High-pressure stability of Ti-Zr-Ni quasicrystals

Radu Nicula and Adrian Jianu

National Institute of Materials Physics, P.O. Box MG-7, 76900 Bucharest-Magurele, Romania

Ulrich Ponkratz and Eberhard Burkel

FB Physik, LS Physik neuer Materialien, Universität Rostock, August-Bebel-Strasse 55, D-18051 Rostock, Germany

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The room-temperature compressibility and stability of single-phase icosahedral Ti-Zr-Ni alloys were investigated for pressures up to 30 GPa, using synchrotron radiation energy dispersive diffraction. The icosahedral Ti-Zr-Ni single phase is stable over this pressure range, no phase transition being noticed. The pressure-volume data were least-squares fitted to a Birch-Murnaghan equation of state to obtain the zero-pressure bulk modulus $B_0 = (173 \pm 5)$ GPa and its pressure derivative $B'_0 = 2.3 \pm 0.5$.

I. INTRODUCTION

Previous experimental work on quasicrystals has focused mainly on the formation, structure, and physical properties of Al-based alloys.^{1,2} The Ti-based icosahedral (*i*) phases form the second largest family of quasicrystalline alloys. Among these, the *i*-TiZrNi phases are the most interesting, mainly due to their high degree of icosahedral perfection and their potential use as efficient hydrogen storage materials.³

Most Ti-based quasicrystalline phases reported to date were produced by rapid quenching techniques, suggesting that they are metastable.⁴ Single or nearly single *i* phases with compositions close to $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}$ and $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ were obtained by melt spinning.⁵ Differential scanning calorimetry studies of the rapidly quenched alloys revealed endothermal transitions, pointing to the *i*-phase stability at the above compositions.⁵⁻⁷ The *i*- $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}$ single phase is stable up to 650 °C.^{5,7} An icosahedral phase with composition $\text{Ti}_{41.5}\text{Zr}_{41.5}\text{Ni}_{17}$ is obtained after annealing of the as-quenched $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ alloy for 64 h at 570 °C.⁶ In spite of the long-term thermal treatment, the annealed samples still contain traces of residual secondary phases.⁶⁻⁸

So far, little is known about the pressure stability and compressibility of non-Al icosahedral phases and approximants. In comparison, the high-pressure properties of quasicrystalline Al-transition-metal alloys have been studied in more detail.⁹⁻¹⁶ In this paper experimental results on the room-temperature high-pressure behavior of *i*-TiZrNi phases are reported. A remarkable result is that quasi-hydrostatic pressure does not induce any phase transition of the *i*- $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}$ single-phase up to 30 GPa. The zero-pressure bulk modulus B_0 and its pressure derivative B'_0 were evaluated using a Birch-Murnaghan¹⁷ equation of state (EOS). The resulting *i*-TiZrNi values $B_0 = (173 \pm 5)$ GPa and $B'_0 = 2.3 \pm 0.5$ are close to the ones quoted for the *i*-AlCuFe phase.¹²

The remainder of the paper is organized as follows. Alloy preparation and the synchrotron radiation diffraction experiments are described in Sec. II. The data analysis procedure and the EOS parameters are presented in Sec. III. The results are discussed and compared with the high-pressure behavior

of several Al-based quasicrystals in Sec. IV. The conclusions are summarized in Sec. V.

II. EXPERIMENTAL PROCEDURES

The *i*-TiZrNi alloys were prepared by melt spinning at the National Institute of Materials Physics (Bucharest, Romania). High-purity elements were used to obtain primary alloy ingots by arc melting in water-cooled copper molds. The ingots were repeatedly melted in order to achieve satisfactory alloy homogeneity. Ribbons 1–10 cm long with an average cross section of 2 mm (width) $\times$ 50 μm (thickness) were obtained by rapid quenching onto a copper wheel in protective Ar atmosphere. An average chemical composition of $\text{Ti}_{52.8}\text{Zr}_{26.2}\text{Ni}_{21}$ was determined by energy dispersive spectroscopy.

Synchrotron radiation angular dispersive diffraction experiments were performed under high-resolution conditions in order to detect the presence of rational approximant phases. The measurements were performed at the B2 and CEMO beamlines of the Deutsches Elektronen Synchrotron DESY/HASYLAB (Hamburg, Germany).¹⁸ The high-resolution experimental setup included a Soller slit system and a Ge analyzer crystal placed in front of the NaI detector. The powder-diffraction pattern of as-quenched *i*- $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}$ (Fig. 1) is shown together with a simulated diffraction pattern corresponding to the 1/1 rational approximant (*W* phase).¹⁹ While a good agreement between the 2 θ positions and linewidths of the strongest icosahedral and *W*-phase diffraction lines can be noticed, the absence of the *W*-phase (600) diffraction line from the experimental diffraction pattern demonstrates the monophasic nature of the samples and the formation of a well-structured icosahedral phase.

The high-pressure synchrotron radiation diffraction experiments were performed at the F3 DESY/HASYLAB beamline. White beam is delivered from a bending magnet radiation source ($E_c = 16.6$ keV). The radiation scattered in the horizontal plane is recorded by an energy sensitive high-purity Ge solid-state detector (Princeton Gamma-Tech) positioned at a fixed scattering angle θ . Tungsten slits are used for primary and diffracted beam collimation. The beam size

FIG. 1. Experimental high-resolution powder-diffraction pattern of the *i*-TiZrNi phase (open circles) and the diffraction pattern of the 1/1 rational approximant (continuous line) calculated using the Rietveld-refined structure data of Ref. 19.

at the sample can be adjusted down to $20 \times 20 \mu\text{m}$; in our experiments the beam size ranged from 80×80 to $120 \times 120 \mu\text{m}$. All diffraction patterns were collected in energy dispersive mode between 13.95 and 68.16 keV. The diffraction angle $\theta = 5.487^\circ \pm 0.002^\circ$ was determined using gold powder ($a_{\text{Au}} = 4.0789 \text{ \AA}$). More details on the experimental setup can be found elsewhere.²⁰

Pressures were generated by a gas-membrane diamond-anvil cell (DIACELL DXR-GMW), equipped with $500 \mu\text{m}$ flat size diamonds. The as-quenched ribbons were dry grinded in an agate mortar to produce a fine powder (average particle size $100 \mu\text{m}$). High-pressure experiments were performed in which a single *i*-TiZrNi $100\text{-}\mu\text{m}$ powder particle was loaded together with silicon oil as pressure transmitting medium and with NaCl as internal pressure standard. The *i*-phase particle was enclosed in a $150\text{-}\mu\text{m}$ diameter hole, mechanically drilled in a $200\text{-}\mu\text{m}$ -thick inconel gasket pre-indented to about $50 \mu\text{m}$. Special care was taken to avoid bridging of the diamonds through the icosahedral phase powder particle. All pressures were determined from the strong (200) reflection of NaCl using the EOS parameters $B_0 = 24.03 \text{ GPa}$ and $B'_0 = 4.74$ obtained from a fit to the data of Decker.²¹ The agreement with pressures determined from the weaker NaCl (220) reflection was always better than 0.5 GPa. Another high-pressure experiment was performed using a 4:1 methanol-ethanol mixture as pressure transmitting medium and the ruby fluorescence method for pressure calibration.

III. DATA ANALYSIS

Cahn (N,M) indices²² were used for indexing the *i*-phase diffraction lines. The indexing procedure allows for the evaluation of the hypercubic lattice constant A according to

$$A = \frac{1}{Q} \cdot \sqrt{\frac{N+M}{2(2+\tau)}} = a\sqrt{2}, \quad (1)$$

where $Q (\text{\AA}^{-1}) = [d_{N,M}]^{-1} = [12.398/E (\text{keV}) \cdot 2 \sin \theta]^{-1}$ is the parallel space momentum transfer, $\tau = (1 + \sqrt{5})/2$ is the

FIG. 2. Energy dispersive spectra of *i*-TiZrNi with increasing pressure. Icosahedral diffraction lines are indexed with Cahn (N,M) indices.

golden mean, $d_{N,M}$ is the interplanar distance for the (N,M) diffraction line, and a is the three-dimensional quasilattice parameter.

Besides the main (18,29), (20,32), and (52,84) *i*-phase diffraction lines, less intense peaks like (14,21), (70,113), (72,116), and (110,177) were observed in the diffraction patterns. These smaller peaks tend to become less pronounced with increasing pressure and in some cases overlap with inconel, NaCl or with the tungsten fluorescence lines from the slit system, their indexing becoming less reliable. For this reason and because the corresponding corrections to the quasilattice parameter values were less than 0.5% at all pressures, only the most intense (18,29), (20,32), and (52,84) *i*-phase diffraction lines were employed for indexing and quasilattice parameter evaluation. Indexing of the zero-pressure *i*-phase diffraction lines lead to a quasilattice constant $a_0 = 5.0589 \pm 0.0048 \text{ \AA}$ and a hypercubic lattice parameter $A_0 = 7.1543 \text{ \AA}$, in close agreement with the results of high-resolution powder diffraction experiments.

The diffraction patterns (Fig. 2) were analyzed using peak fitting and profile deconvolution procedures. The difference between observed and calculated *i*-phase diffraction line positions was less than 90 eV at all pressures.

The pressure-volume relationship was obtained from the d spacings of the icosahedral phase using the assumption of isotropic compression. This assumption is valid for high-symmetry cubic and icosahedral structures⁹ and allows for sample volume evaluation using $V(P) \sim d(P)^3$. The isotro-

FIG. 3. Plot of the observed d spacings ratios calculated from NaCl and i -TiZrNi diffraction lines vs pressure. The $d(200)/d(220)$, $d(18,29)/d(20,32)$, and $d(18,29)/d(52,84)$ ratios are pressure independent within 0.3%, indicating isotropic compression conditions. Lines are guides to the eye.

pic compression hypothesis was tested through the pressure dependence of the d -spacings ratio $d(200)/d(220)$ of NaCl and of the i -phase $d(18,29)/d(20,32)$ and $d(18,29)/d(52,84)$ ratios (Fig. 3). These ratios are pressure independent within the 0.3% error of the present experiments. The pressure-dependent volume ratios can consequently be calculated from the icosahedral phase d spacings according to $V/V_0 = (d/d_0)^3$.

An alternative method for estimating the V/V_0 volume ratio is to use the pressure dependence of the quasilattice parameter a , i.e., $V/V_0 \sim (a/a_0)^3$. The resulting V/V_0 values are in excellent agreement with the ones obtained using the d spacings of the main icosahedral diffraction lines (18,29), (20,32), and (52,84). Accordingly, the zero-pressure volume V_0 is proportional to $a_0^3 = 129.46 \text{ \AA}^3$. The pressure dependence of the average volume calculated from both interplanar distances d and i -phase quasilattice constant a is shown in Fig. 4. We also note that the volume compression of the $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}$ i phase for the highest pressure attained in the present experiments (29.8 GPa) is $\sim 14\%$.

The zero-pressure bulk modulus B_0 and the pressure derivative B'_0 were determined from a least-squares fit to a second-order Birch-Murnaghan EOS:

$$P = \frac{3}{2} B_0 \cdot \left[\left(\frac{V_0}{V} \right)^{7/3} - \left(\frac{V_0}{V} \right)^{5/3} \right] \cdot \left[1 + \frac{3}{4} (B'_0 - 4) \cdot \left(\frac{V_0}{V} \right)^{2/3} \right]. \quad (2)$$

For the experiments in which the specimen was embedded in a mixture of silicon oil and NaCl powder (Fig. 4), we used the pressure-volume data above 8 GPa and B_0 , B'_0 , and V_0 as variable fit parameters to obtain the zero-pressure bulk

FIG. 4. Relative change of the i -TiZrNi quasilattice constant a and d spacings for the (18,29), (20,32), and (52,84) diffraction lines (top). Relative variation of the average volume with increasing pressure (bottom). Experiments were performed using silicon oil as pressure transmitting medium and NaCl for pressure calibration.

modulus $B_0 = 166 \pm 13$ GPa and its pressure derivative $B'_0 = 1.9 \pm 0.6$. The initial sample volume estimated from the least-squares EOS fit equals $V_0 = 132.18 \text{ \AA}^3$, which would in turn correspond to a zero-pressure quasilattice constant $a_0 = \sqrt[3]{V_0} = 5.094 \text{ \AA}$. The difference between the actual quasilattice parameter and the a_0 value estimated from the EOS fit is less than 1% and is presumably due to fitting only the experimental pressure-volume data above 8 GPa. For fixed $B'_0 = 2$ we obtain a bulk modulus $B_0 = (163 \pm 3)$ GPa. The EOS fit does not extrapolate to $V/V_0 = 1$ at zero pressure, in spite of the fact that the value of the quasilattice parameter is exactly recovered after pressure release (Fig. 6). We attribute this effect to the presence of uniaxial stress components.²³ In our scattering geometry, the incident x-ray beam is parallel to the main load axis of the diamond anvil cell, i.e., the normal to the plane of the diamond anvils. Due to the use of a small scattering angle the set of atomic planes satisfying the diffraction condition lie almost parallel to the incident beam direction. The uniaxial stress components acting on the diffracting planes are of expansive nature and thus determine an apparent increase of the quasilattice parameter with increasing pressure. This consequently results in a shift of the EOS towards higher V/V_0 values. The polycrystalline nature of the specimen together with the elastic isotropy of the quasicrystalline structure ensure that the same compression behavior is observed along any icosahedral symmetry axis (Fig. 3).

The effect of uniaxial stress components transmitted through the compression medium is significantly reduced when using an 4:1 methanol-ethanol mixture as pressure

FIG. 5. Relative variation of the average volume with increasing pressure. Experiments were performed using a 4:1 methanol-ethanol mixture as pressure transmitting medium. The ruby fluorescence method was used for pressure calibration.

transmitting medium. Pressure calibration was in this case performed using the ruby fluorescence method. The pressure-volume data for this experiment is shown in Fig. 5. The corresponding EOS with parameters $B_0 = 173 \pm 5$ GPa and $B'_0 = 2.3 \pm 0.5$ extrapolates to $V/V_0 = 1$ at zero pressure.

IV. DISCUSSION

Icosahedral phases are traditionally grouped into two structural classes. The first group comprises i -AlMn(Si), i -Al-Cu-TM (TM: 3d transition metals) and i -AlPdMn. The second group includes the i -GaMgZn and i -AlLiCu phases. A recent classification scheme based on the nature of constituent atomic clusters has been proposed by Kim *et al.*¹⁹

The compression behavior of i -AlMn and i -AlCuFe phases was studied in more detail. It was found that i -Al₈₆Mn₁₄ is stable under pressures as high as 28 GPa ($B_0 = 117.6 \pm 16.8$ GPa, $B'_0 = 6$).⁹ Mixtures of i -AlMn and fcc crystalline α phase usually form in alloys with compositions Al₇₅Mn₂₅ and Al₇₉Mn₂₁ and are stable under pressure up to 47 GPa ($B_0 = 146 \pm 10$ GPa, $B'_0 = 1.7$).¹⁰ Extended x-ray-absorption fine-structure¹¹ and x-ray-diffraction¹² studies of single-phase i -AlCuFe and crystalline approximants were performed for pressures up to 35 GPa. Least-squares analysis of the i -AlCuFe data using a Birch-Murnaghan EOS with B_0 and B'_0 as variable fit parameters leads to $B_0 = 165 \pm 10$ GPa and $B'_0 = 1.15 \pm 0.6$. The i -Al₆₂Cu_{25.5}Fe_{12.5} single phase is stable up to 33.5 GPa. *In situ* high-pressure energy dispersive diffraction experiments similar to the ones described here were performed by Amazit *et al.* on 10- μ m i -AlPdMn powder particles obtained from fragments of a large Al_{68.7}Pd_{21.7}Mn₉₆ stable quasicrystal.¹³ The pressure-volume data (up to 40 GPa) for these fine powdered samples follow a Birch-Murnaghan EOS with parameters $B_0 = 133 \pm 5$ GPa and $B'_0 = 5 \pm 1$.

The i phases of the second structural class seem less stable at high pressures.^{14–16} First experiments indicated that both i -AlLiCu and the cubic R -AlLiCu rational approximant phases become amorphous: the R phase at 23.5 GPa and the i phase above 10 GPa. For the latter, a transition to a crystalline phase occurs at 28 GPa. More recent results of Itie

FIG. 6. Plot of the i -phase energy dispersive spectra before compression (top) and 30 min after pressure release (bottom).

et al. concerning a pure i -AlLiCu phase (without Al contamination) indicate the occurrence of a phase transition to an unknown crystalline structure at 16 GPa.¹⁶

At difference to other Ti-based i phases, the structure of i -TiZrNi appears to be similar to the structure of i -GaMgZn and i -AlLiCu.^{5,19} The high-pressure behavior of i -AlLiCu (Refs. 14 and 16) would consequently suggest that a pressure-induced transition to an amorphous or crystalline state may be expected also for i -TiZrNi. The broadening of the main i -phase diffraction lines with increasing pressure leads to the severe superposition of the (18,29) and (20,32) diffraction lines above 20 GPa. Whether the i -TiZrNi undergoes a structural phase transition at pressures above 30 GPa needs to be examined in a future experiment. The i -TiZrNi phase diffraction lines can be clearly identified in the energy dispersive spectra taken at the highest pressure attained (29.8 GPa) as well as 30 min after pressure release (Fig. 6). The positions of the main icosahedral diffraction lines are the same at zero pressure and after decompression, meaning that the quasilattice parameter recovers its initial value upon pressure release. Pressure-induced defects are “frozen” in the icosahedral phase structure upon pressure release, as evidenced by the residual broadening of the diffraction lines (Fig. 6).

V. CONCLUSION

The high-pressure properties of single-phase i -Ti₅₃Zr₂₇Ni₂₀ alloys were investigated using synchrotron radiation energy dispersive diffraction. The i -TiZrNi sample was loaded together with silicon oil and NaCl in the diamond-anvil high-pressure cell. The pressure-volume data

above 8 GPa were then least-squares fitted to a second-order Birch-Murnaghan EOS and the zero pressure values of the *i*-TiZrNi bulk modulus ($B_0 = 166 \pm 13$ GPa) and its pressure derivative ($B'_0 = 1.9 \pm 0.6$) were obtained. A shift of the EOS towards higher V/V_0 values was also observed and attributed to nonvanishing uniaxial stress components. The effect of uniaxial stresses is reduced when using a 4:1 methanol-ethanol mixture as pressure transmitting medium. Values for the bulk modulus ($B_0 = 173 \pm 5$ GPa) and its pressure derivative ($B'_0 = 2.3 \pm 0.5$) were obtained from the Birch-Murnaghan EOS fit. Both experiments prove that the *i*-Ti₅₃Zr₂₇Ni₂₀ single-phase is stable up to 30 GPa. Upon pressure release, the quasilattice parameter recovers its zero-

pressure value, however, defects are “frozen” in the icosahedral structure. The overall behavior is similar to the *i*-AlCuFe phase in spite of their different chemical constitution. This might be related to the occurrence of similar local atomic environments^{24–26} in both alloy structures.

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- ¹*Proceedings of the 5th International Conference on Quasicrystals, 1995*, edited by C. Janot and R. Mosseri (World Scientific, Singapore, 1995).
- ²*Proceedings of the 6th International Conference on Quasicrystals, 1997*, edited by S. Takeuchi and T. Fujiwara (World Scientific, Singapore, 1998).
- ³K. F. Kelton and P. C. Gibbons, *MRS Bull.* **22**, 69 (1997).
- ⁴K. F. Kelton, in *Intermetallic Compounds: Principles and Practice*, edited by J. H. Westbrook and R. L. Fleischer (Wiley, New York, 1995), p. 453.
- ⁵R. M. Stroud and K. F. Kelton, in *Proceedings of the 5th International Conference on Quasicrystals, 1995* (Ref. 1), p. 253.
- ⁶K. F. Kelton, W. J. Kim, and R. M. Stroud, *Appl. Phys. Lett.* **70**, 3230 (1997).
- ⁷R. M. Stroud, K. F. Kelton, and S. T. Misture, *J. Mater. Res.* **12**, 434 (1997).
- ⁸W. J. Kim, P. C. Gibbons, and K. F. Kelton, in *Proceedings of the 6th International Conference on Quasicrystals, 1997* (Ref. 2), p. 47.
- ⁹Y. Sato-Sorensen and L. B. Sorensen, *Phys. Rev. B* **39**, 2654 (1989).
- ¹⁰E. Johnson, J. Staun Olsen, J. V. Wood, and L. Gerward, *Mater. Sci. Eng.* **99**, 403 (1988).
- ¹¹A. Sadoc, J. P. Itie, A. Polian, S. Lefebvre, M. Bessiere, and Y. Calvayrac, *Philos. Mag. B* **70**, 855 (1994).
- ¹²S. Lefebvre, M. Bessiere, Y. Calvayrac, J. P. Itie, A. Polian, and A. Sadoc, *Philos. Mag. B* **72**, 101 (1995).
- ¹³Y. Amazit, B. Perrin, M. Fischer, J. P. Itie, and A. Polian, *Philos. Mag. A* **75**, 1677 (1997).
- ¹⁴Y. Akahama, Y. Mori, M. Kobayashi, H. Kawamura, K. Kimura, and S. Takeuchi, *J. Phys. Soc. Jpn.* **58**, 2231 (1989).
- ¹⁵R. R. Winters and W. S. Hammack, *Science* **260**, 202 (1993).
- ¹⁶J. P. Itie, S. Lefebvre, A. Sadoc, M. J. Capitan, M. Bessiere, Y. Calvayrac, and A. Polian, in *Proceedings of the 5th International Conference on Quasicrystals, 1995* (Ref. 1), p. 168.
- ¹⁷F. Birch, *J. Geophys. Res.* **83**, 1257 (1978).
- ¹⁸R. Nicula, C. Kumpf, and E. Burkel, *DESY-HASYLAB Annual Report, 1997* (unpublished), Vol. I, p. 540.
- ¹⁹W. J. Kim, P. C. Gibbons, K. F. Kelton, and W. B. Yelon, *Phys. Rev. B* **58**, 2578 (1998).
- ²⁰J. W. Otto, *Nucl. Instrum. Methods Phys. Res. A* **384**, 552 (1997).
- ²¹D. L. Decker, *J. Appl. Phys.* **42**, 3239 (1971).
- ²²J. W. Cahn, D. Shechtamn, and D. Gratias, *J. Mater. Res.* **1**, 13 (1986).
- ²³A. K. Singh, *J. Appl. Phys.* **73**, 4278 (1993).
- ²⁴E. Cockayne, R. Philips, X. B. Kan, S. C. Moss, J. L. Robertson, T. Ishimasa, and M. Mori, *J. Non-Cryst. Solids* **153-154**, 140 (1993).
- ²⁵A. Katz and D. Gratias, in *Proceedings of the 5th International Conference on Quasicrystals, 1995* (Ref. 1), p. 164 and references therein.
- ²⁶V. Elser, *Philos. Mag. B* **73**, 641 (1996).