

# Icosahedral Ti–Zr–Ni and hydrogenated Ti–Zr–Ni quasicrystals under high pressure

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## Abstract

We present results from the first X-ray diffraction studies under high pressure in icosahedral Ti–Ni–Zr quasicrystals (QCs). The icosahedral  $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}$  phase and an icosahedral  $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$  phase that also contains 0.32 hydrogen atoms for each metal atom were investigated. The icosahedral QC structure is retained up to the highest pressures used. The six-dimensional (6D) lattice parameters were obtained as a function of pressure. The zero-pressure bulk modulus and its pressure derivative were determined for the different samples by fitting the 6D parameter change to a Murnaghan-type equation of state. It is worthwhile mentioning that the hydrogenated sample appears more compressible than the one without hydrogen. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Quasicrystal; Hydrogen; High pressure; X-ray diffraction; Ti–Ni–Zr

## 1. Introduction

The most exciting feature of the new Ti/Zr-based quasicrystals (QCs) is their ability to reversibly store hydrogen [1]. As these QCs are potential materials for hydrogen storage and battery application, it is important to know their thermodynamical properties, in particular, under pressure. In this paper, in situ X-ray diffraction studies are reported for the first time in icosahedral Ti–Ni–Zr QCs under high pressure in quasihydrostatic conditions. The icosahedral  $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}$  phase (i-Ti–Ni–Zr) and an icosahedral  $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$  phase that also contains 0.32 hydrogen atoms for each metal atom (i-Ti–Ni–Zr+H) were investigated.

## 2. Experimental

Samples of the icosahedral phase  $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}$  (Ti–Zr–Ni), and icosahedral  $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$  (Ti–Zr–Ni+H) that also contain approximately 0.32 hydrogen atoms for each metal atom (H/M=0.32) were prepared and characterized at Washington University (St. Louis, MO). Rapidly-quenched ribbons of the QCs were produced

by melt-spinning onto a copper wheel. The resulting  $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$  i-phase ribbons were plasma-etched, coated with a thin layer of Pd, and hydrogenated by direct exposure to hydrogen gas (as discussed elsewhere [2,3]) to an H/M value of approximately 0.32. Small flakes of  $\text{Ti}_{53}\text{Zr}_{27}\text{Ni}_{20}$  ribbons and some grains of Ti–Zr–Ni+H fined-grained powder were used for the high-pressure diffraction experiments. The X-ray diffraction experiments, carried out at LURE using the DCI synchrotron radiation facility, were recorded, in the energy dispersive mode, on the experimental station DW11, using a germanium solid-state detector. Nitrogen was used as a pressure-transmitting medium inside the diamond-anvil cell. The pressure was measured by the shift of the luminescence peaks of a ruby chip added to the sample. The diffraction pattern was recorded from ambient pressure to 26 GPa for Ti–Ni–Zr and to 15 GPa in the case of Ti–Ni–Zr+H, and also at ambient pressure after coming back to zero pressure after the high-pressure cycle. The Bragg relation between the interplanar distance  $d$  and the energy  $E$  is given by

$$d(\text{\AA}) = \frac{12.398}{2 \sin \theta E(\text{keV})} \quad (1)$$

where  $\theta$ , the fixed angle between the incident X-ray beam and the sample plane, was close to  $6^\circ$ . Due to the size of the beam ( $50 \mu\text{m} \times 50 \mu\text{m}$ ), the number of crystals which can

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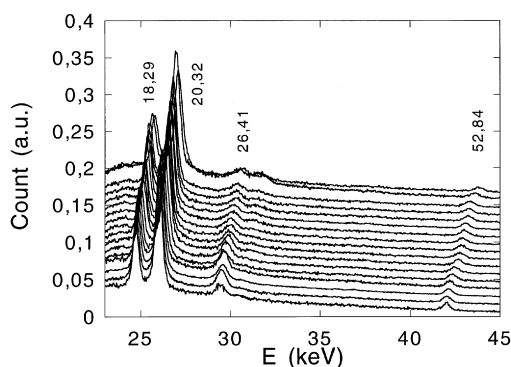


Fig. 1. X-ray diffraction spectra of Ti-Ni-Zr vs. pressure, from ambient (below) up to 26 GPa; the Bragg peaks are indexed following Cahn et al. [4].

diffract is very small and the intensities of the Bragg peaks are therefore sensitive to the orientation of the sample.

Diffraction patterns are shown in Fig. 1 for Ti-Ni-Zr with the indexing. Similar spectra were obtained for Ti-Ni-Zr+H. The Bragg peaks shift monotonously to higher  $E$  values when the pressure increases. No peak disappears, nor does any new peak appear, so that the alloys remain icosahedral. After release of pressure, the Bragg peaks recover their initial position. The indexing of the diffraction patterns was performed using the six-dimensional (6D) scheme proposed by Cahn et al. [4] with two integers  $N$  and  $M$ . Four Bragg peaks were measured: (18, 29), (20, 32), (26, 41) and (52, 84). The 6D lattice parameter  $A$  is given by

$$A = \frac{1}{Q_{//}} \frac{\sqrt{N + M\tau}}{2\sqrt{2 + \tau}} \quad (2)$$

where  $\tau$  is the golden mean and  $Q_{//}$ , the projection in parallel space of a 6D reciprocal lattice vector, is equal to the inverse of the interplanar distance  $d$ . The  $A$  parameter can be derived, for each  $(N, M)$  Bragg peak from the peak positions in the energy scale. The variations of  $A$  with pressure are compared in Fig. 2 for the two samples. A Murnaghan equation of state was adjusted to the values of lattice parameter:

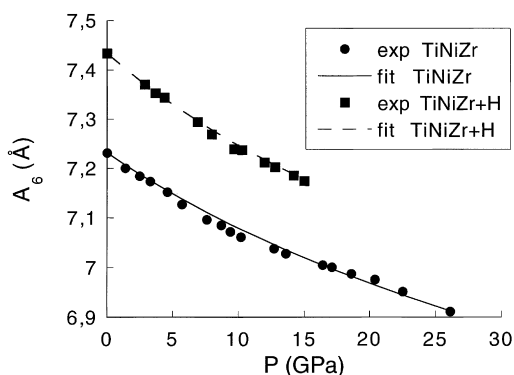


Fig. 2. Variation of the six-dimensional parameter vs. pressure for Ti-Ni-Zr and Ti-Ni-Zr+H. Solid line: Murnaghan fit.

$$A = A_0 \left( 1 + \frac{B'_0 P}{B_0} \right)^{-1/(3B'_0)}$$

where  $A_0$  is the 6D parameter at ambient pressure,  $B_0$  the bulk modulus at zero pressure and where  $B'_0$  is its pressure derivative. The  $B_0$  values were found to be  $130 \pm 10$  GPa for Ti-Ni-Zr and  $105 \pm 10$  GPa for the hydrogenated sample for the same value of the  $B'_0$  derivative equal to  $5.5 \pm 1$ . Therefore, the sample containing hydrogen appears to be more compressible at ambient pressure than the alloy without hydrogen, as is clearly evident in Fig. 2. The value found in Ti-Ni-Zr for the bulk modulus is very similar to those found in icosahedral Al-Pd-Mn [5] and Al-Cu-Ru ([6] and references therein) ( $B_0 = 128$  GPa), which are perfect QCs and are also stable under high pressure. The behaviour of icosahedral Al-Li-Cu appears very particularly with a phase transition under high pressure and a high compressibility ( $B_0 = 71$  GPa) [7–9,10].

### 3. Conclusions

As found previously in several QCs [5,6], the Ti-Ni-Zr and Ti-Ni-Zr+H alloys remain icosahedral up to the highest pressure. The 6D parameter decreases monotonously for both alloys but more in the hydrogenated alloy. More experiments in other hydrogenated alloy are needed to confirm this tendency.

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