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# Frustration of the stable Zr-Ti-Ni quasicrystal as the basis of glass formation

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The origin of glass formation and the systematics of quasicrystal formation in Zr-Ti-Ni-(Cu-Be)-based metallic glasses is unraveled. Both are found to rely on frustration of the stable $Zr_{41.5}Ti_{41.5}Ni_{17}$ quasicrystal. A systematic change in composition of the stable Zr-Ti-Ni quasicrystal prevents icosahedral order from direct growth in the deeply undercooled liquid and induces the glass transition. Quasicrystals form in the amorphous phase to reduce frustration, i.e., to recover the ideal symmetry and composition of the stable Zr-Ti-Ni quasicrystal. This relation is established especially by the discovery of a new type of sequential phase transformations of icosahedral quasicrystalline phases involving chemical redistribution.

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It is now well established that many undercooled metallic liquids exhibit a tendency to form icosahedral short-range order (ISRO) that increases with the level of undercooling.[1–4] This ISRO increases the energetic barrier for the nucleation of crystalline phases and thereby enables undercooling of metallic liquids,[4] as it was first suggested by Frank in 1952.[5] Following the concept of *geometrical frustration*,[6–9] glass formation in metallic alloys results from this increased level of ISRO with undercooling. The impossibility of the growth of a locally favored icosahedral order into a nonicosahedral liquid leads to an increase in the "line-defect" (disclination) density, i.e., the density of nonicosahedral symmetry lines that separate the icosahedral ordered regions. At the glass transition then the disclination density becomes maximized, so that the kinetics dramatically slows down and the system freezes into a glassy phase. Generally, a glass thereby is described as being frustrated with respect to an ideal and frustration-free reference system. In metallic systems, thermodynamically stable icosahedral quasicrystals (QCs) that exhibit perfect icosahedral long-range order could represent such a frustration-free reference system.

In fact, in many metallic glasses signatures for icosahedral short- and/or medium-range order were found[1,3,10] and icosahedral-like cluster-based packing models for the structure of metallic glasses lead to reasonable agreement to glass-forming compositions[11] and to experimental structural data.[3] In some metallic glasses even icosahedral long-range order, i.e., icosahedral quasicrystals, form in the amorphous phase during thermal annealing slightly above the glass transition temperature $T_g$ (see, e.g., Ref. 12). While the quasicrystals in most cases differ in composition from the initial amorphous phase, in some cases they even form polymorphously, i.e., without a change in composition from the amorphous phase, such as, e.g., in Pd-U-Si,[13] Al-Cu-V,[14] or Zr-Ti-Ni-Cu (Ref. 15) glasses.

Nevertheless, although first indications for a frustration-based approach for glass formation in a Zr-Ti-Ni-Cu-Al bulk metallic glass (BMG) (Ref. 1) as well as in a Zr-Ti-Ni-Cu-Be BMG (Ref. 15) were found recently, neither a necessary direct link between metallic glasses and thermodynamically stable icosahedral quasicrystals nor a systematics of the decomposition tendencies during quasicrystal formation could be obtained up to now. Moreover, quasicrystals can form from the amorphous phase either by grain growth or by a nucleation-based process. This raises the question of whether a specific amorphous metallic phase is in fact of microquasicrystalline or true glassy, more disordered nature.[16]

Here such a relation between Zr-Ti-Ni-Cu-Be as well as Zr-Ti-Ni(-Cu)-based metallic glasses and the thermodynamically stable $Zr_{41.5}Ti_{41.5}Ni_{17}$ quasicrystal[17,18] is established and related to the role of geometric frustration in glass formation and crystallization of the amorphous phase. The Zr-Ti-Ni(-Cu-Be) system is the ideal candidate for such studies, as it contains all the elements of the stable quasicrystal and shows a strong tendency for decomposition during quasicrystal formation.[19–21]

The BMG $Zr_{41}Ti_{14}Ni_{10}Cu_{12.5}Be_{22.5}$ (V1) as well as several Zr-Ti-Ni-Cu and Zr-Ti-Ni alloys have been produced as described earlier.[15,22] The critical cooling rate for amorphization of the Be-free alloys is much higher than for the BMG V1. Fully amorphous thin sheets of Zr-Ti-Ni and Zr-Ti-Ni-Cu alloys of a thickness of 30–50 $\mu$m were therefore produced in a Buehler splat-quenching device. The crystallization behavior of the amorphous alloys was investigated *in situ* during heating of the amorphous samples by means of x-ray diffraction (XRD) using synchrotron radiation with an energy of 8 kV at beamline KMC-II at BESSY-II Berlin, Germany and by differential scanning calorimetry (DSC, Perkin Elmer Pyris 1). Special emphasis was laid on the formation of quasicrystalline phases that evolve from the amorphous phase that were characterized in *ex situ* annealed samples by transmission electron microscopy (TEM, Philips CM 30 and FEI Tecnai F20), XRD (Bruker D8 Advance) and extended x-ray adsorption fine-structure analysis (EXAFS) at the *K* edge of Ni at beamline KMC-I at BESSY-II. The composition of quasicrystals was characterized by means of energy-dispersive x-ray spectroscopy (EDXS) and electron energy-loss spectroscopy (EELS) in TEM. Table I displays the compositions of the different Be-free alloys investigated in this study as well as of the different quasicrystalline phases which appear during crystallization of their amorphous phases as measured by EDXS in TEM.

The formation of quasicrystals in the $Zr_{41}Ti_{14}Ni_{10}Cu_{12.5}Be_{22.5}$ (V1) BMG [which differs only slightly from Vitreloy1 (Ref. 23)] has been reported before.[21,23] In accordance with these studies, we found that during isothermal annealing of the glass at temperatures of up to 693 K (i.e., 83 K above $T_g$=610 K) icosahedral qua-

TABLE I. Composition (in at. %) of the different Be-free alloys investigated in this study, V4-0-N, V4-0, V1-QC-N, and V1-QC. Also included are the compositions of the different quasicrystalline phases V1-QC-I, V1-QC-II, and V1-QC-III that appear in the microstructure of amorphous V1-QC during heating with 4 K/min, as measured by EDXS in TEM. For these measurements an amorphous sample of V1-QC has been used as a standard so that relative changes in the concentration of the constituents can be detected with high accuracy.

| | Zr | Ti | Ni | Cu |
|---|---|---|---|---|
| V4-0-N | 64.5 | 11.4 | 24.1 | |
| V4-0 | 64.5 | 11.4 | 13.8 | 10.3 |
| V1-QC-N | 50.5 | 25.3 | 24.2 | |
| V1-QC | 50.5 | 25.3 | 11.3 | 12.9 |
| V1-QC-I | 50.3 | 25.2 | 12.1 | 12.4 |
| V1-QC-II | 50.0 | 28.0 | 11.3 | 10.7 |
| V1-QC-III | 45.6 | 34.4 | 13.9 | 6.1 |

sicrystals (in the following referred to as V1-QC) with a size of about 60 nm are formed (not shown here). Here, a composition of the quasicrystals V1-QC of $Zr_{50.5}Ti_{25.3}Ni_{11.3}Cu_{12.9}$ was found by means of EDXS in TEM (by which Be cannot be detected). Complementary qualitative EELS measurements yielded that the quasicrystals are largely depleted in Be. Probably the quasicrystals are even Be free, similar to the quasicrystals that form in the closely related BMG $Zr_{46.8}Ti_{8.2}Ni_{10}Cu_{7.5}Be_{27.5}$ (V4) (Ref. 19) [which differs only slightly from Vitreloy4 (Ref. 23)]. Therefore, in the following only Be-free alloys were investigated.

Amorphous V1-QC exhibits a complicated crystallization behavior during heating with a constant heating rate of 4 K/min, as demonstrated by the *in situ* XRD analysis displayed in Fig. 1. For temperatures of up to 660 K the diffractogram shows only a broad diffraction maxima centered around $2\Theta = 37.3°$ indicating the lack of long-range order as it is characteristic for an amorphous phase. At about 660 K two sharp Bragg reflections become visible and are getting sharper with increasing temperature, until at about 765 K a phase transformation occurs. The TEM bright field (BF) image in Fig. 2(a) shows the microstructure of the alloy after heating the amorphous sample up to $T_{max} = 753$ K, i.e., slightly below the onset of the phase transformation, and subsequent quenching to room temperature. The selected area electron-diffraction (SAED) pattern in Fig. 2(b) exhibiting a twofold-symmetry pattern was taken on the dark crystal in the center of Fig. 2(a). The corresponding tenfold and sixfold patterns of an icosahedral quasicrystalline phase were also observed. No other phase than the quasicrystals was found in the sample by TEM or XRD. Thus, during heating, the amorphous phase of V1-QC transforms at first polymorphous into one single quasicrystalline phase (in the following termed V1-QC-I). It is noted that with $T_{max} = 714$ K (and probably even at lower temperatures), the transformation into quasicrystals is already completed. The quasicrystals here have only a size of 10–20 nm. Between 714 and 753 K only grain growth occurs.

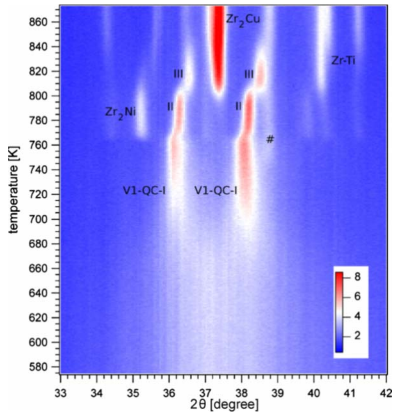

FIG. 1. (Color online) XRD evolution plot of the crystallization of amorphous $Zr_{50.5}Ti_{25.3}Ni_{11.3}Cu_{12.9}$ (V1-QC) taken *in situ* during heating with 4 K/min. The amorphous phase transforms into a single quasicrystalline phase V1-QC-I, that at about 765 K decomposes into a $Zr_2Ni$-type phase and a second quasicrystalline phase V1-QC-II. At about 800 K a further transformation occurs that leads to formation of a $Zr_2Cu$-type phase and a third quasicrystalline phase V1-QC-III that is stable up to 840 K. The Bragg reflection at about $2\Theta = 38.7°$ (#) is due to an oxygen-stabilized cubic $Ti_2Ni$ phase that forms at the surface but cannot be found in the bulk.

With the phase transformation at 765 K new Bragg reflections evolve, e.g., at $2\Theta = 35.2°$, that can be assigned to a $Zr_2Ni$-type phase. The Bragg reflections of the quasicrystalline phase V1-QC-I shift to higher scattering angles, indicating the transformation into a new quasicrystalline phase V1-QC-II. The corresponding TEM BF and SAED images in Figs. 2(c) and 2(d) taken after heating the amorphous phase up to $T_{max} = 786$ K prove the quasicrystalline nature of V1-QC-II. At about 800 K a further phase transformation occurs in the sample (see Fig. 1). Now the reflections from the $Zr_2Ni$ phase and the quasicrystals V1-QC-II vanish, while reflections of a $Zr_2Cu$ type like phase (e.g., at $2\Theta = 37.4°$) and of another quasicrystalline phase (V1-QC-III) appear. The existence of the latter is again proven by the TEM im-

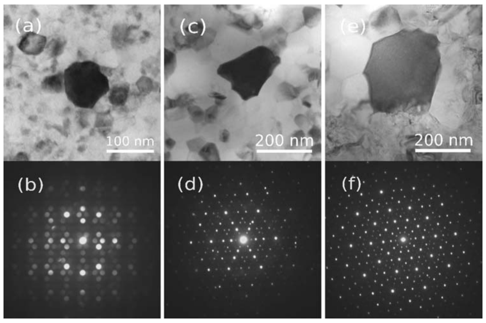

FIG. 2. The microstructure of V1-QC after heating of the amorphous phase to selected temperatures $T_{max}$ that characterize the different quasicrystalline phases that appear in the microstructure with $T_{\mathrm{max}}$ for (a) and (b) of 753 K (V1-QC-I), (c) and (d) 786 K (V1-QC-II), and (e) and (f) 828 K (V1-QC-III), according to Fig. 1. The corresponding SAED patterns stem from the respective quasicrystalline particles showing (b) a twofold, (d) a sixfold, and (f) a tenfold symmetry axes of an icosahedral phase with primitive hyperlattice.

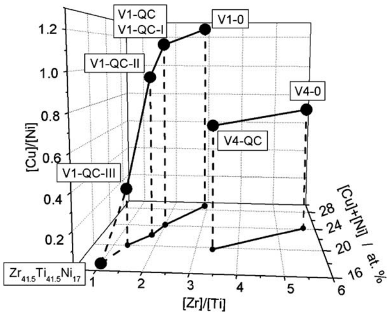

FIG. 3. Three-dimensional representation of the compositions of the different quasicrystals V1-QC-I, V1-QC-II, and V1-QC-III that form in V1-QC during heating of the amorphous phase (compositions are parametrized by [Zr]/[Ti], [Cu]/[Ni], and [Cu]+[Ni]). Also included are the compositions of the V1 BMG (without Be), the stable $Zr_{41.5}Ti_{41.5}Ni_{17}$ quasicrystal, the V4 BMG (without Be), and the quasicrystals V4-QC that form in V4 (Refs. 19 and 20).

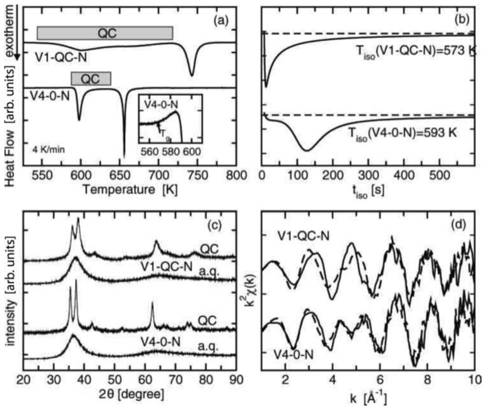

FIG. 4. (a) and (b) characterize the crystallization behavior of the amorphous phases of $Zr_{50.5}Ti_{25.3}Ni_{24.2}$ (V1-QC-N) and $Zr_{64.5}Ti_{11.4}Ni_{24.1}$ (V4-0-N) as measured by DSC during heating with 4 K/min (a) as well as during isothermal annealing after heating with 80 K/min to the annealing temperature (b). The temperature range of quasicrystal formation is indicated by QC in (a). The inset in (a) shows the DSC signal enlarged around the glass transition temperature $T_g$ for the alloy V4-0-N. The dashed lines in (b) represent the zero value for the heat release for both isothermal measurements, respectively. (c) X-ray diffraction patterns of the alloys V1-QC-N and V4-0-N in the a.q. amorphous state and in the fully QC state after heating with 4 K/min to 713 K and 631 K, respectively. (d) shows the $k^2$-weighted EXAFS spectra for the Ni $K$ edge for the amorphous (dashed line) and quasicrystalline states (solid line) of V1-QC-N and V4-0-N as in (c).

ages in Figs. 2(e) and 2(f). Finally, at about 840 K the reflections of the quasicrystals V1-QC-III vanish and reflections of a hexagonal Zr-Ti phase appear (e.g., at $2\Theta = 40.4°$).

It is noted that for V1-QC the fully quasicrystalline state V1-QC-I is also obtained directly in the as-quenched (a.q.) state for sample thicknesses of more than 50 $\mu$m, i.e., formation of quasicrystals is the limiting factor for amorphization during quenching of the alloy, as it was also observed for $Zr_{64.5}Ti_{11.4}Ni_{13.8}Cu_{10.3}$ (V4-0).[15] Moreover, for V1-QC, for sample thicknesses of about 150 $\mu$m a phase mixture of mainly quasicrystals V1-QC-III and $Zr_2Cu$ is formed. This implies that the crystallization sequence during quenching of the liquid alloy resembles that of the amorphous phase during heating, as shown in Fig. 1.

The compositions of the different quasicrystalline phases, V1-QC-I, V1-QC-II, and V1-QC-III in comparison to the nominal composition of V1-QC are given in Table I. According to the polymorphous transition of amorphous V1-QC into the quasicrystals V1-QC-I no significant difference in composition between these two phases exists. In contrast, for the quasicrystals V1-QC-II and even more prominent for V1-QC-III the compositions change systematically, i.e., with the phase transformations of the quasicrystals they become mainly enriched in Ti and depleted of Zr and Cu while the Ni content increases only slightly.

The systematics of the change in composition of the quasicrystals becomes more clear when the composition of the different phases is plotted as the ratio of Zr and Ti content: [Zr]/[Ti] versus the ratio of Cu and Ni: [Cu]/[Ni] and versus the total amount of Cu and Ni: [Cu]+[Ni], see Fig. 3. Also the compositions of the stable quasicrystal $Zr_{41.5}Ti_{41.5}Ni_{17}$ (Refs. 17 and 18) and of the BMG V1 (when Be is neglected) are added in the figure. Starting from V1 the compositions of quasicrystals that form in the amorphous phases change with each step of transformation straight in direction of the stable $Zr_{41.5}Ti_{41.5}Ni_{17}$ quasicrystal. The quasicrystals that form in the BMG V4 (Refs. 19 and 20) show the same tendency.

This decomposition tendency indicates that the Zr-Ti-Ni-Cu-Be BMGs are closely related to the stable Zr-Ti-Ni quasicrystal. Apparently, due to the low-temperature stability of the Zr-Ti-Ni quasicrystal[17,18] and the general tendency of an increase in icosahedral order of the liquid phase with deeper undercooling[1–4] the amorphous phase tends to recover the composition of the stable quasicrystal by rejection of elements such as Cu and Be and adjustment of the content of Zr, Ti, and Ni during annealing. Consequently, in between the compositions of the stable quasicrystal and the Zr-Ti-Ni-Cu-Be alloys the thermal properties of the alloys have to change from a "quasicrystallinelike" behavior to a "glasslike" behavior, i.e., at some point the glass transition has to emerge.

We found that this change can even be located between two ternary Zr-Ti-Ni alloys that differ only in their Zr/Ti ratio: $Zr_{50.5}Ti_{25.3}Ni_{24.2}$ (V1-QC-N) and $Zr_{64.5}Ti_{11.4}Ni_{24.1}$ (V4-0-N). These two alloys were derived from the Cu-containing alloys $Zr_{50.5}Ti_{25.3}Ni_{11.3}Cu_{12.9}$ (V1-QC, this study) and $Zr_{64.5}Ti_{11.4}Ni_{13.8}Cu_{10.3}$ [V4-0, Ref. 15)] by replacing Cu with Ni. In both ternary alloys the amorphous phase also transforms completely into a quasicrystalline phase, but via different mechanism, as will be shown in the following.

Figures 4(a) and 4(b) are showing thermograms taken by DSC of amorphous V1-QC-N and V4-0-N with a heating rate of 4 K/min and during isothermal annealing at 573 K and 593 K, respectively. For V1-QC-N, the formation of quasicrystals from the amorphous phase during heating occurs within a broad temperature region of about 180 K [see upper curve in Fig. 4(a) and the corresponding XRD patterns in Fig. 4(c)]. Even at high heating rates of about 100 K/min the signal is qualitatively the same, i.e., an endothermic increase in the heat release that would indicate a glass transition is not observed.

During isothermal annealing of amorphous V1-QC-N [see upper curve in Fig. 4(b)] an exothermic heat release that indicates the formation of quasicrystals sets in immediately once the annealing temperature is reached and then only decreases monotonically to become negligible. Similar results are obtained for the amorphous phases of V1-QC and the stable Zr-Ti-Ni quasicrystal (not shown here).

According to Ref. 24 this indicates that nuclei of the quasicrystals are already present in the amorphous phase and that the quasicrystals form in a grain-growth process. The corresponding high degree of ISRO in the amorphous phase of V1-QC-N is reflected in the similarity of the EXAFS spectra of the Ni *K* edge of the amorphous and the quasicrystalline phases in Fig. 4(d). The main difference between the amorphous and the quasicrystalline phases thereby is the larger correlation length in the grains of the quasicrystalline phase compared to the icosahedral clusters in the amorphous phase. The "amorphous" phases of these alloys therefore should be more precisely named a microquasicrystalline phase.[24]

On the other hand, in V4-0-N the polymorphous formation of quasicrystals occurs within a rather narrow temperature range of only 50 K [see lower curve in Fig. 4(a) and the corresponding XRD patterns in Fig. 4(c)]. In contrast to V1-QC-N, an endothermic increase in the signal before the onset of the exothermic formation of the quasicrystals, i.e., a glass transition is observed for V4-0-N [see inset in Fig. 4(a)]. Here the endothermic glass transition is not fully developed as it is partially masked by the exothermic formation of quasicrystals. This means that these alloys, V4-0-N and V4-0, form true metallic glasses.

Furthermore, within the isothermal annealing [see lower curve in Fig. 4(b)] the heat release exhibits a distinct exothermic peak, i.e., it increases only after a certain incubation time. According to Ref. 24 this can be attributed to a necessary nucleation for the formation of the quasicrystals from the amorphous phase. A similar behavior as for V4-0-N has also been observed for the alloy V4-0.[15]

Thus, within the composition range between V1-QC-N ($Zr_{50.5}Ti_{25.3}Ni_{24.2}$) and V4-0-N ($Zr_{64.5}Ti_{11.4}Ni_{24.1}$), i.e., due to the dissimilarity of Zr and Ti, microstructural changes occur that prevent local icosahedral arrangements from free propagation in the undercooled liquid and the amorphous phase of V4-0-N (and similar in V4-0). Nevertheless, the amorphous phases of V4-0 (Ref. 15) and V4-0-N still show a high degree of ISRO. For V4-0-N this is indicated by the similarity of the EXAFS spectra of the Ni *K* edge of the amorphous and quasicrystalline phase in Fig. 4(d).

However, for V4-0-N and also for V4-0 (Ref. 15) the glass-forming ability is limited by the polymorphous formation of quasicrystals during quenching of the liquid phase. In order to achieve a higher glass-forming ability and thermal stability of the glass the formation of quasicrystals should be retarded. One way is to introduce a considerable amount of Be into the composition of V4-0. For a Be content of 27.5 at. % this directly yields the composition of the BMG $Zr_{46.8}Ti_{8.2}Ni_{10}Cu_{7.5}Be_{27.5}$ (V4) which exhibits an extended stability of the undercooled liquid phase.[15,23] In this BMG the icosahedral ordering is considerably altered[15] and quasicrystals that form only after prolonged annealing times at temperatures near the glass transition[22,23] are Be free.[19] Nucleation and growth of icosahedral quasicrystals is thereby further deferred by the necessary time consuming long-range diffusion of Be, while the formation of crystalline phases such as $Be_2Zr$ still is hampered by the tendency for icosahedral ordering.[5]

In conclusion, in terms of the concept of geometrical frustration,[6–9] for the Zr-Ti-Ni(-Cu-Be)-based metallic glasses the stable Zr-Ti-Ni quasicrystal can be regarded as the frustration free reference system that the glasses tend to recover during thermal annealing. Glass formation seems to result from the impediment of the growth of local icosahedral order into the bulk liquid, i.e., from frustration of icosahedral order. Frustration here is determined by the degree of change in composition of the stable Zr-Ti-Ni quasicrystal and by addition of further elements. In other words, glass formation and the thermal stability of the glass is linked to the destabilization of the stable quasicrystal. Thus, in some respect, these Zr-Ti-Ni(Cu-Be)-based metallic glasses should be considered to be highly defective or "oversaturated" quasicrystals.

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