(r)$ is the *pair density function* with $g(r)$ the *pair correlation function* [Ega03]. $G(r)$ can be interpreted as the distribution of probability of finding the centre of another atom at distance r from an arbitrarily chosen atom (at $r = 0$ Å) and can directly provide an insight into the typical shell-like structure of a amorphous materials (liquid, undercooled liquid, glass). Due to the lack of knowledge of $\rho_0(T)$ results in real space will be discussed in terms of $G(r)$. All functions $G(r)$, $g(r)$ and $\rho(r)$ provide comparable information and associate the shell-like structure with deviations from the average density ρ_0 to higher *as well as to lower* values. Therefore, the shell/anti-shell concept (Ch. 5) will be adopted for the present discussion, i.e. the regions with $G(r) > 0$ will be called nearest-neighbour (NN) *shells*. There the local density $\rho(r)$ is higher than the average density ρ_0 . Analogous to the reciprocal-space structural metrics in real space will be obtained from these regions. Complementary, the regions with $G(r) < 0$ are called anti-shells (Ch. 5). No background-subtraction will be used for both $G(r)$ and $S(Q)$ and, with only a few exceptions, no fit procedures will be employed which reduces subjectivity during data analysis and discussion immensely. Discussion of centres of mass of peaks is preferred over that of the positions of their maxima as the former involves integration over a complete peak, i.e. does not rely on a single value only. This not only reduces uncertainty but also characterises the complete peak, i.e. halo or NN shell, instead of singling out a partial contribution. In general, metrics involving an integration over an entire peak in a function $f(x)$ (e.g. $S(Q)$ or $G(r)$), e.g. the position of its centroid

$$x_c = \frac{\int_{\text{peak}} f(x) x dx}{\int_{\text{peak}} f(x) dx} \tag{7.2}$$

or its second moment (related to the variance) [Lan16]

$$\sigma^2 = \frac{\int_{\text{peak}} f(x)(x - x_c)^2 dx}{\int_{\text{peak}} f(x) dx} \quad (7.3)$$

as measure of its width should be favoured. Using the second moment instead of the full width at half maximum (FWHM) Γ to measure the width also helps to capture changes of the peak shape that may take place below the half of the maximal height. Those changes that can occur especially in asymmetric peaks would be missed by the FWHM. Nevertheless, it is sometimes necessary to investigate the origin of specific sub-features of a peak, for instance if a high asymmetry, shoulders or splits occur. In this case the use of a fitting procedure may be necessary.

7.3 Results

Following the direction imposed by the experiment, the results are discussed from high T towards low T also reflecting the evolution of the structure during glass formation and glass transition.

A necessary prerequisite for vitrification is that the alloy can be undercooled in its liquid state below T_l and down to T_g without crystallisation. Figure 7.2 shows the temperature-time profiles $T(t)$ ("cooling curves") of all three alloys $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$, $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ and $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ during free cooling after switching off the heating lasers. The absence of recalescence phenomena points to successfully achieved vitrification. Hence, the diffraction data taken in parallel reflect the alloys being in an amorphous state along the complete pathway including vitrification (for $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ below $T \approx 950$ K a limited number of $S(Q)$, showing minor non-amorphous features of unknown origin, were exempted from further analysis).

To facilitate the presentation of the results symbols used in plots are chosen according to the number of components in the alloys, i.e. triangles ($\blacktriangle, \triangle$) for the ternary alloy $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$, squares ($\blacksquare, \square$) for the quaternary alloy $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ and pentagons ($\blacklozenge, \lozenge$) for the quinary alloy $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$. Different colours are used when more than one structural metrics of the same alloy are plotted in a single figure. Relevant parameters, like characteristic temperatures, for the three alloys are compiled in Tab. 7.1. Presentation of the results will commence in reciprocal space.

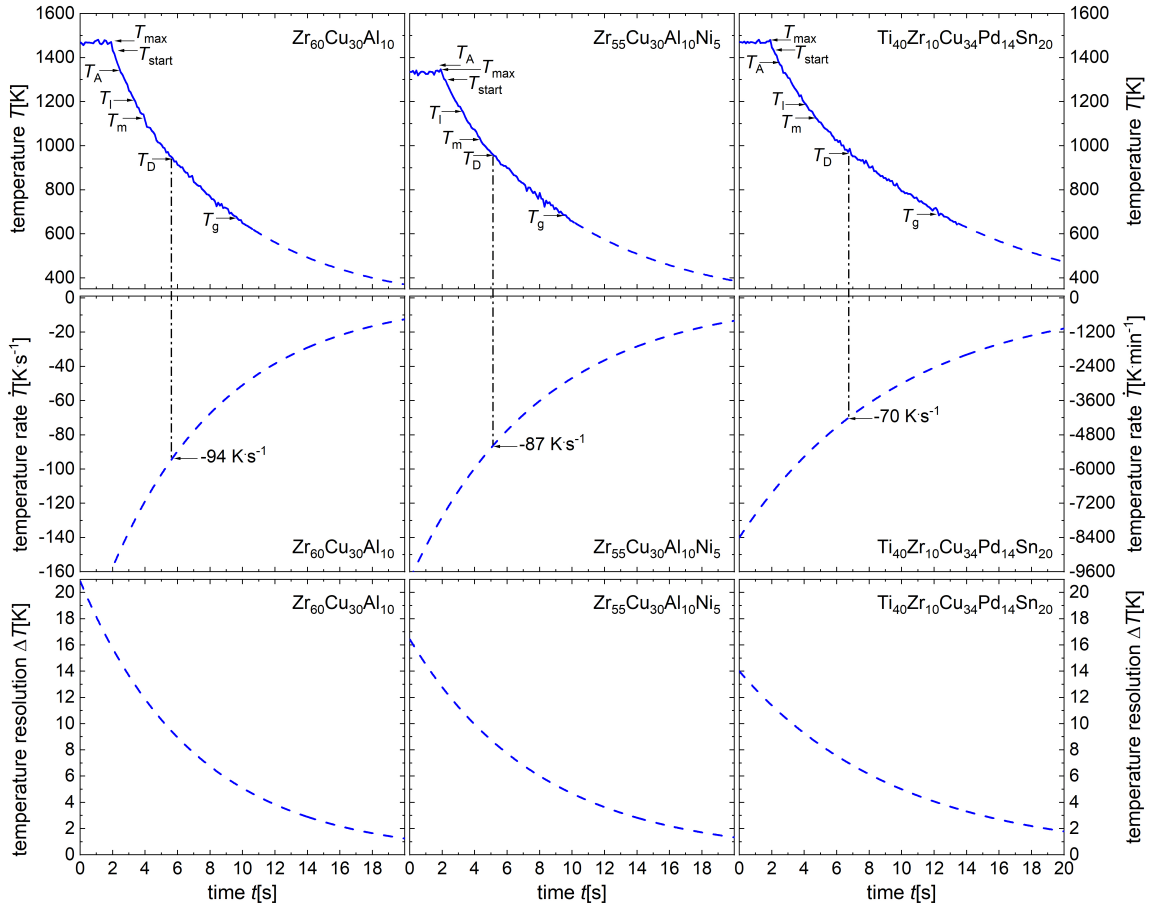


Figure 7.2: The temperature-time profiles $T(t)$ ("cooling curves"; first row) and temperature rates $\dot{T}(t)$ ("cooling rates"; second row) of the three alloys $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$, $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ and $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ upon free cooling. The absence of recalescence phenomena (sudden steep rises in temperature) indicates successful vitrification during the experiments. Temperatures below 620 K were calculated from a fit to measured data at higher T . Arrows mark characteristic temperatures for each alloy (cf. Tab. 7.1): the highest occurring temperature T_{max} , the highest temperature for which data is discussed T_{start} , the "cooperativity-onset temperature" $T_A = 2 T_g$ [Gan17, Kel17], the liquidus temperature T_L , the melting temperature T_m , the "backbone temperature" $T_D = 1.4 T_g$ [Sok16, Kel17], the glass-transition temperature T_g . The rates $\dot{T}(t)$ are the first derivative of said exponential fit. The right y-axis for the temperature rates shows the values in K/min for comparison as often in literature this unit is chosen since for experiments not using aerodynamic levitation only much smaller cooling rates are achievable (cf. Ch. 2). The vertical dash-dotted lines point to the temperature rate the samples experience when passing through T_D . The bottom row shows the uncertainty ΔT in the temperature determination caused by the by the finite acquisition time of 100 ms of the detector ($\Delta T(t) = \dot{T}(t) \cdot 100 \text{ ms}$).

7.3.1 Reciprocal space

To give an overview of the evolving atomic structure during cooling the first row of Fig. 7.3 shows a three-dimensional (3D) plot of the temperature-dependent structure factor $S(Q, T)$. Prominent in this representation, and common to all three alloys, is the development and increase of a split in the second halo upon cooling. Projection of all structure factors onto one plane for each alloy provides a better view of this behaviour and the evolution of further details (Fig. 7.3, second row). In addition, the Supplementary Material contains the same data visualised as movies (Sec. 7.6.3). For all alloys it is mainly the low- Q feature of the second halo that develops while the feature at higher Q stays almost constant. Furthermore, an increase of the height, as well as a shift to higher Q , of the first halo is salient. Additionally, also the halos beyond the second halo increase in intensity upon progressing undercooling. To emphasise these changes more clearly the differences compared to $S(Q)$ at the respective maximal temperature T_{start} at the beginning of the cooling process can be calculated according to $\Delta S(Q, T) = S(Q, T) - S(Q, T_{\text{start}})$. These functions are plotted in the third row of Fig. 7.3. The changes over a wide Q -range point to changes over a wide r -range in real space.

Figure 7.4 displays several metrics derived from the peak representing the first halo of $S(Q)$. The relevant portion of the peak that is used is shown schematically in the inset of the top-left figure. As function of T for the three alloys, the maximal heights $S(Q_{1,m})$ (first row) and the positions of the centroids $Q_{1,c}$ as well as that of the maxima $Q_{1,m}$ (second row) are shown. These metrics exhibit a "kink" at the respective T_g which is most distinct for $S(Q_{1,m})$. Such a change in structural metrics at T_g is well known (Ch. 2) and has first been reported for metallic glasses investigated upon heating [Mat03, Mat04, Yav04, Yav05, Mat07b, Jia10, Mat12, Mau13, Mau13a, Mau14, Joh14]. The main drawback of heating experiments is the intervention of crystallisation resulting in a large T -range in which the alloy cannot be investigated in an amorphous state until it liquefies at much higher T . The according gap in the data severely hampers the reliable determination of a functional relationship describing the data. Often a linear behaviour with a single slope above T_g was assumed [Mat02, Mat03, Mat04, Jia10], but already on closer inspection of such data a non-linear behaviour appears probable (cf. Fig. 7.11). However, only experiments upon rapid cooling, avoiding crystallisation, can reliably fill the gap with continuously measured data of the sample being in an amorphous state at all times. By a direct comparison of the three alloys $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$, $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$,

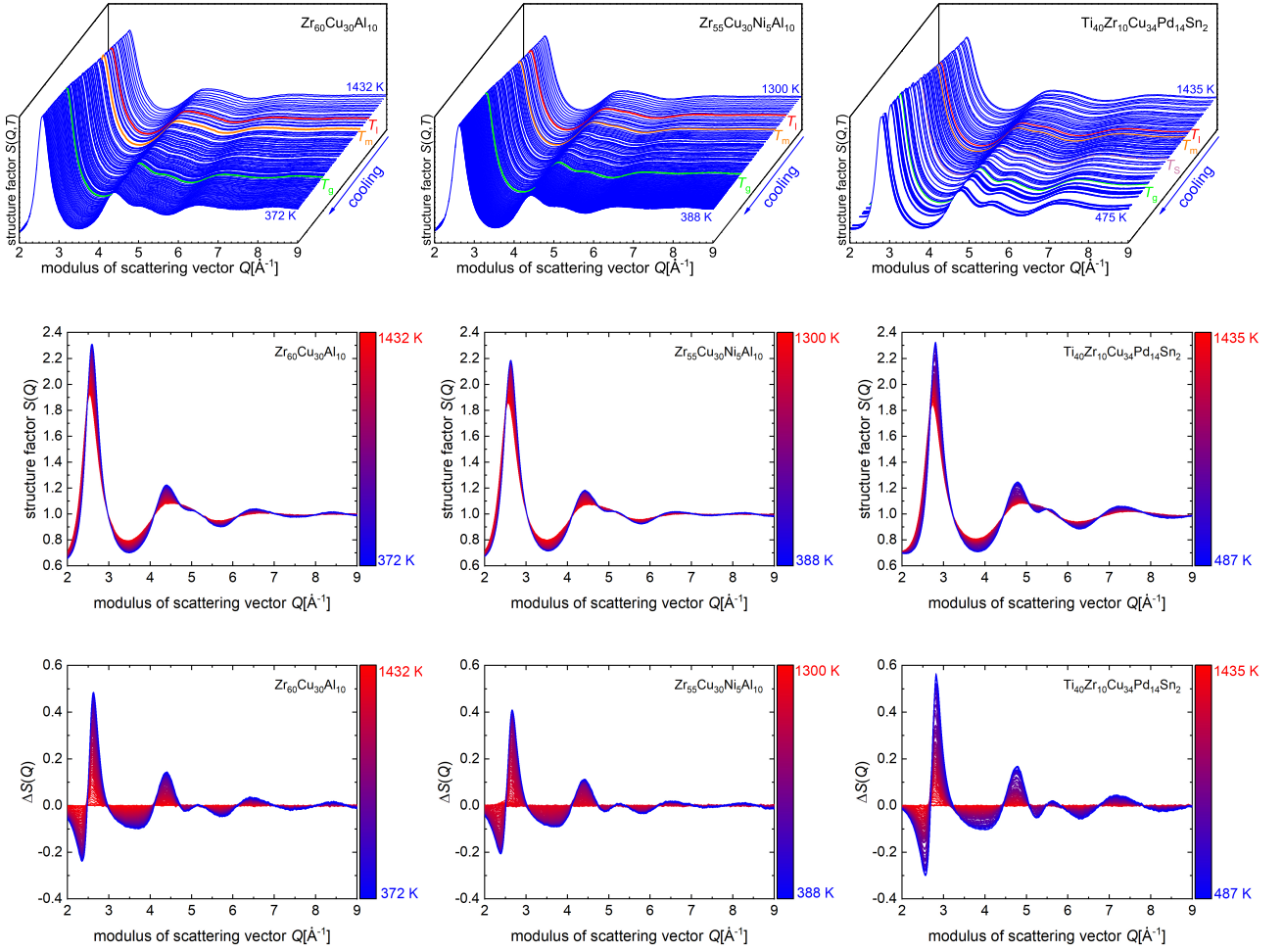


Figure 7.3: Temperature-dependent structure factors $S(Q, T)$ of $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$, $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ and $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ (from left to right) as 3D waterfall (first row), projected onto one plane (second row) as well as changes $\Delta S(Q, T) = S(Q, T) - S(Q, T_{\text{start}})$ (third row). Structure factors (first row) for special temperatures are highlighted by colours: $S(Q, T_l)$ (red), $S(Q, T_m)$ (orange), $S(Q, T_s)$ (lilac; for $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ only) and $S(Q, T_g)$ (green). In the second and third row a continuous low T .

and $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ (Fig. 7.4 first and second row) it becomes obvious that a single smooth and non-linear functional relation could be able to describe both the T -dependence of the position of the first peak in $S(Q)$ as well as its height from high T down to the glass transition (Sec. 7.4). Only $Q_{1,m}(T)$ for $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ poses an exception showing a kink for $T > T_g$ (but none at T_g). To get further insights a measure of skewness by combining $Q_{1,c}$ and $Q_{1,m}$ can be defined by

$$\Lambda(T) = \frac{Q_{1,c}(T) - Q_{1,m}(T)}{Q_{1,m}(T)} . \quad (7.4)$$

If a peak is highly symmetrical Λ would be very close to 0, i.e. the position of centroid

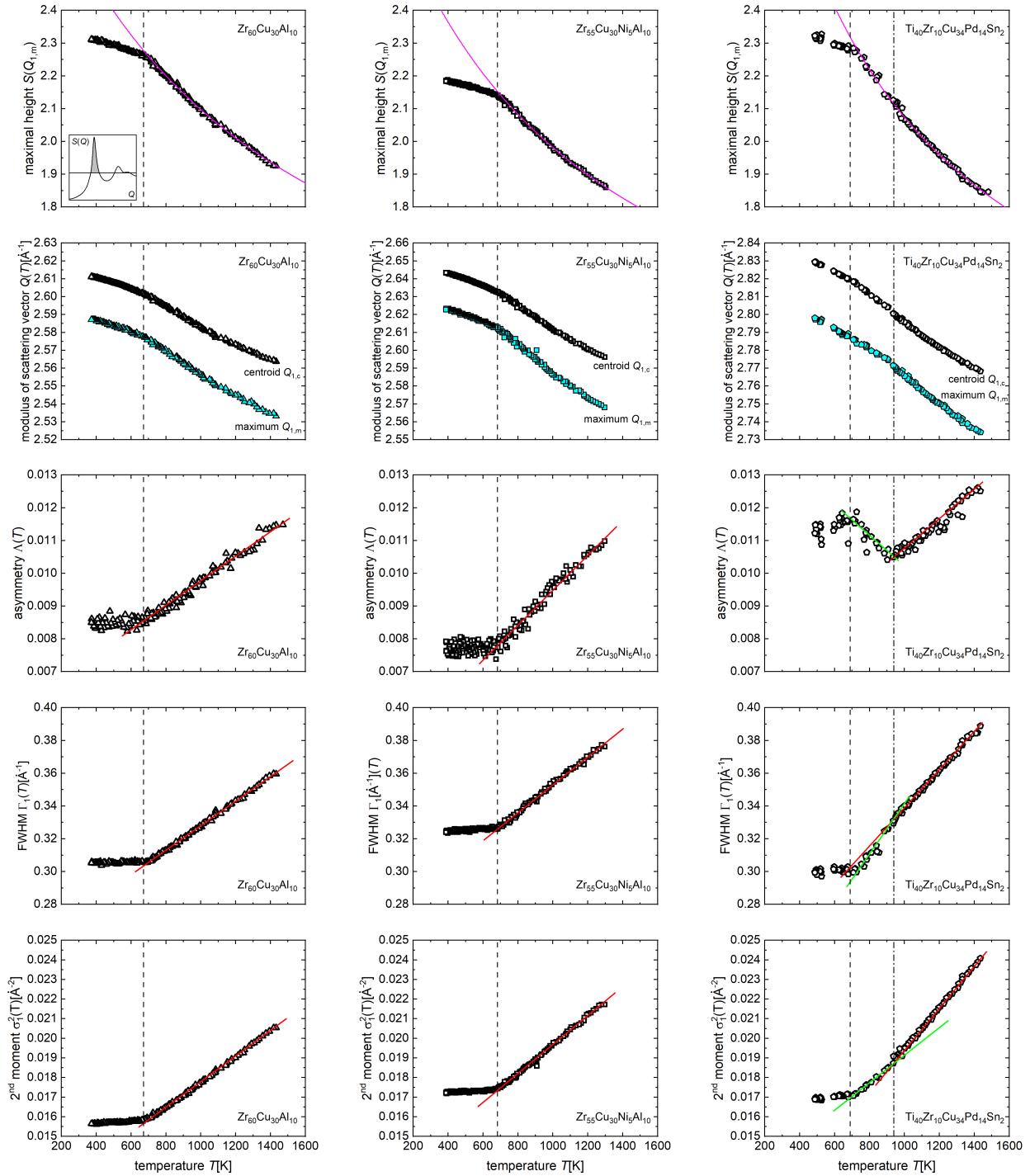


Figure 7.4: Metrics of $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$, $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ and $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ derived from the first peak in $S(Q)$ (first halo; cf. inset in the top right figure for a schematic $S(Q)$ showing the relevant portion from which the metrics are derived). First row: height $S(Q_{1,m})$ of the first peak, second row: position of centroids $Q_{1,c}$ (open symbols) and maxima $Q_{1,m}$ (black-blue symbols), third row: peak asymmetry $\Lambda(T)$, fourth row: FWHM $\Gamma_1(T)$ and fifth row: second moment $\sigma_1^2(T)$. The magenta lines in the first row are derived from fits of Eq. (7.5) to $S(Q_{1,m}) - 1$. The red and green lines in rows three to five are guides for the eye.

and maximum would be very close to each other. The values according to Eq. (7.4) are shown in the third row of Fig. 7.4. From Fig. 7.4 it can be inferred that for all three alloys an asymmetry exists which decreases during undercooling and remains about constant after vitrification. The latter may indicate that the structural evolution during undercooling ceases around T_g . While for the two Zr-based alloys a monotonous evolution in the liquid and undercooled liquid takes place a different behaviour for $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ can be observed: initially the asymmetry decreases as well, but below a characteristic temperature $T_S \approx 940 \text{ K} \approx 1.36 T_g$ (dash-dotted vertical line in Fig. 7.4) a renewed increase of the asymmetry occurs. In the further discussion it needs to be investigated if this distinct difference between $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ and the Zr-based alloys as well as the characteristic temperature $T_S \approx 940 \text{ K} \approx 1.36 T_g$ is reflected in other metrics as well and what the underlying reason might be. A change in peak asymmetry is likely to be accompanied by a change in the peak width, i.e. its second moment σ^2 (Eq. (7.3)). Figure 7.4 (bottom row) shows $\sigma_1^2(T)$ as function of T for the first halo of the three alloys. For $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ and $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ a monotonous and almost linear decrease of $\sigma_1^2(T)$ with undercooling towards T_g is obvious, i.e. the peaks representing the first halo become narrower upon cooling indicating an increase in structural order by means of the structural correlation length in real space [Oss91]. While initially $\sigma_1^2(T)$ for $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ behaves similar to the two Zr-based alloys, below T_S (vertical dash-dotted line in Fig. 7.4) the narrowing of the peak is slower upon further cooling. As expected $\Gamma_1(T)$ and $\sigma_1^2(T)$ provide comparable information, the latter exhibits less scatter as can be seen in the last two rows of Fig. 7.4. However, it is interesting to note that for $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ both quantities show an opposite change in behaviour at T_S . This indicates a more complex change of peak shape along the pathway for $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$. The different behaviour of $Q_{1,c}(T)$ in comparison to that of $Q_{1,m}(T)$ for $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$, causing the non-monotonous change of Λ in the first place, gives a glimpse of this complexity which might be related to the partial structure factors and their individual evolution during cooling. For $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$, with its 15 atomic pairs (Fig. 7.1, Tab. 7.2), 15 partial structure factors need to be assessed (compared to 10 for $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ and 6 for $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$). Their interplay, reflecting chemical ordering along the pathway, may be key in understanding LLCs and possibly vitrification itself. Unfortunately, their experimental determination is severely hampered by several challenges (Ch. 2). Future molecular dynamics (MD) and reverse monte-carlo (RMC) simulations (cf. Ch. 2) might be able to aid a better understanding.

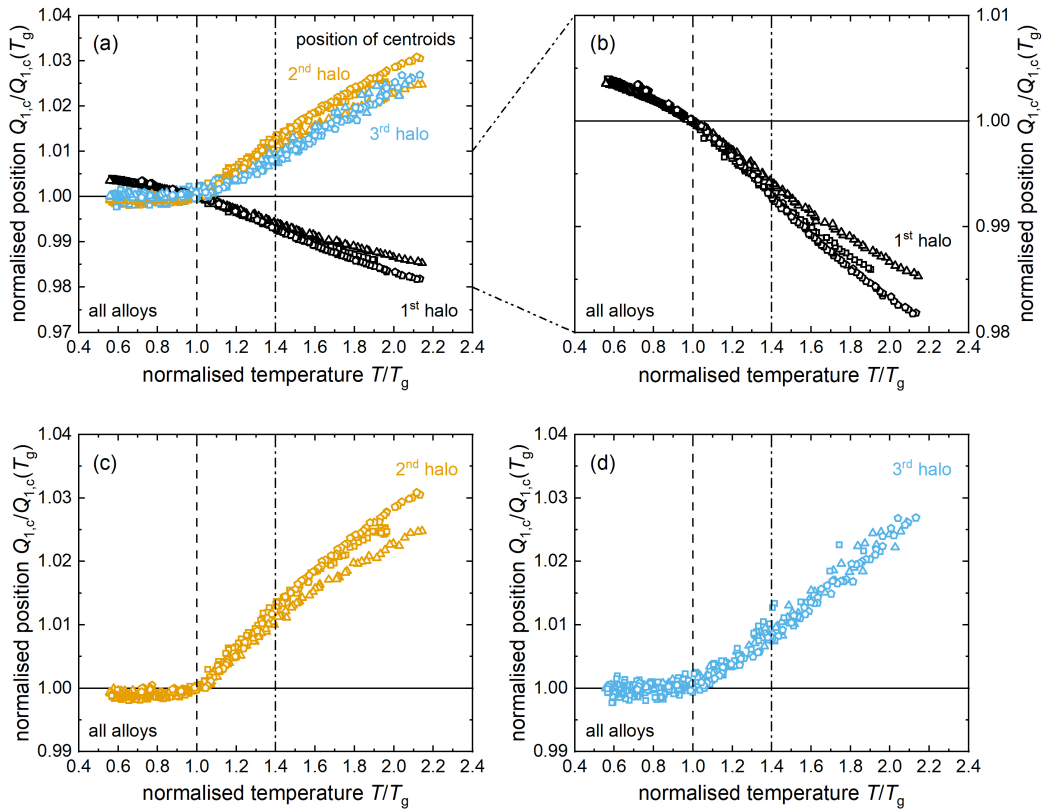


Figure 7.5: The positions of the centroids for halos 1, 2 and 3 of $Zr_{60}Cu_{30}Al_{10}$, $Zr_{55}Cu_{30}Ni_5Al_{10}$ and $Ti_{40}Cu_{34}Pd_{14}Zr_{10}Sn_2$ normalised to their respective values at T_g plotted versus the normalised temperature T/T_g . For halo 3 of $Zr_{55}Cu_{30}Ni_5Al_{10}$ a relatively strong scatter of data occurs and several outliers are not shown for clarity. The vertical dashed and dash-dotted lines mark T_g and $1.4 T_g$, respectively.

At T_g the decrease of $\sigma_1^2(T)$ and $\Gamma_1(T)$ abruptly stops and both become almost constant in the glassy state (Fig. 7.4) indicating again that the structural evolution has largely come to an end and the observed changes in $S(Q)$, and subsequently in real space as well, are mainly due to thermal excitations (DEBYE-WALLER factor [Ega03]; also cf. Sec. 7.4.2). Apart from the anomalous behaviour at T_s for $Ti_{40}Cu_{34}Pd_{14}Zr_{10}Sn_2$ the metrics presented so far reveal many commonalities between the three alloys. For a closer comparison it useful to normalise the T -axes to the respective T_g and the y-axes to the values of the metrics to their values at the respective T_g . This may also shed more light on the special behaviour of $Ti_{40}Cu_{34}Pd_{14}Zr_{10}Sn_2$.

Figure 7.5a shows the normalised positions of the centroids for halos 1 (un-normalised in Fig. 7.4) and, in addition, those of halo 2 and 3 of $Zr_{60}Cu_{30}Al_{10}$, $Zr_{55}Cu_{30}Ni_5Al_{10}$ and $Ti_{40}Cu_{34}Pd_{14}Zr_{10}Sn_2$. The scatter in the experimental data for all higher halos prevents a meaningful discussion. Halo 1 shifts with T opposite to that

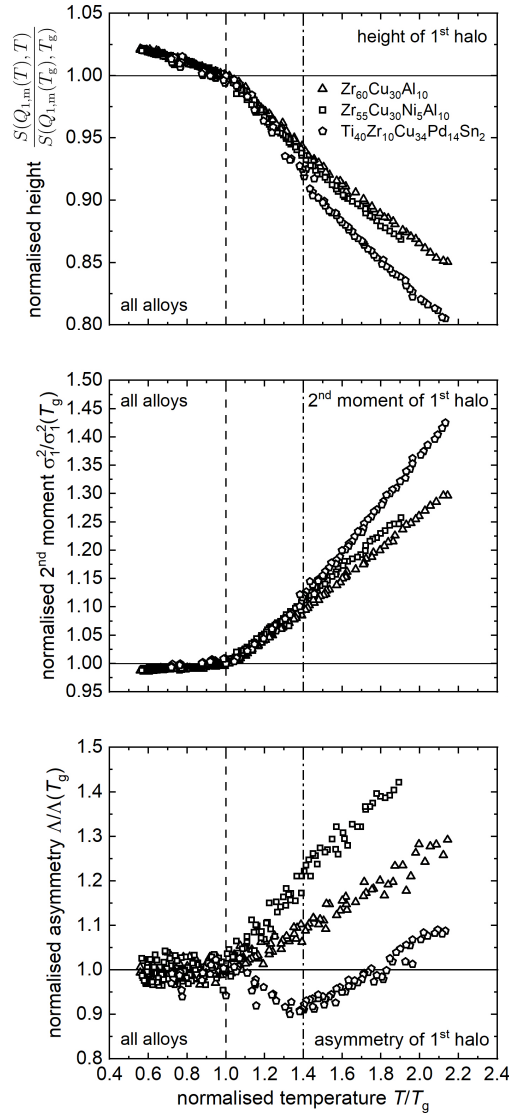


Figure 7.6: Normalised metrics of the first halo of $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$, $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ and $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$: height $S(Q_{1,m}(T), T)/S(Q_{1,m}(T), T_g)$, second moment (variance) $\sigma_1^2(T)/\sigma_1^2(T_g)$ and asymmetry $\Lambda(T)/\Lambda(T_g)$ plotted versus the normalised temperature T/T_g . The vertical dashed and dash-dotted lines mark T_g and $1.4 T_g$, respectively.

of halos 2 and 3. The shift in halo 1 which represents the high- r part of $G(r)$ in real space [Car75, Ryu20] is related to thermal expansion [Yav05]. While the observed shift of halo 1 points to a "normal" (positive) thermal expansion for these distances the opposite behaviour of halos 2 and 3 indicates different behaviour at lower distances in real space (see below). Figure 7.5b-c shows enlarged views for the individual halos. In addition to the vertical line at T_g (dashed) another vertical line at $1.4 T_g$ (dash-dotted) is shown which is inspired by reports of a characteristic temperature during glass formation, as found in simulations, below which individual clusters or smaller cluster assemblies rapidly interconnect to create a backbone eventually per-

colating the complete sample [Sok16, Kel17]. Interestingly, the latter is also close to $T_S \approx 1.36 T_g$ found here. The normalised plots exhibit an intriguing similarity among the three alloys. While for halo 3 a virtually identical behaviour can be seen in all three alloys over the complete investigated T -range, for halos 1 and 2 this is the case only for deep undercooling and in the glass phase. As a characteristic temperature below which the three alloys show unified behaviour again $T \approx 1.4 T_g$ seems to be an appropriate choice. Normalising the metrics for height and width of the peaks as well supports again $T \approx 1.4 T_g$ being a characteristic temperature (Fig. 7.6a,b). The normalised peak asymmetry (Fig. 7.6c) shows common behaviour for all three alloys below T_g but exhibits special behaviour at $T \approx 1.4 T_g$ only for $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ as already mentioned above. With the exception of $\Lambda(T)$ these results point to possible universalities in the structural behaviour along the pathway of liquid metallic alloys to vitrification which needs to be verified by future investigations of more alloys.

7.3.2 Real space

The reduced pair correlation functions $G(r)$ of the three alloys obtained using Eq. (7.1) are shown as 3D waterfall plot as well as projected plot in Fig. 7.7. Furthermore, the Supplementary Material contains the functions visualised as movies (Sec. 7.6.3). All $G(r)$ show the shape typical of amorphous materials with oscillations representing the shell-like structure up to high distances. For all three alloys an increasing split of the second NN shell with increasing undercooling is visible. The most prominent difference between $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ and the two Zr-bearing alloys is the developing shoulder on the low- r part of the first NN shell for the latter two alloys (Fig. 7.7 second row). To highlight these changes more clearly difference functions according to $\Delta G(r) = G(r, T) - G(r, T_{\text{start}})$ were calculated (Fig. 7.7 bottom row).

In the following structural metrics derived from the peaks in $G(r)$ using the shell/anti-shell concept (Ch. 5) will be discussed. Compared to the reciprocal space a bigger number of peaks (representing NN shells) for each alloy will need to be compared and discussed. Therefore only normalised data that will be considered here. Figure 7.8 shows the positions of the centroids $r_{n,c}(T)$ of the first 8 NN shells ($n = 1 \dots 8$) for the three alloys ($n = 8$ only for $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ due to strong scatter for the other two alloys) in various compositions to facilitate the discussion. The comparison of all NN shells in Fig. 7.8a immediately shows the first NN shell to behave very differently from all other NN shells, especially in the undercooled liquid regime where an *apparent* negative thermal expansion seems to take place

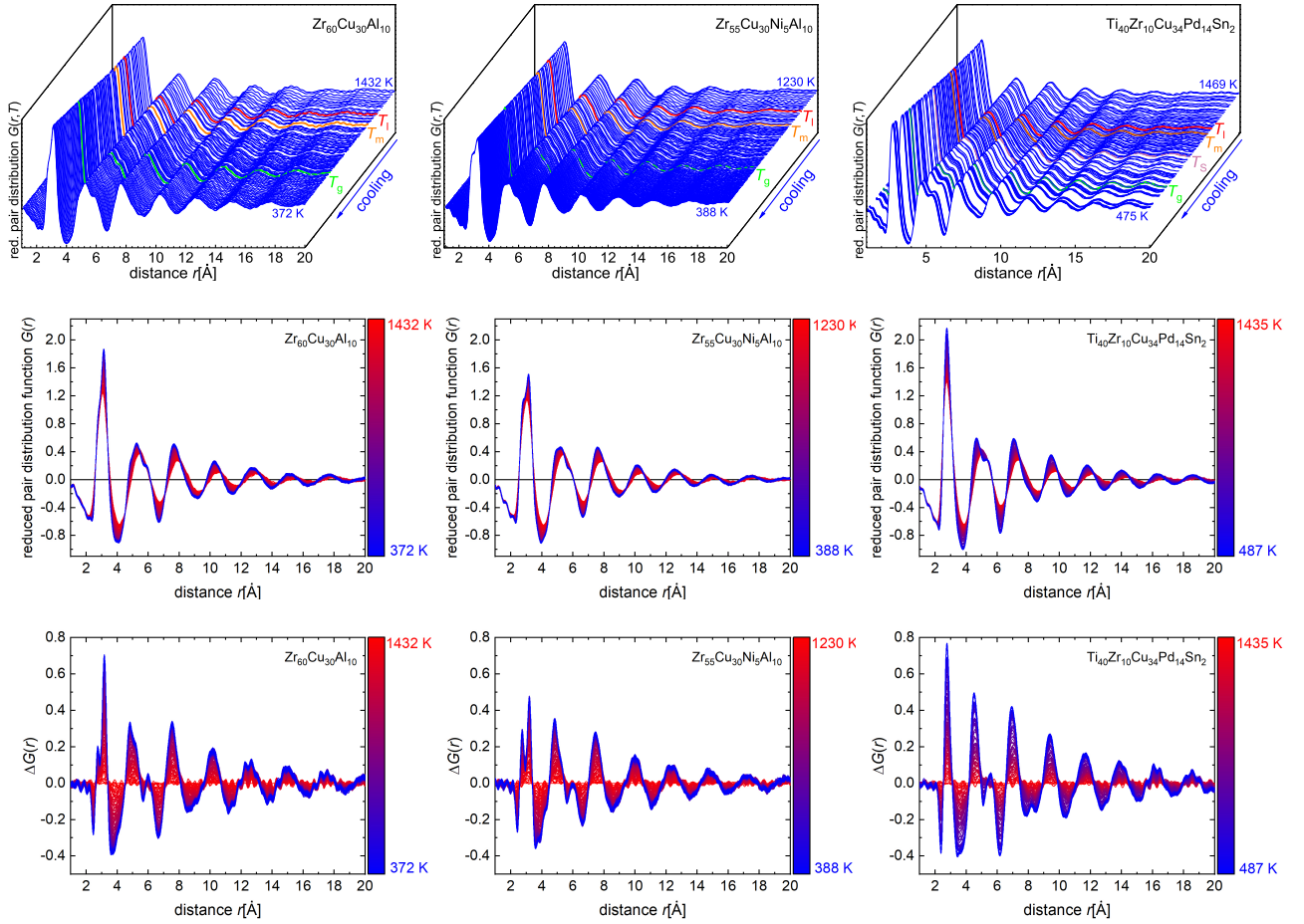


Figure 7.7: Temperature-dependent reduced pair distribution functions $G(r)$ of $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$, $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ and $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ as 3D waterfall (first row), projected onto one plane as well as changes $\Delta G(r, T) = G(r, T) - G(r, T_{\text{start}})$. Structure factors (first row) for special temperatures are highlighted by colours: $G(r, T_l)$ (red), $G(r, T_m)$ (orange), $G(r, T_s)$ (lilac; for $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ only) and $G(r, T_g)$ (green). In the second and third row a continuous colour scale is used to indicate the temperature change (from red at high T to blue at low T .)

[Mat03, Jia10, Geo11, Lou13, Mat13, Din14a, Geo15]. In Fig. 7.8b, and magnified in Fig. 7.8c, only data for the first NN shells are shown revealing a sharp change from apparent negative to positive thermal expansion at T_g . All other NN shells show positive thermal expansion for the complete investigated T -range. In computer simulations distances in the second NN shell where associated with the interconnection of coordination polyhedra (clusters) sharing different number of atoms [Ben72, Din15]. According to these simulations, atoms in the second NN shell can be found at distances $2r_{1,c}$, $\sqrt{3}r_{1,c}$, $\sqrt{\frac{8}{3}}r_{1,c}$ or $\sqrt{2}r_{1,c}$ if their coordination polyhedra share 1, 2, 3 or 4 atoms with coordination polyhedra of atoms located at $r = 0$ Å, respectively. Given the opposite shift of NN shells 1 and 2 for $T > T_g$ these relations are not valid in the undercooled liquid. Figure 7.8d-f shows the positions of the centroids for NN shells 2 and 3. Two "branches" seem to exist (Fig. 7.8d). For $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ and $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ data for

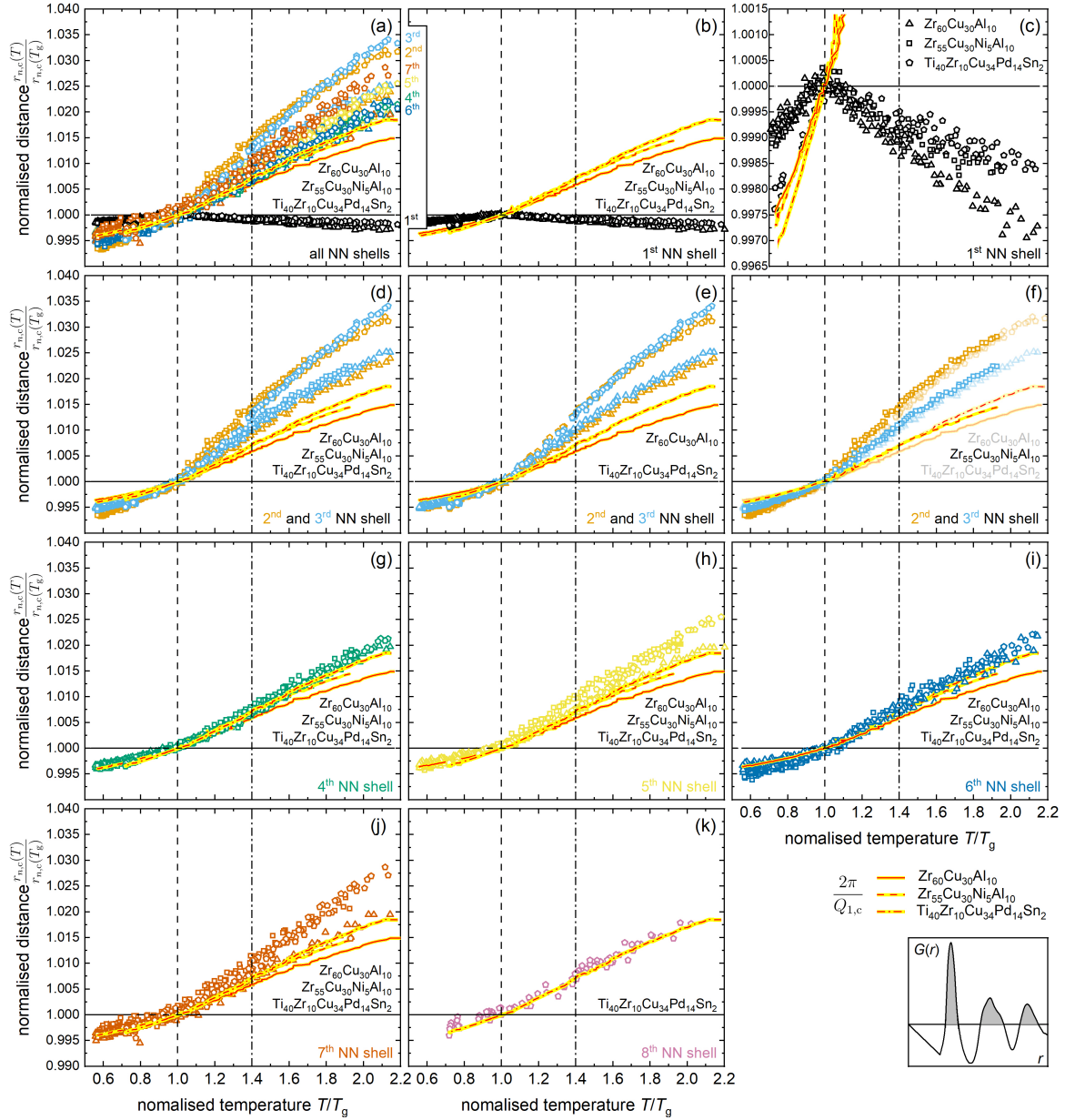


Figure 7.8: Temperature-dependent distances of centroids of the NN shells for the three alloys $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$, $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ and $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$. The temperature axis is normalised to the respective T_g and the distances to their respective values at T_g . For comparison the distances for all NN shells (1 through 8) are shown in (a). The values for the first NN shell shown in (b) are magnified in (c) to highlight the change from negative to positive thermal expansion at T_g . In (d), (e) and (f) values for NN shells 2 and 3 are shown in different combinations. Values for NN shells 4,5,6 and 7 are shown in (g), (h), (i) and (j). Due to strongly scattered data for $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ and $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ values for NN shell 8 (i) are only shown for $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$. In all sub-figures red lines showing $2\pi/Q_{1,c}(T)$ (normalised to their values at T_g) are plotted for $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ (solid), $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ (dashed) and $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ (dash-dotted). A yellow background is used to enhance visibility of these lines. The schematics in the bottom right shows the areas (grey) of $G(r)$ integrated (Eq. (7.2)) to obtain the positions of the centroids.

NN shells 2 and 3 is located on the same branch for each alloy (Fig. 7.8e). Contrary to that, for $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ data of NN shells 2 and 3 *do not* behave identical (Fig. 7.8f) and NN shell 2 of $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ behaves like NN shell 2 for $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ whereas NN shell 3 of $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ like NN shell 3 for $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ (Fig. 7.8f). While for NN shell 4 and 6 all three alloys behave virtually identical, for NN shell 5 and 7 $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ show somewhat lower values compared to the two other alloys. It is currently not clear whether the latter is a structural effect or an artifact only. In summary, the three alloys mainly differ in the first three NN shells whereas for higher NN shells a more or less common behaviour can be noted, corroborating earlier findings (Ch. 5 and 6).

Figure 7.9 shows the heights of the peaks representing the NN shells. In contrast to the position of the centroid (Fig. 7.8) which represent the entire peak (Eq. (7.2)) the heights may relate to a dominant partial contribution (partial pair distribution) only. This is schematically shown in the inset in Fig. 7.9e where for the second NN shell the height is dominated by the feature in the centre of the peak but the shoulders at the low- and high- r side (and their origin) would be neglected by this metric. Although the salient asymmetry of the first NN shell of the two Zr-based alloys sets them apart from $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ (Fig. 7.7) the normalised heights evolve strikingly similar, again especially for $T < T_g$ (Fig. 7.9). Nevertheless, $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$, exhibiting the most pronounced split in the first NN shell, deviates somewhat from $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ and $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ which behave very similar to each other. For the second NN shells again a comparable behaviour of all three alloys is visible, where it is now $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ which deviates the most probably owing to its most pronounced split there. Furthermore, a change of behaviour around $1.4 T_g$ is visible. It is interesting to note the normalised heights of all three alloys for NN shells 1 and 2 are very close to each other (Fig. 7.9c-f). From NN shell 3 onwards a different behaviour, i.e. stronger T -dependence above T_g , but common for all three alloys can be observed (Fig. 7.9g-k). Especially for NN shell 4 and beyond all NN shells evolve similar (Fig. 7.9l), but the strong scatter of the data prevents a more detailed analysis. Still, this corroborates the observed common behaviour of many glasses for higher distances in real space (NN shell 4 and beyond) [Ryu20] where individual atomic properties have averaged out (Ch. 5). Given the characteristic shapes of the first three NN shells, strongly influenced by the partial pair distribution functions due to the many different elemental pairs, it might not be meaningful to compare the height of the peaks for the according distances at all.

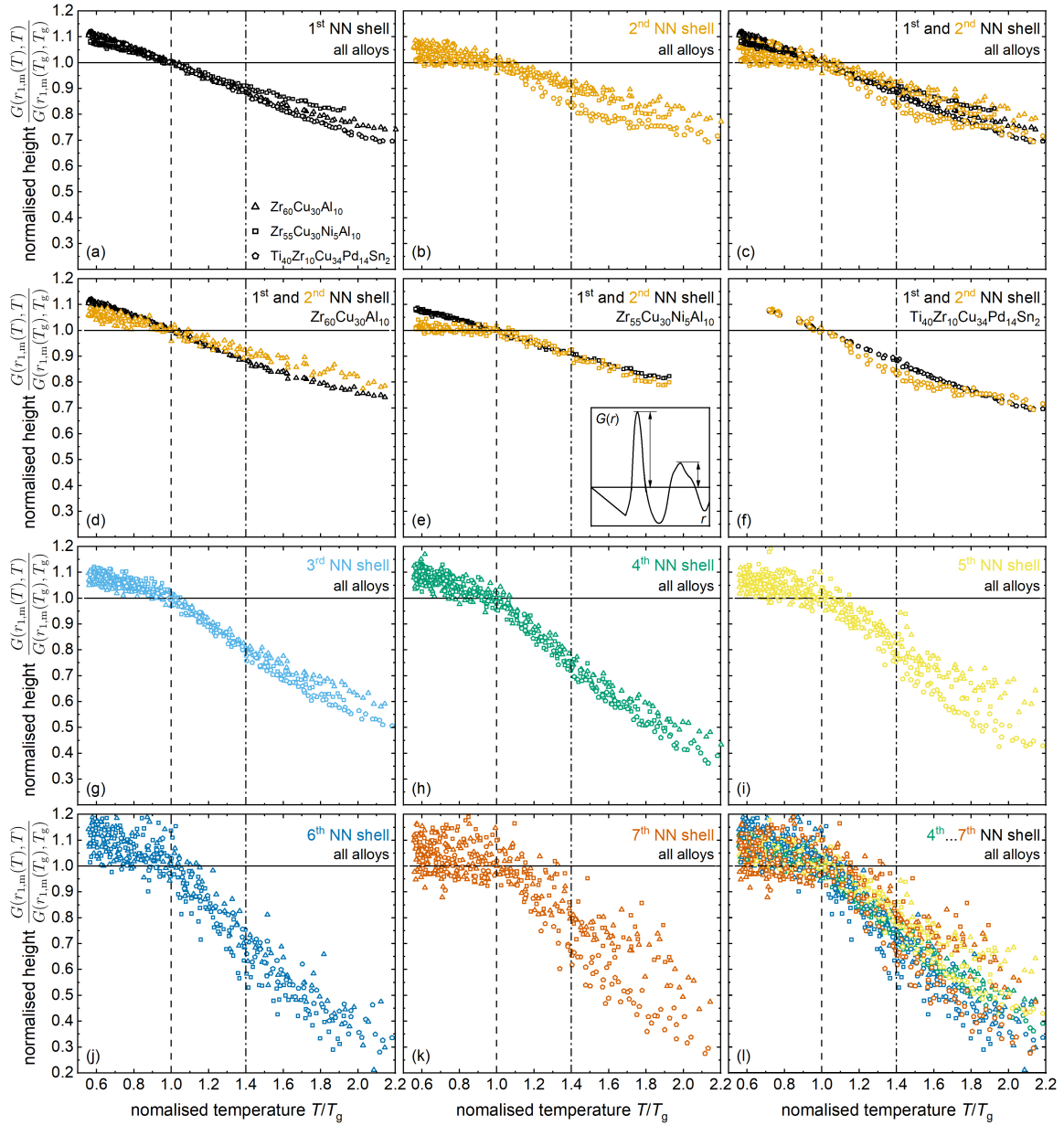


Figure 7.9: Temperature-dependent heights of NN shells 1 to 7 for the three alloys $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$, $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ and $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$. The temperature axis is normalised to the respective T_g and the heights to their values at T_g . For better comparison values for NN shells 1 and 2 are shown in different combinations in **a-f**. In **(l)** the values for NN shells 4-7 for all three alloys are shown together. The inset in **(e)** shows schematically what "height of a peak" refers to.

Figure 7.10 shows the normalised second moments as measure for the width of the peaks representing the NN shells. Due to strong scatter of data for higher NN shells Fig. 7.10a-e only depicts data for NN shells 1...5. Increasing structural order during undercooling is expected to cause a reduction of the width of peaks (cf. e.g.

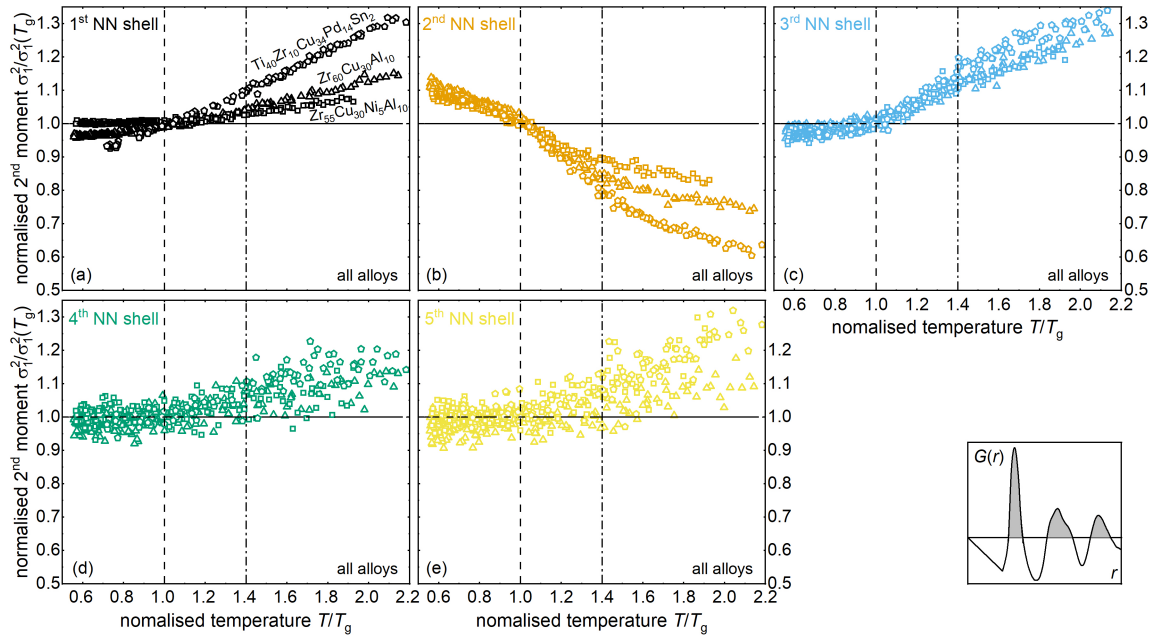


Figure 7.10: Temperature-dependent second moments (variance) of the peaks representing the NN shells. Data for NN shells 6 and above exhibits scatter too strong for a meaningful discussion. The schematics in the bottom right shows the areas (grey) of $G(r)$ integrated (Eq. (7.3)) to obtain the second moments of the centroids.

Ch. 5 or refs. Dmo07 and Ton15). Indeed, this can be observed for most of the shells (Fig. 7.10). Interestingly, the second moment of the second shell increases with progressing undercooling, which is probably related to its more complex structure with developing shoulders and an increasing split (Fig. 7.7). Also for the second moment $1.4 T_g$ seems to be a special temperature below which data for all alloys converge to the same T -dependent behaviour (especially visible for second and third NN shell, Fig. 7.10b,c). For higher NN shells an identical trend can be surmised, but the strong scatter prevents a more detailed analysis. The main differences between the alloys are again visible for the first and second NN shell. Reviewing the information gathered by analysis of the structural metrics so far, it seems that $1.4 T_g$ [Sok16] indeed plays a special role. This is most pronounced in $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ and an identification with the characteristic temperature $T_S \approx 1.36 T_g$ seems conclusive. Revisiting the waterfall plots in Fig. 7.7 (lilac curve) it seems $1.4 T_g$ might also be related to the $G(r)$ for which the split of the second NN shell in $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ becomes recognisable.

quantity	Zr ₆₀ Cu ₃₀ Al ₁₀	Zr ₅₅ Cu ₃₀ Ni ₅ Al ₁₀	Ti ₄₀ Cu ₃₄ Pd ₁₄ Zr ₁₀ Sn ₂
d_c	8 mm [Zha10]	30 mm [Ino96]	12 mm [Zhu12]
$T_{\max}$	1476 K	1348 K	1480 K
T_{start}	1432 K	1300 K	1435 K
T_A	1342 K	1366 K	1378 K
T_l	1207 K [Geo15]	1156 K [Har10]	1187 K [Zhu08]
T_m	1123 K (Ch. 5)	1028 K [Har10]	1126 K [Zhu08]
T_D	939 K [Geo15]	956 K [Har10]	964 K [Zhu08]
T_X	755 K [Zha10]	751 K [Har10]	739 K [Zhu08]
T_g	671 K [Geo15]	683 K [Har10]	689 K [Zhu08]
ΔT_X	84 K	68 K	50 K [Zhu08]
T_g/T_m	0.598	0.664	0.612
T_g/T_l	0.556	0.591	0.580
$\bar{\Theta}_{D,c}$ [Ho74]	282 K	286.75 K	325.98 K
$\Theta_{D,g}$	(311 ± 8) K	(342 ± 6) K	(305 ± 7) K
$\Theta_{D,l}$	(163 ± 9) K	(158 ± 9) K	(164 ± 10) K
T_{IG}	(−1332 ± 14) K	(−1142 ± 15) K	(−677 ± 15) K
C	(2560 ± 16) K	(2103 ± 15) K	(1801 ± 16) K

Table 7.1: Characteristic data of Zr₆₀Cu₃₀Al₁₀, Zr₅₅Cu₃₀Ni₅Al₁₀ and Ti₄₀Cu₃₄Pd₁₄Zr₁₀Sn₂ from this work as well as the literature: the critical casting diameter d_c for bulk glassy structure, the highest sample temperature $T_{\max}$ reached, the highest temperature for which data is discussed here T_{start} , the onset temperature $T_A = 2 T_g$ for cooperativity [Blo15, Jai16, Sok16, Gan17], the liquidus temperature T_l , the melting temperature T_m , the backbone temperature $T_D = 1.4 T_g$ [Sok16, Lan16, Gan17] the crystallisation temperature T_X , the glass-transition temperature T_g , the undercooled liquid region $\Delta T_X = T_X - T_g$, the reduced glass-transition temperatures T_g/T_m and T_g/T_l , the composition-averaged DEBYE-temperature $\bar{\Theta}_D$ [Ho74], the quasi DEBYE-temperature in the glassy state $\Theta_{D,g}$, the quasi DEBYE-temperature in the liquid state $\Theta_{D,l}$, the ideal-glass temperature T_{IG} (Eq. (7.5)) [Ryu19], the quasi CURIE-constant C (Eq. (7.5)) [Ryu19]. The shown characteristic temperatures T_l , T_m , T_X and T_g where obtained by differential scanning-calorimetry (DSC).

7.4 Discussion

Despite some characteristic differences the similarity of the three alloys Zr₆₀Cu₃₀Al₁₀, Zr₅₅Cu₃₀Ni₅Al₁₀ and Ti₄₀Cu₃₄Pd₁₄Zr₁₀Sn₂ in many different metrics in reciprocal as well as real space is intriguing and suggest possible universalities in the (structural) behaviour of metallic glasses during glass formation.

7.4.1 Structural CURIE-WEISS behaviour

Most notably such a universal behaviour becomes visible in $S(Q_{1,m}(T), T)$ (Fig. 7.5 first row), or $S(Q_{1,m}(T), T) - 1$, which was recently [Ryu19] shown to be describable by a

CURIE-WEISS-like behaviour according to

$$S(Q_{1,m}(T), T) - 1 = \frac{C}{T - T_{IG}} \quad . \quad (7.5)$$

Such a behaviour is originally known from the description of magnetic ordering [Ash76]. Here T_{IG} is a characteristic temperature at which $S(Q_{1,m}(T), T) - 1$ diverges (IG stands for *ideal glass* [Ryu19]) and C is an alloy-specific constant (analogous to the CURIE constant in the magnetic case). As T_{IG} was found to be exclusively negative [Ryu19] for a range of different metallic glasses (mostly MD-simulated) it seems that the evolution of structural order during undercooling can be likened to antiferromagnetic or spin-glass behaviour. Fitting Eq. (7.5) to $S(Q_{1,m}(T), T) - 1$ in the present case yields the magenta solid curves in Fig. 7.4 (first row) (parameters in Tab. 7.1). The excellent agreement highlights that the evolution of the structure, in particular the distance ranges represented by the first halo in $S(Q)$ [Car75], can be described as a smooth (non-linear) behaviour with an increasing slope upon progressing undercooling. This hints an acceleration of the ordering processes taking place as already pointed out in previous studies (experiment as well as simulation) [Che08, Lou11, Zha11, Sok13, Geo15] (cf. also Ch. 2). However, the excellent applicability of Eq. (7.5) contradicts previous studies where linear functions were used to fit the data (with a single slope due to insufficient data [Mat03, Mat04, Jia10, Joh14]; with a change of slope or the departure from a linear function at a certain T to model possible LLCs in complete datasets [Geo15, Lan16]). In other studies linear fits were used to extrapolate $S(Q_{1,m}(T), T)$ at high T towards T_g showing a mismatch with available data at T_g [Mau14, Kel17]. The extent of this mismatch was used to construct a structural measure of fragility [Mau13, Mau13a]. Although this already indicated that somewhere during undercooling a change in behaviour, especially an accelerated ordering, must occur a deeper understanding was, and actually still is, missing. With the knowledge of the non-linear behaviour of $S(Q_{1,m}(T), T)$ the validity, in a quantitative way, of this measure of fragility is questionable as its value depends on the temperature interval from which the supporting points for the fit are taken. Not only in this respect it would be desirable to probe in future experiments up to which T a description in terms of Eq. (7.5) is valid. Comparison of $S(Q_{1,m}(T), T)$ for $Zr_{60}Cu_{30}Al_{10}$ in Fig. 7.4 with results published previously for this alloy [Geo15], where two linear functions were used to fit the data, highlights the great care that needs to be taken when interpreting T -dependent structural data. To emphasise this Fig. 7.11 shows several examples for fits of Eq. (7.5) to published

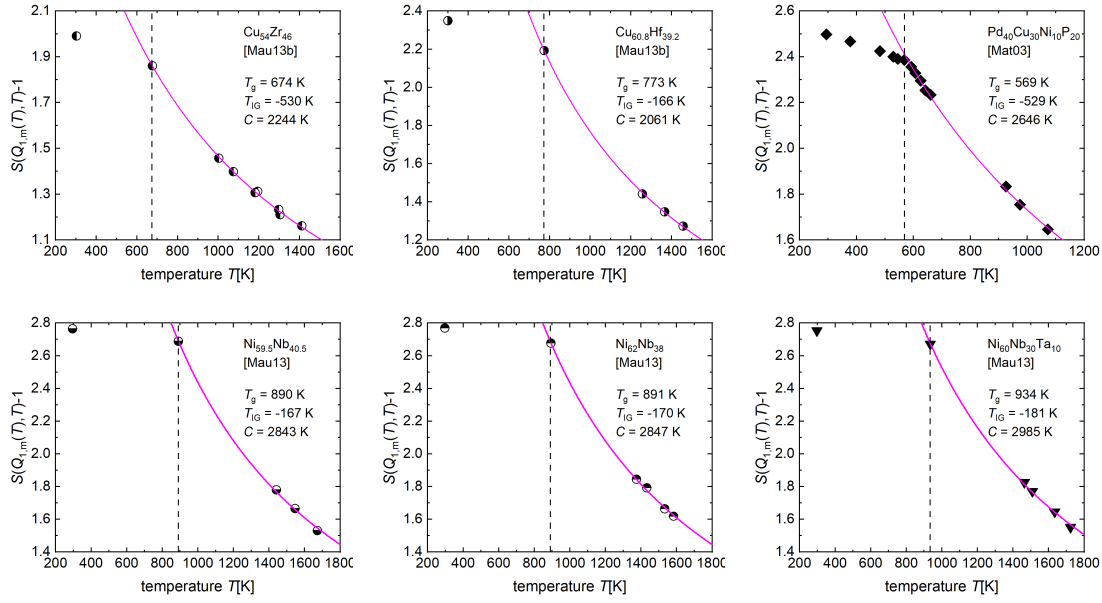


Figure 7.11: Fits of Eq. (7.5) to data above T_g for several different metallic glasses taken from the literature [Mat03, Mau13, Mau13b]. The resulting parameters C and T_{IG} are shown next to the graphs for each alloy. The vertical lines mark the according T_g .

data of $S(Q_{1,m}(T), T)$ taken during experiments upon heating where previously linear dependences were assumed. For a more quantitative analysis the parameters C and T_{IG} derived from the fits would need to be correlated to T_g as well as the viscosity η . Unfortunately, $S(Q_{1,m}(T), T)$ is much more susceptible to different experimental conditions than e.g. the peak position which makes a comparison of data taken by different authors less reliable. However, the general applicability of Eq. (7.5) still shows the smooth non-linear behaviour of $S(Q_{1,m}(T), T)$. Harnessing the very similar experimental conditions for the three alloys in focus here, indeed a (linear) correlation of C and T_g seems to occur (Tab. 7.1) where a higher C correlates with a lower T_g after $T_g \approx -0.024C + 733$ K. Other things being equal, the quasi CURIE-constant C describes the accelerated increase of $S(Q_{1,m}(T), T)$ upon cooling where a bigger C means a stronger "upturn", i.e. faster structural evolution. Such a behaviour bears some resemblance with the temperature dependence of the viscosity related to the fragility of an undercooled melt [Ang88]; a bigger C (assuming constant T_{IG}) might be related to a higher fragility. A close relation between the structural evolution and viscosity has been reported before based on structural metrics in real space for $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ [Lou11]. The present analysis hints at a relation with structural metrics in reciprocal space. With further experimental input it might be possible to construct a quantitative structural measure of viscosity valid for many metallic-glass forming alloys. For a more

detailed comparison $\eta(T)$ needs to be known over a T -range comparable to that for structural data (currently $\eta(T)$ is known for a few 100 K for each of the three alloys only [Yam05, Mau14, Geo15] and Ch. 6). With above relation between C and T_g higher fragility might be directly related to a lower T_g and a more direct link between accelerated ordering during undercooling and glass formation / transition may be established. Furthermore, this would allow to predict T_g of an alloy even if a sample crystallises during undercooling if available data for $S(Q_{1,m}(T), T)$ at high T are sufficient for a reliable fit of Eq. (7.5). A possible correlation of T_{IG} and T_g may be possible too, but its mathematical structure seems less obvious. It needs to be kept in mind that the structural changes during undercooling are a sum of both thermal vibration (DEBYE-WALLER) and structural evolution and both will enter C and T_{IG} which complicates their interpretation. Currently, Eq. (7.5) was rationalised for $S(Q_{1,m}(T), T)$ only [Ryu19] but the curvature in the other structural metrics, showing a similar curvature, should be related.

Taking only the observed behaviour of $S(Q_{1,m}(T), T)$ into consideration no LLCs seems to occur in any of the three alloys investigated here, i.e. with the applicability of Eq. (7.5) no distinct temperature where a change from one linear function to another or deviation from linear behaviour occurs [Geo15, Lan16] can be identified. However, in the case of $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ a clear change of slope appears in the asymmetry $\Lambda(T)$ (Figs. 7.4 and 7.6) at $T_S = 1.36 T_g$ (being close to $T_D = 1.4 T_g$) which is also reflected in other metrics for this alloy. This points to a possible LLC in the case of $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ after all which might be related to a fragile-to-strong transition (Ch. 6). The question that remains is if the two Zr-based alloys do not exhibit a similar effect or if it is too subtle to be recognised. For other Zr-based alloys a strong cooling-rate dependence of LLCs could be shown [Jon19], where with increasing cooling rates the visibility of LLCs in structural metrics decreases. Since the aerodynamic levitation technique employed here results in much higher cooling rates compared to other investigations reported in literature possible LLCs may be bypassed altogether (cf. Ch. 2). Interestingly, the smallest cooling rates near T_S in the present study indeed occur for $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ (Fig. 7.2). Although, they are still much higher than those for reports in the literature this may still be a clue as to why it is only $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ that shows signs of an LLC among the three alloys in the focus here. The existence of T_S for $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ hints at three distinct non-crystalline structural regimes during vitrification (high-temperature liquid (HTL) for $T \gtrsim T_S$; low-temperature liquid (LTL) for $T_S \gtrsim T \gtrsim T_g$; glass for $T_g \gtrsim T$) in this alloy. This resembles ANGELL's three

domains of interest for non-crystallising liquids [Ang08] which has been pointed out before [Geo15] (cf. also Ch. 6). The absence of equally as clear indications of LLCs for $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ and $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ does not exclude the presence of the three regimes in these alloys altogether. Experiments with smaller cooling rates are constrained by the high critical cooling rates to prevent crystallisation. However, it may still be possible to reduce the cooling rate in the expected temperature range for the LLC ($\approx 1.4 T_g$) since in this respect the goal of in-situ-monitored vitrification would be subordinate. Vice versa, it would be interesting to use aerodynamic levitation to investigate if the alloys studied in ref. Jon19 still show structural signs of an LLC at considerably higher than the reported cooling rates.

7.4.2 DEBYE-like behaviour

The temperature range below T_g , where the almost constant width of the first halo (Fig. 7.6) points to mainly thermal vibrations having an effect on the atomic structure, can be fitted to obtain DEBYE-like characteristic temperatures Θ_D of the alloys [Nag77, Man84, Sin89, Mat03]. Assuming a constant Θ_D in the temperature interval $T_1 \leq T \leq T_2$ a structure factor $S(Q, T_2)$ can be calculated from $S(Q, T_1)$ by [Sin89]

$$S(Q, T_2) - 1 = (S(Q, T_1) - 1)e^{-2[W(Q, T_2) - W(Q, T_1)]} \quad (7.6)$$

with

$$W(Q, T) = \frac{3}{2} \frac{\hbar^2 Q^2}{M k_B \Theta_D} \left(\frac{T}{\Theta_D} \right)^2 \int_0^{\frac{\Theta_D}{T}} \left(\frac{1}{2} + \frac{1}{e^z - 1} \right) dz \quad (7.7)$$

where $e^{-2W(T)}$ is the DEBYE-WALLER factor, $\hbar$ the reduced PLANCK constant, k_B the BOLTZMANN constant and M the average atomic mass of the alloy. This method has been applied for several different amorphous alloys [Sin89, Mat02, Mat03, Mat07a, Mau13, Mat13, Jia10]. Vice versa, known structure factors $S(Q, T_1)$ and $S(Q, T_2)$ can in principle be used to determine Θ_D of an alloy [Sin89, Mat02, Mat03, Mat13, Mau13a]. Following the procedure outlined in ref. Mat03 a least-squares fit of Eq. (7.6) to the complete range of structural data for $T < T_g$ has been performed for the three alloys. The values for the resulting $\Theta_{D,g}$ can be found in Tab. 7.1 and are comparable to average values calculated from the DEBYE temperatures of the crystalline elements [Ho74]. This

shows the validity of the approach. Accordingly, the calculation of a structure factor for a chosen $T < T_g$ by extrapolating another one in the glassy state yields good agreement in terms of peak height. However, this method does not take into account the shifting peak position due to thermal expansion, let alone that during structural evolution in the undercooled liquid state. Nevertheless, the literature reports cases where this method has also been applied for $T > T_g$ in order to distinguish the effect of thermal vibrations from that of structural changes in the undercooled liquid [Mat02, Mat03]. However, the determination of a $\Theta_{D,l}$ in the same way as used for $\Theta_{D,g}$ is questionable since due to the structural changes a "new" material with a different Θ_D at each $T > T_g$ emerges. The fit procedure used "is not aware" of this circumstance and assumes a constant Θ_D over the complete fitted T -range. This leads to $\Theta_{D,l}$ being different from $\Theta_{D,g}$ by about a factor 2 in the literature [Mat02, Mat03] as well as in the present case (Tab. 7.1). At best, an $S(Q, T)$ for $T < T_g$ could be extrapolated to one for $T > T_g$ using $\Theta_{D,g}$ for qualitative assessment of structural changes there. This again neglects the changing peak positions which can shift in opposite directions for different Q regions in $S(Q)$ (Fig. 7.5). It should be mentioned that a fit of Eq. (7.6) to the structural data for $T > T_g$ yields a curved function that can approximate the measured $S(Q_{1,m}(T), T)$ virtually equally as good as the CURIE-WEISS law (Eq. (7.5)) discussed above. The latter may even define an inherent temperature scale for the structural changes taking place during undercooling and glass-formation. While both Eq. (7.5) and Eq. (7.7) describe $S(Q_{1,m}(T), T) - 1$, not $S(Q_{1,m}(T), T)$, the former focusses on the structural evolution neglecting the thermal oscillations of the atoms the situation is reversed for the latter. A correct description would need to incorporate both effects as a separation solely based on experimental data seems impossible. In simulations, however, the structural evolution could be stopped at any temperature along the pathway and thermal vibrations be analysed independently for the according instantaneous structure.

7.4.3 Relations between real and reciprocal space

Comparison of all normalised metrics in reciprocal as well as real space exhibits that $T = 1.4 T_g$ is not only special in the case of $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ but seems to be a characteristic temperature for all three alloys below which the metrics converge and show universal behaviour independent of the particular alloy. The higher the distance in real space the less pronounced is the change of behaviour at $T = 1.4 T_g$ and from the fourth NN shell onwards all alloys are virtually indistinguishable in their normalised

metrics over the complete investigated T range (Figs. 7.8, 7.9, 7.10). This also confirms earlier observations whereafter the real-space structure at high distances is less strongly dependent on the particular composition of a (metallic) glass [Ryu20]. If, however, it would solely be the first halo in $S(Q)$ that represents the r -range from NN shell 3 and beyond [Car75, Ryu20] its T -dependence should be identical among the three alloys which is not the case. The Supplementary Material (Sec. 7.6.1) contains a movie which uses a varying $Q_{\max}$ (Eq. (7.1)) in the FOURIER transform to illustrate the relation between Q -ranges in reciprocal space and r -ranges in real space (Sec. 7.6.1). From this it can be seen that not only the first halo but also (parts of) the second halo are necessary to correctly determine the structural features at distances related to NN shell 3 and beyond. Comparing the positions of the first and second halo (Fig. 7.5) an opposite variation with T can be seen, where the combined effect may cause the similar structural evolution for all three alloys at high distances in real space (Fig. 7.8). The T -dependence of the position of halos and NN shells also helps to establish the relation between relevant Q and r ranges even further. Halo 1 in reciprocal space shifts to higher Q upon cooling and NN shells for higher distances in real space accordingly shift to lower r . Halos 2 and 3 shift to higher Q and accordingly NN shell 1, at least above T_g , shifts to higher r . This not only illustrates the reciprocal relationship between both spaces but at the same time also a symmetry between them which is indicated by the shift of the positions of the first halo/shell being opposite to that of the higher halos/shells (Figs. 7.5 and 7.8). Such results can only be obtained by temperature-dependent structural measurements. The almost T -independent positions of halos 2 and 3 below T_g point to an almost fixed structure for small distances (short-range order, SRO) in real space in the glassy state. This may correlate with the short-range structures being dominated by relatively rigid clusters [Mir04] while thermal expansion is determined mainly by the inter-cluster length scale, i.e. medium-range order (MRO). Indeed, below T_g NN shell 1 shows a much weaker expansion behaviour than the higher NN shells (Fig. 7.5). Above T_g less strongly bound atoms can be expelled from the clusters allowing denser packing and causing the apparent negative thermal expansion of the first NN shell [Lou13]. The red lines in Fig. 7.5 show the (normalised) inverse position of the first halo in $S(Q)$. Provided that the shift of the first halo is related to the macroscopic thermal expansion [Yav05] it is NN shells 4 and beyond, but not the first three NN shells, that are responsible for expansion in real space for the glassy state ($T < T_g$). For $T > T_g$ the distances are influenced by a blend of thermal expansion and structural evolution which is reflected by a weaker correlation between

the shift of the first halo (red lines in Fig. 7.5) and that of NN shells 4 and beyond. No correlation with the behaviour of the first three NN shells ($T > T_g$) is visible. The relatively good agreement of the red lines with the positions of the higher NN shells (Fig. 7.5) also points to a possible global electronic influence on the structure formation in $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$, $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ and $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$.

7.4.4 The influence of global electronic interactions

As previously shown for $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ (Ch. 6) the distances of the NN shell can be described by invoking the effect of global electronic interactions on structural ordering in amorphous materials [Nag75, Hau92, Now99, Sti19]. For the undercooled liquid this was the case only for distances starting from the fourth NN shell. Pivotal for the analysis of the influence of global electronic interactions are the positions Q_1 of the first halo in $S(Q)$ and their change with temperature. The positions of the NN shells should then be describable by [Hau92]

$$r_n = \left(\frac{1}{4} + n \right) \frac{2\pi}{Q_1} \quad . \quad (7.8)$$

Comparing the positions of the centroids of the NN shells to $\frac{2\pi}{Q_{1,c}(T)}$ (normalised to the values at the respective T_g) is a simple way of testing the validity of this concept (red lines on yellow background in Fig. 7.8; $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$: full, $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$: dashed, $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$: dash-dotted). Contrary to the assumption of previous studies [Hau92, Hau05, Gil16] that did not have access to the T dependence, not all NN shells follow the distances prescribed by the Eq. (7.8). It is mainly the positions of NN shells 4 and above that show according agreement even if not over the complete T -range. The agreement is worst at high temperatures but becomes better during progressing undercooling, especially below $\approx 1.4 T_g$. In the glass phase a very good agreement is obvious (Fig. 7.5). This corroborates the conjecture that a global electronic description is limited to higher distances in $G(r)$ (Ch. 6). Discussing measurements in the glass phase at constant T cannot provide this information and misinterpret the extent of the global electronic influence on structure formation.

7.4.5 Short range order versus medium range order

In literature a distinction between SRO and MRO is frequently made where often only the first NN shell is referred to as SRO [She06, Ma15, Yan21]. Considering the

T dependence of the centroids of the NN shells (Fig. 7.8) the unique (expansion) behaviour of the first NN shell would support this view. However, in comparison to all other NN shells, also NN shells 2 and 3 behave differently (from NN shell 1 as well as from all higher NN shells) as is obvious from several metrics (Figs. 7.8,7.9,7.10). This view is also supported by measurements in the glass phase at constant T but varying composition, in particular analysing the influence of small addition of Ni or Co to $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ (Ch. 5). This questions the "traditional" demarcation between SRO and MRO between the first and second NN shell. Given the similar behaviour of NN shells 2 and 3, but at the same time the differences in their behaviour compared to NN shell 1 as well as 4 and beyond, a future classification may distinguish further categories. As a proposal, MRO would only comprise NN shells 2 and 3 while NN shells 4 and beyond could for instance be referred to as ERO (extended-range order). There the individual properties due to many different atomic pairs have averaged out and global electronic influences play a major role (Sec. 7.4.4). Aspects of these different length scales may have different influence on GFA. In this respect it is interesting to note that for $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$, having the best GFA among the three alloys considered here (see d_c in Tab. 7.1), the normalised positions of the centroids of NN shells 2 and 3 *do not* coincide, contrary to those of $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ and $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ (Fig. 7.8). To investigate the underlying reason for this difference and its possible connection to GFA knowledge of the partial structure factors and pair distribution functions seems to be essential. Given the number of components and the related experimental complexity (cf. Ch. 2) future atomistic simulations are inevitable for their determination.

7.5 Conclusions

Results originating from a comparative study of the atomic structure of $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$, $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ and $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ monitored in-situ along their pathways from the high-temperature equilibrium liquid, during undercooling, through their vitrification and in the subsequent glassy state were presented. Despite an overall very similar behaviour of $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$, $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ and $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ several characteristic differences exist. Normalised to their values at the glass-transition temperature many of the structural metrics analysed point to universal behaviour among the three alloys. The validity of a recently proposed structural analogue to the CURIE-WEISS law could be shown in all three alloys and a possible correlation with the glass-transition temperature be suggested. The main property that sets $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$, having the

highest glass-forming ability, apart from the other two alloys is the different behaviour of the temperature-dependent positions of the second and third nearest-neighbour shells upon cooling. This also breaks the expected trend of increasing glass-forming ability from $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ over $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ to $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ suggested by INOUE's empirical rules. Once again, this highlights that quantities and properties beyond the number of components, their different sizes and enthalpies of mixing among them need to be considered when assessing glass-forming ability. Prominent indications for a possible liquid-liquid crossover at $T \approx 1.4 T_g$ could only be found in $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$. Nevertheless, $T \approx 1.4 T_g$ seems to be a characteristic temperature for all three alloys below which the universal behaviour becomes particularly obvious. In the literature, this temperature has been associated with the onset of the rapid formation of backbones from previously isolated individual clusters or smaller cluster assemblies. It could, therefore, be argued that during this process an alloy's individuality is replaced by universality. For further insights the pathway of more alloys, spanning a wide range of glass-forming ability, needs to be investigated as well as simulations be performed. The latter is especially necessary to unveil the distinct influence of partial structure functions. Temperature-dependent measurements of structural metrics are key in understanding the extent of global electronic influences on structure formation along the pathway and also help to clarify the relation of structural features in real and reciprocal space. Using structural metrics that involve an integration over peaks, i.e. second moment instead of the FWHM or positions of centroids instead of maxima, should be favoured. This does not only reduce scatter but also provides physical information about the entire halo or nearest-neighbour shell represented by that peak instead about dominant individual features only.

7.6 Supplementary Material

7.6.1 Visualising the FOURIER transform

The movie under cord.cranfield.ac.uk/account/projects/121164/articles/16406340 shows $G(r)$ calculated with varying $Q_{\max}$ in Eq. (7.1) (moving vertical line in the inset for $S(Q)$) for glassy $\text{Zr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ at room temperature (raw data taken from Ch. 5).

7.6.2 Atomic pair data

Table 7.2 shows the interatomic distances [Mir10] d_{at} , enthalpies of mixing ΔH_{mix} [Tak05] according to MIEDEMA's model, FABER-ZIMAN weights W_{ij} (Eq. (5.2)) and probabilities for random contact P_{ij} (Eq. (5.3)) [Jel14, Ton16] for all atomic pairs in $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$, $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ and $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$.

alloy	pair i - j	d_{at} [Å]	W_{ij}	P_{ij}	ΔH_{mix} [kJ/mol]
$\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$	Zr-Zr	3.16	0.498	0.360	0
	Cu-Zr	2.84	0.361	0.360	-23
	Cu-Cu	2.52	0.065	0.090	0
	Al-Zr	2.99	0.054	0.120	-44
	Al-Cu	2.67	0.020	0.060	-1
	Al-Al	2.82	0.001	0.010	0
$\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$	Zr-Zr	3.16	0.434	0.303	0
	Cu-Zr	2.84	0.343	0.330	-23
	Cu-Cu	2.52	0.068	0.090	0
	Al-Zr	2.99	0.051	0.110	-44
	Al-Cu	2.67	0.020	0.060	-1
	Al-Al	2.82	0.002	0.010	0
	Ni-Zr	2.84	0.055	0.055	-49
	Ni-Cu	2.52	0.022	0.030	4
	Ni-Al	2.67	0.003	0.010	-22
	Ni-Ni	2.52	0.002	0.003	0
$\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$	Ti-Ti	2.84	0.085	0.160	0
	Cu-Ti	2.68	0.192	0.272	-9
	Cu-Cu	2.52	0.107	0.116	0
	Pd-Ti	2.84	0.125	0.112	-65
	Pd-Cu	2.68	0.140	0.095	-14
	Pd-Pd	2.84	0.046	0.020	0
	Zr-Ti	3.00	0.078	0.080	0
	Zr-Cu	2.84	0.087	0.068	-23
	Zr-Pd	3.00	0.057	0.028	-91
	Zr-Zr	3.16	0.018	0.010	0
	Sn-Ti	2.97	0.019	0.016	-21
	Sn-Cu	2.81	0.022	0.014	7
	Sn-Pd	2.97	0.014	0.006	-34
	Sn-Zr	3.13	0.009	0.004	-43
	Sn-Sn	3.10	0.001	0.000	0

Table 7.2: Interatomic distances [Mir10] d_{at} , enthalpies of mixing [Tak05] ΔH_{mix} , FABER-ZIMAN weights W_{ij} (Eq. (5.2)) and probabilities for random contact P_{ij} (Eq. (5.3)) [Jel14, Ton16] for all atomic pairs in $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$, $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ and $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$.

7.6.3 Visualising the structural pathway

Movies showing $S(Q, T)$ and $G(r, T)$ along the pathways of the three alloys in an animated way can be found as follows:

$\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$:

$S(Q)$: cord.cranfield.ac.uk/account/projects/121164/articles/16449033,

$G(r)$: cord.cranfield.ac.uk/account/projects/121164/articles/16449012,

$\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$:

$S(Q)$: cord.cranfield.ac.uk/account/projects/121164/articles/16449087,

$G(r)$: cord.cranfield.ac.uk/account/projects/121164/articles/16449069,

$\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$:

$S(Q)$: cord.cranfield.ac.uk/account/projects/121164/articles/16432536,

$G(r)$: cord.cranfield.ac.uk/account/projects/121164/articles/16432581.

The structure functions are coloured in red for $T > T_l$, in blue for $T_l > T > T_g$ and in green for $T_g > T$.

8 Conclusions

The structure of binary, ternary, quaternary and quinary metallic glasses has been analysed. By variation of temperature on the one hand or of composition on the other, structural aspects that may influence glass-forming ability (GFA) were investigated.

Monitoring the structural pathway of the three liquid alloys $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$, $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ and $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ in situ by synchrotron X-ray diffraction upon cooling revealed that structural metrics follow a smooth, but non-linear, relation from well above their liquidus temperatures T_l down to their glass-transition temperatures T_g . Judging from this observation an acceleration of structural ordering, as previously reported in literature, does not start below a particular temperature during undercooling but takes place along the complete pathway of the liquid metallic melt towards vitrification. This behaviour, although amplified by many orders of magnitude, is paralleled by the expected temperature dependence of viscosity in the same interval. Future investigations are needed to decide how closely both are connected and to derive a possible quantitative relation between them. Extending the structural measurements to temperatures much higher than T_l may show if a change in the temperature dependence of the metrics at $T_A = 2 T_g$, the temperature associated with the onset of cooperativity at the atomic scale in metallic liquids, takes place.

Although indications for possible liquid-liquid-crossovers (LLC) could only be found in $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$, occurring at about $1.4 T_g$, most metrics in reciprocal as well as real space show universal behaviour among the three alloys below that temperature. Since $1.4 T_g$ has also been associated with the enhanced formation of "backbones", i.e. extended networks of atomic clusters, this could signify that around this temperature individual behaviour of an alloy is replaced by a universal behaviour as common prerequisite for vitrification. In $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$ this may cause a particularly strong response causing the LLC. To check if a relation with a change in fragility exists viscosity measurements in this temperature range are inevitable. A decreased cooling rate close to $1.4 T_g$ may help to reveal indications of LLCs in the two Zr-based alloys as well if crystallisation could still be avoided.

No single structural property that can conclusively signify high GFA could be pinpointed and probably does not exist at all. Nevertheless, small structural details like the temperature dependence of the position of the second and third nearest-neighbour (NN) shell in $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$, which differs from that of $\text{Zr}_{60}\text{Cu}_{30}\text{Al}_{10}$ and

$\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$, can provide important clues in this respect. The difference is likely related to the interplay between the partial structures of the alloys hinting at structural diversity as its underlying cause. Diversity in various properties of atomic species as basis of "confusion", competition or frustration can be associated with enhanced GFA, but adjusting only an isolated source of diversity, e.g. in the atomic sizes of an alloy's components, may not necessarily add to this effect. Various sources of diversity like the different electronic structures of the components, resulting in different bonding behaviour, competing crystalline ordering mechanisms or the interplay between local and global electronic effects need to be considered as well. Diversity in a property can also emerge upon alloying due to the interaction between the components. Increasing structural disorder by varying the composition of an alloy is able to increase GFA only if at the same time not other factors, causing a decrease of GFA, are affected as well.

The analysis of the structure and changes thereof can be facilitated by the novel concept of the atomic "anti-shell" complementing the NN shell. This recognises that order does not only mean local deviations from the average density to higher but also to lower values. In combination with the use of metrics that involve an integration over a complete peak, like centroids and second moments, enables to waive fit procedures in many cases and substantially reduces subjectivity. The first NN shell, commonly associated with polyhedral clusters, shows weaker thermal expansion below T_g when compared to the other NN shells. Thermal expansion seems to be mainly related to inter-cluster distances rather than to intra-cluster distances. While below T_g the number of atoms in clusters stays constant, above T_g weakly bound atoms can be expelled from them allowing denser packing. This effect supersedes the actual thermal expansion above T_g for the first NN shell and causes its often-reported apparent negative thermal expansion there. In general, the reaction of the NN shells to changes in temperature or composition suggests to change the "traditional" division of real space into short (SRO) and medium-range order (MRO) by introduction of a third category, perhaps to be designated as extended-range order (ERO), where MRO only comprises NN shells two and three. The range of the second and third NN shell may be especially important for GFA and it is also this distance range where a competition between local and global electronic interaction would cause the biggest confusion. While SRO would still refer to the first NN shell ERO comprises NN shells four and beyond where individual properties of atoms and their various pairs have been averaged out and a description in terms of coarse-grained density fluctuations and global electronic influences takes

over. Structure formation at smaller distances, especially for the SRO, is dominated by other factors, e.g. local electronic interactions related to the shape of the interatomic potentials. The distances of the ERO reflect the macroscopic thermal expansion below T_g and approximately also above T_g .

The correlation of global electronic effects with other properties could be shown in binary Ni-Zr as well as Cu-Zr glasses and should be considered an additional factor that needs to be considered when GFA of metallic-glasses forming alloys is assessed. In this framework, an average valence of 1.5 electrons per atom showed to be pivotal for the binary glasses as well as for $\text{Ti}_{40}\text{Cu}_{34}\text{Pd}_{14}\text{Zr}_{10}\text{Sn}_2$. Exactly how global interactions between the electronic and atomic structure can enhance GFA needs to be explored in more detail by analysing additional data.

Many of the aspects discussed in this thesis need further validation by investigation of other metallic-glass forming alloys along their pathways. Furthermore, several aspects like the length scales related to global electronic interactions or thermal expansion can only be identified by temperature-dependent measurements. Therefore, the development of experimental methods allowing for a higher throughput in "pathway studies" should be approached. Extensive simulations to determine partial structure functions are necessary as well. Structural investigations need to be accompanied by measurements of other quantities, foremost viscosity, over the complete temperature interval of the pathway. Analysis of anti-shells (and anti-halos) in future studies will provide an additional set of parameters that may give further insights into the structural evolution in relation to GFA. Reduced cooling rates could be used to deliberately cause crystallisation of a sample. The occurring crystal structures can be compared to those occurring during annealing of a glass of same composition. This is interesting in terms of investigation of nucleation but also helps to identify competing structures that may help to enhance GFA by increased confusion. Diversity, confusion and frustration need to be defined in a more quantitative way to better establish connections between them.

A Publications and conference contributions

Publications and conference contributions related to the present PhD project are listed below.

Conference contributions

- *Structural features of binary amorphous Zr-TM and Al-TM alloys as an aid towards a better understanding of multinary bulk metallic glasses*, Martin E. STIEHLER, Mark R. JOLLY and Konstantinos GEORGARAKIS, oral, The 25th International Symposium on Metastable, Amorphous and Nanostructured Materials (IS-MANAM 2018), 2018, Rome, Italy.
- *Caught in the act: The glass transition in undercooled metallic liquids observed in-situ by synchrotron X-ray diffraction*, Martin E. STIEHLER, Mark R. JOLLY and Konstantinos GEORGARAKIS, oral, The 17th international conference on Liquid and Amorphous Metals (LAM17), 2019, Lyon, France.
- *Spicing up: The influence of Fe, Co or Ni additions on the structure of Zr-Cu-Al-based bulk metallic glasses*, Martin E. STIEHLER, Nikolaos T. PANAGIOTOPOULOS, A. Lindsay GREER, Mark R. JOLLY and Konstantinos GEORGARAKIS, poster, The 17th international conference on Liquid and Amorphous Metals (LAM17), 2019, Lyon, France.
- *Beating crystallisation with speed: Rapid solidification and vitrification monitored in-situ using high-energy synchrotron X-ray diffraction*, Martin E. STIEHLER, Mark R. JOLLY and Konstantinos GEORGARAKIS, poster, European congress and exhibition on advanced materials and processes (EUROMAT 2021), 2021, virtual.
- Further contributions have been postponed due to the COVID-19 pandemic.

Publications

- *On the impact of global interactions on the structure of metallic glasses*, Martin E. STIEHLER, Mark R. JOLLY and Konstantinos GEORGARAKIS, Journal of Alloys and Compounds **782** (2019) 496 (doi:[10.1016/j.jallcom.2018.12.086](https://doi.org/10.1016/j.jallcom.2018.12.086)) [Sti19] (maps on Ch. 4 of this thesis).

- *The effect of Ni or Co additions on the structure of $Zr_{60}Cu_{30}Al_{10}$ bulk metallic glass revealed by high-energy synchrotron radiation*, Martin E. STIEHLER, Nikolaos T. PANAGIOTOPOULOS, Dean S. KEEBLE, Yurii P. IVANOV, Melita MENELAOU, Mark R. JOLLY, A. Lindsay GREER and Konstantinos GEORGARAKIS (doi:[10.1016/j.mtcomm.2022.103531](https://doi.org/10.1016/j.mtcomm.2022.103531)) available online in *Materials Today Communications* (maps on Ch. 5 of this thesis).
- Manuscripts related to the other chapters of this thesis are currently under preparation for submission.

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