Decoupling of Component Diffusion in a Glass-Forming $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ Melt Far above the Liquidus Temperature

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We report ^{95}Zr and ^{57}Co radiotracer diffusivities and viscosity data in the equilibrium liquid state of a bulk metallic glass forming $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ melt (Vitreloy 4) far above the liquidus temperature T_l that are not affected by convection, as evidenced via quasielastic neutron scattering. Zr diffusion is strongly decoupled from diffusion of the smaller components by more than a factor of 4 at T_l, although it obeys the Stokes-Einstein equation. The results suggest that, in the present Zr-based metallic glass forming systems, diffusion and viscous flow start to develop solidlike, i.e., energy-landscape-controlled, features already in the stable liquid state more than 300 K above the mode coupling temperature T_c.

Metallic glasses and particularly the multicomponent bulk metallic glasses are very interesting engineering materials. They are stronger than most steels and can be molded like plastics. In addition, they exhibit intriguing functional properties [1–3]. During recent years, advanced multicomponent glass forming alloys with excellent glass forming ability also received much attention in the glass community as model systems for studying the glass transition, which is currently a very active research topic in physics [4–8]. The attraction of metallic glass formers also for researchers working on ceramic or molecular glasses or on the dynamics of liquids and melts lies in their simple structure being made up of spherical atoms without or with relatively weak directional bonding, rotational degrees of freedom, or side chains, for instance. The glass forming ability of multicomponent metallic glass formers neither arises from strong directed covalent bonding, as in the traditional oxide glasses or amorphous semiconductors, nor does it arise from structural asymmetry, as in single component molecular glass formers, but it is due to dynamic asymmetry which mainly originates from size disparity and short-range order [7,9–11]. Additional thermodynamic aspects [12–14] and the "confusion principle" [15,16] also play a role.

In an ideal liquid at high temperatures, diffusion proceeds via uncorrelated binary collisions between the atoms, and in this liquidlike diffusion regime, dynamic asymmetry should be absent, as reflected in the Stokes-Einstein relation [see Eq. (1) below] [17]. In contrast, the dynamic asymmetry is very strong in the glassy state where the atoms have to overcome high activation barriers by local hopping, and diffusivities of the larger and smaller atoms can differ by many orders of magnitude. This has already been investigated intensively in binary Zr-based glasses such as *a*-Co-Zr and *a*-Ni-Zr [18–20]. Here, even different

diffusion mechanisms were proposed for the larger Zr atoms and the smaller Co or Ni atoms. For the smaller atoms, a direct highly collective diffusion mechanism involving hopping of a large number of atoms was proposed based on the vanishing isotope effect [18] and pressure dependence [21], as well as on molecular dynamics simulations [22], where chainlike collective displacements were seen, for instance. In contrast, for the much larger Zr atoms, a pronounced activation volume of the order of an atomic volume was observed [20], suggesting a different mechanism based on the thermally activated opening of the nearest-neighbor cage which can be envisioned as being assisted by thermally generated smeared-out free volume.

A strong decoupling of the diffusivities of the larger Pd atoms and the smaller components was also seen in the supercooled liquid state of multicomponent Pd-based glass forming alloys below the critical temperature T_c of the mode coupling theory reaching 4 orders of magnitude at the caloric glass transition temperature T_g [7]. This was attributed to the freezing in of liquidlike diffusion at T_c–well above the caloric glass transition temperature—and the existence of a pronounced energy landscape and dynamic heterogeneities. Strong decoupling of the component diffusivities was also reported in Zr-based bulk glass forming alloys in the deeply supercooled liquid state [23–26]. In the equilibrium melt far above the liquidus temperature, however, the energy-landscape theory describes atoms as diffusing almost freely well above the peaks and valleys of the energy landscape, seeing only shallow minima [27]. In accord with this expectation, the diffusivities of all components of the above-mentioned Pd-based glass forming alloy were found to merge close to T_c. On the other hand, recent investigations on molecular glass formers indicate characteristics of glassy dynamics even above the melting temperature [28].

Here we report on radiotracer measurements of ^{95}Zr and
^{57}Co diffusion in the stable liquid state of a multicomponent
bulk metallic glass forming $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$
melt above the liquidus temperature. ^{57}Co is used as a
convenient and well-established tracer for Ni diffusion [4,7].
The results are compared with viscosity data obtained by an
elaborate containerless electrostatic levitation technique.
While diffusion of the large Zr atoms obeys the Stokes-
Einstein equation, a pronounced decoupling is observed
between Zr diffusion and diffusion of the smaller Co
atoms. This suggests that some signature of the aforemen-
tioned different diffusion mechanisms of the large Zr atoms
and the smaller atoms observed in the glassy state, and,
hence, strong influences of the energy landscape on dif-
fusion, is still preserved even in the stable liquid state far
above the liquidus temperature. The contrasting behavior
with respect to the Pd-based glass forming alloy mentioned
above will be discussed in terms of the sharply contrasting
electronic properties of the very reactive Zr which has
partially occupied d orbitals and can form directed bonds,
and the noble metal palladium.

The $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ glass forming alloy
(known as Vitreloy 4) was prepared and characterized as
reported previously [29]. The caloric glass transition
temperature T_g of 580 K (at 20 K/ min) and the quasieu-
tectic melting temperature T_m of 1050 K were determined
by means of differential scanning calorimetry (DSC) at a
heating rate of 20 K/ min. Microscopic dynamics in the
equilibrium liquid were studied by quasielastic neutron
scattering (QNS) and were shown to be in accordance with
the predictions of the mode coupling theory. The temper-
ature dependence of the structural relaxation times as well
as the temperature dependence of the amplitude and time
scale of a localized cage motion (fast beta relaxation)
extrapolate consistently to a T_c at 875 K [30]. For the
diffusion measurements, the radiotracer technique in com-
bination with serial sectioning and an elaborate encapsu-
lation technique in a graphite container were employed.
Radiotracer ^{57}Co was commercially available (Eckert &
Ziegler, Braunschweig, Germany), and ^{95}Zr was obtained
from neutron irradiation of enriched ^{94}Zr at Helmholtz
Zentrum Berlin. Prior to the deposition of the tracers,
cylindrical samples with 8 mm diameter and ~1 mm
thickness were polished mirrorlike at one base. The
deposition of ^{95}Zr was done electrochemically as des-
cribed, e.g., in Ref. [20], and ^{57}Co was evaporated as
described, e.g., in Ref. [7]. Because of the large penetration
depth, serial sectioning was performed by mechanical
grinding. Most of the diffusion measurements with ^{57}Co
and ^{95}Zr were carried out separately in alloys from the same
batch. Thus, possible errors due to slight variations in the
alloy composition [31] were eliminated. To rule out effects
of systematic errors, particularly in temperature, some ^{57}Co
and ^{95}Zr diffusivities were also measured simultaneously
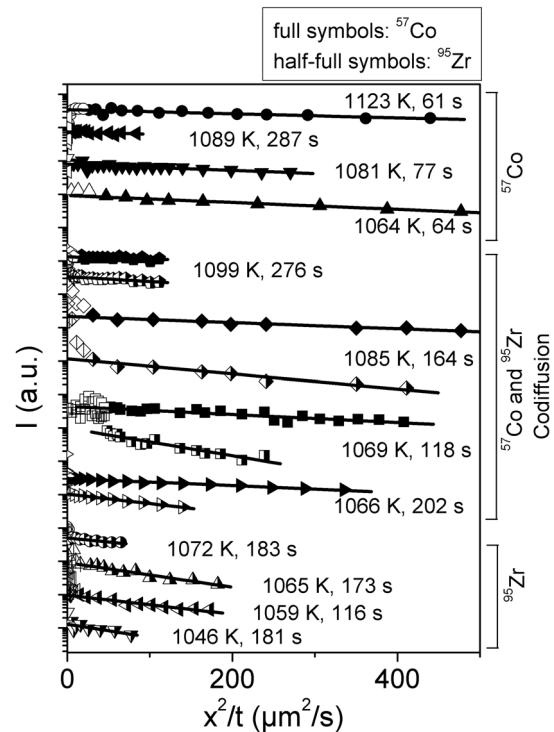(see Fig. 1 middle and Fig. 2). All the diffusion profiles are

FIG. 1. ^{95}Zr and ^{57}Co penetration profiles. The activity of ^{95}Zr
and ^{57}Co is plotted on a semilog scale vs the square of the
penetration depth divided by the annealing time. Full and half-full
symbols display ^{57}Co and ^{95}Zr diffusivities, respectively. Data
points with open symbols close to the surface are affected by
surface hold up and were not taken into account. Note that the
profiles in the central part were obtained from simultaneous
diffusion of both tracers to rule out systematic errors.

shown in Fig. 1. Tracer diffusivities were obtained via the
thin film solution of Fick's second law from the slopes
and the annealing times as described in Ref. [32]. Since the
comparison of ^{57}Co and ^{95}Zr diffusion is crucial for the
present work, surface hold-up effects caused by the bottom
tracer layer on the diffusion of the top layer were ruled
out via measurements with either ^{57}Co or ^{95}Zr as the top
layer and otherwise identical conditions (see Fig. 2). These
experiments also demonstrate the reproducibility of the
diffusion measurements with error margins of the order of
20% for the same alloy.

The viscosity measurements were performed in an
electrostatic levitator using the oscillating drop technique
[6,33]. The samples of 2–3 mm in diameter were levitated
under high vacuum ($<1 \times 10^{-4}$ Pa) and molten with infra-
red lasers. The sample temperature was recorded with
pyrometry. The excitation of the dipole oscillation was
achieved by superimposing a small sinusoidal alternating
electrical field onto the static levitation field. The frequency
of the field was set to the eigenfrequency of the droplet. The
damping of the oscillation, which was used to determine
the viscosity, was recorded with a high-speed camera.
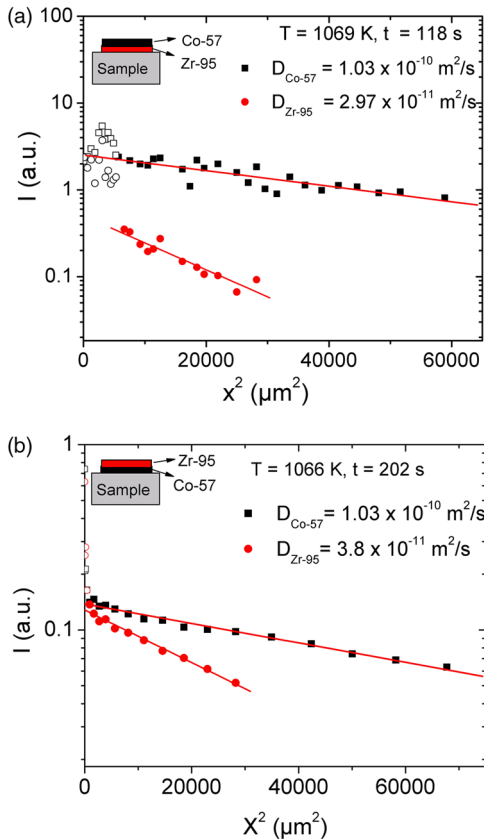Details are published elsewhere [34].

FIG. 2 (color online). ^{95}Zr and ^{57}Co penetration profiles from simultaneous diffusion of both tracers with different sequence of the tracer layers and otherwise identical conditions. (a) ^{57}Co layer on top of ^{95}Zr layer and (b) ^{95}Zr layer on top of ^{57}Co layer. Note the good agreement which allows hold-up effects caused by the bottom layer on diffusion of the top layer to be excluded.

Figure 3(a) shows the ^{95}Zr and ^{57}Co diffusivities reported here, together with radiotracer diffusivities of various elements taken from the literature. A magnified view of the most interesting range in the stable liquid state is displayed in Fig. 3(b). These figures also depict the results from quasielastic neutron scattering mentioned above, which essentially represent diffusivities of Cu and Ni (and, hence, of ^{57}Co taken here as a tracer for Ni), because of the small coherent neutron cross section of Zr, as also confirmed earlier by comparison with radiotracer experiments [7,29]. The good agreement seen in Fig. 3 between the diffusivities from the QNS and the present ^{57}Co diffusivities has to be pointed out because the QNS measurements are not affected by convection [7,26], which often severely influences diffusion measurements in ordinary liquids and melts under gravity. Thus, convection effects on the present measurements can be ruled out even in the stable liquid state investigated here. This can be attributed to the high viscosity of bulk glass forming alloys [7]. The absence of convection was also corroborated through comparison with radiotracer experiments, which we performed by means of the long capillary technique.
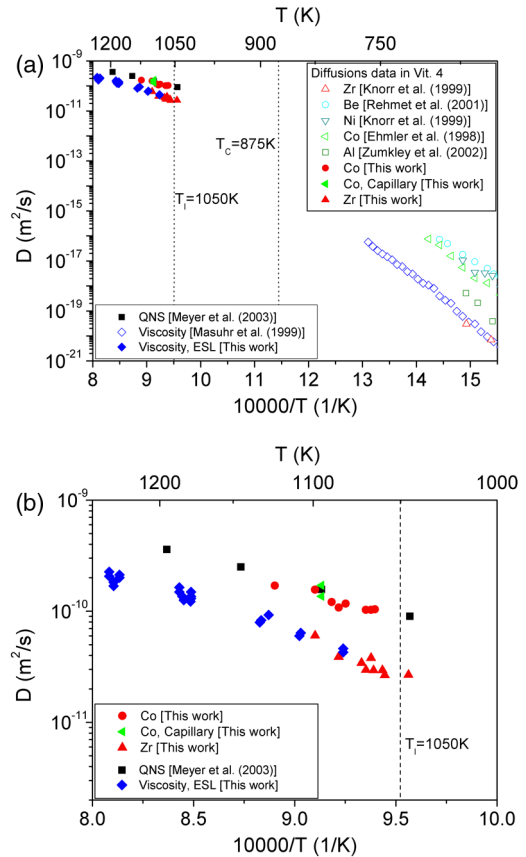

FIG. 3 (color online).   (a) Arrhenius plot of diffusion in $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ (Vitreloy 4) in the stable and in the supercooled liquid state. The present ^{95}Zr and ^{57}Co diffusivities, including data points obtained with the long capillary technique (green triangles), are shown together with diffusivities from QNS [29] and tracer diffusivities from the literature (Knorr et al. [23], Rehmet et al. [24], Ehmler et al. [25], and Zumkley et al. [26]). The QNS data essentially represent diffusivities of Cu and Ni [29,30]. Also shown are diffusivities converted via the Stokes-Einstein equation from the present viscosity data measured using electrostatic levitation. The radius of 145 pm was taken, which represents Zr atoms; however, taking radii of the smaller components would not lead to any significant changes on the present log scale. Dashed lines mark the quasieutectic melting temperature T_m and the critical temperature T_c of the mode coupling theory determined form quasielastic neutron scattering. The caloric glass transition temperature T_g (not shown) is 580 K (from DSC at 20 K/min). (b) Magnified view of (a) showing only the range of the stable liquid state.

This technique is a well-known method to minimize convection [35]. The resulting diffusivities are included in Fig. 3. and are in excellent agreement with the other data. Details will be reported elsewhere.

The striking observation in Figs. 3(a) and 3(b) is the decoupling of Zr diffusion from the diffusion of the smaller components in the stable liquid state reaching a factor as large as 4 at the liquidus temperature. The decoupling decreases at higher temperatures, and extrapolation of the

data in Fig. 3 suggests a value smaller than a factor of 2 above 1250 K. This is in line with the previous QNS results [36] showing that at 1255 K, the measured density correlation function decays completely to zero on a time scale of about 20 ps and does not exhibit a very strong stretching behavior. On the other hand, the QNS experiment could not reveal a slow Zr dynamics at the liquidus temperature, which exceeds the experimental time window.

We point out that one has to discriminate between the observed decoupling of the diffusion of different species, here referred to as component decoupling in contrast to viscous decoupling between viscosity and the diffusivities. The viscous decoupling could be regarded as just a consequence of the effect of the broadening of the distribution of mobilities and the different ways transport and relaxation sample that distribution; i.e., viscous decoupling (because it involves two qualitatively different physical quantities) may be considered as reflecting something rather general about the statistics of dynamics. In contrast, the component decoupling must have an explicit structural origin and reveals information on the relation between composition and atomic dynamics.

As mentioned earlier, component decoupling is not expected in stable liquids exhibiting ordinary liquidlike diffusion governed by uncorrelated binary atomic collisions. A commonly used relation which connects diffusivity and liquid viscosity is the Stokes-Einstein (SE) equation,

$$D = \frac{k_B T}{6\pi \eta r}, \qquad (1)$$

according to which diffusivities should scale with $1/r$, and, hence, the diffusivities of all components should essentially be equal. In Eq. (1), D is the diffusion coefficient, η is the viscosity, k_B the Boltzmann constant, and r the particle radius. The decoupling of Zr diffusion from diffusion of the small components is even more striking in view of the fact that the SE equation is well obeyed for Zr diffusion. This is also shown in Figs. 3(a) and 3(b) where the viscosity data obtained from the present electrostatic levitation measurements based on the oscillating drop technique (see above) were converted into diffusivities via the SE equation. Together with the converted viscosity data of Masuhr et al. [37] and the Zr diffusion data of Knorr et al. [23] close to the caloric glass transition temperature, Fig. 3 suggests the SE equation to hold in the whole temperature range from the stable equilibrium melt down to T_g encompassing more than 10 orders of magnitude. The validity to the SE equation for the large alloy component was also reported earlier for Pd in Pd-based glass formers and was interpreted in terms of the existence of a slow subsystem made up by the large atoms that has to rearrange for structural relaxation and viscous flow [7]. The formation of the slow subsystem was attributed to the interplay of size disparity and chemical short-range order.

Within this notion, the present investigations show that the decoupling of diffusion of the small components from the slow Zr subsystem is still preserved in the stable liquid state at least 150 K above the liquidus temperature and, as suggested by an extrapolation of the data in Figs. 3(a) and 3(b), even at much higher temperatures. Apparently, the diffusion of the large Zr atoms is still strongly affected by the energy landscape more than 300 K above T_c, where liquidlike diffusion is expected to freeze in [38]. This suggests that the gradual decay of the diffusion barriers, which was observed to set in at T_c [7], extends over several hundred K in the present multicomponent metallic glass forming alloy. Consequently, Zr and the small components still seem to diffuse via different mechanisms in the stable liquid state well above T_l. This lends support to the model of local configurational excitations in the atomic connectivity network recently proposed by Egami and co-workers based on molecular dynamics simulations on metallic melts, including Zr based alloys [39]. In these terms, Zr atoms in the melt form significantly stronger temporary nearest-neighbor bonds that have to be broken by thermal activation compared to the other atoms. The Egami model is also nicely confirmed by comparing the present data with those obtained in the Pd-based glass forming melt discussed above [7]. The very reactive Zr has partially occupied d orbitals and can form directed bonds, whereas the noble metal Pd is expected to form much weaker nondirected bonds. Hence, Zr atoms in the melt should form significantly stronger temporary nearest-neighbor bonds that have to be broken by thermal activation compared to Pd. This explains why for the Pd-based glass forming melt, the influence of the energy landscape is much smaller.

In conclusion, the present results show that both diffusion and viscous flow start to develop solidlike, i.e., energy-landscape-controlled, features upon cooling far above the liquidus temperature and many hundred K above the mode coupling T_c in the multicomponent glass forming alloy investigated here.

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