

# 27 Ab-initio Study of the Ground-State Phase Diagram of the Icosahedral Ti-Zr-Ni Quasicrystal

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**Abstract.** In this work the structure and energy of the icosahedral TiZrNi quasicrystal and its approximants are investigated. First, a combined approach of a least-squares analysis of experimental diffraction data and ab-initio relaxations is used to study the structure of the icosahedral Ti-Zr-Ni quasicrystal. Second, the ground state phase diagram of the ternary Ti-Zr-Ni system is investigated by total energy calculations for approximants to the icosahedral quasicrystal and a large number of binary and ternary phases. The refined decoration model is found to be energetically stable for the approximant structures of the quasicrystal.

## 27.1 Introduction

Quasicrystals are solids which combine long-range translational order with rotational symmetries that forbid *periodic* translational symmetry. Despite much progress in recent years, the atomic structure of quasicrystals still remains an unsettled question. The aperiodic nature of quasicrystals requires new method for structural analysis. For certain quasicrystals, single grain samples of up to several millimeter size allow the measurement of single crystal diffraction data; several approaches have been suggested and applied to these systems [1–4].

Much less work has been devoted to quasicrystalline alloys with grain sizes so small that only powder diffraction data are available. Such a system is the icosahedral TiZrNi quasicrystal (*i*-TiZrNi) [5,6], which is formed by either rapid quenching or solid state reactions at temperatures of 500°C to 600°C, generally leading to a fine microstructure of quasicrystal and crystal phases and a small coherence length of about 350 Å. Therefore, an atomic structure determination by diffraction experiments alone is hardly possible. There is hope of obtaining information on the atomic arrangement in *i*-TiZrNi by studying the structure of related periodic “approximants”, meaning crystal structures whose unit cells are fragments of some quasicrystal.

The *W*-TiZrNi phase is closely related to the quasicrystal phase [7,8]. They both form at similar compositions and temperature ranges and grow with a coherent crystallographic orientation. EXAFS studies [9] indicate a similar local structure in both phases. The presence of a reversible phase

transformation between the icosahedral phase and the  $W$ -phase at about  $600^{\circ}\text{C}$  indicates that  $i$ -TiZrNi is a low-temperature phase, in contrast to most other quasicrystals [10]. This opens the exciting possibility that an (aperiodic)  $i$ -TiZrNi quasicrystal, or a very similar large-cell crystal, could be a ground state phase. We conjecture that the small coherence length of  $i$ -TiZrNi is due to the sluggish nature of its formation and is not inherent to the structure. The goal of our work is to model the ideal structure and to investigate its energy.

## 27.2 Structural Model of $i$ -TiZrNi

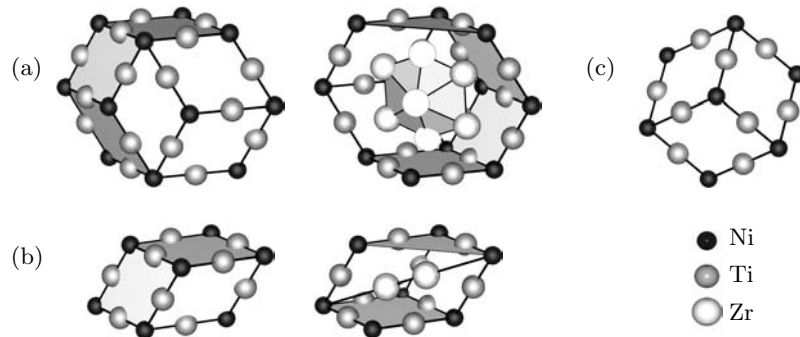
Various methods have been developed for the analysis of powder diffraction data for periodic crystals, including reverse Monte Carlo and maximum entropy methods [11]. These methods are particularly useful to study disordered systems. A different approach, however, is used in this work since our emphasis is not a description of the disorder present in the quasicrystal.

Powder diffraction studies remain one of the main methods of obtaining quantitative structural information for this system. The limited number of measurable structure factors necessitates replacing conventional least-squares structure fitting by a modified approach. For quasicrystals, a combined approach of total energy calculations and diffraction refinements is highly desirable [4,12,13]. This work implements that idea by employing ab-initio relaxation studies to resolve additional details of the structure. The results from the ab-initio relaxations are incorporated as structural constraints into the least-squares analysis.

The structural model is formulated as a decoration of the “canonical cell tiling” [14], meaning that space is filled by several kinds of cells, each of which is given by discrete sites and species occupations, in analogy to the unit cell of an ordinary crystal. The approximant phases are simpler arrangements of the same cells, and our method depends on switching from one approximant to another to perform different steps, while keeping the same decoration.

The decoration sites were chosen to closely correspond to those in the approximant phase  $W$ -TiZrNi [8], which has a cubic structure with the space group  $Im\bar{3}$ , a lattice constant of  $14.3\text{ \AA}$  and 162 atoms in the cubic unit cell. The main structural feature of the  $W$  phase is the occurrence of a double-shell icosahedral Bergman cluster (see Fig. 27.2a), which is likely to dominate the structure of the quasicrystal too.

In the first step, only the chemical occupations of the sites on each cell are refined by a least-squares fit to experimental neutron and x-ray diffraction data. The second step is to relax the atomic positions used in small periodic crystalline approximant structures by ab-initio calculations. These positions are then used as an input into step 1, and this process is iterated until the decoration of the sites does not change significantly.



**Fig. 27.1.** Decoration of (a) the RD, (b) the PR and (c) the OR. The pictures on the right of the RD and PR show the same decorations with interiors visible

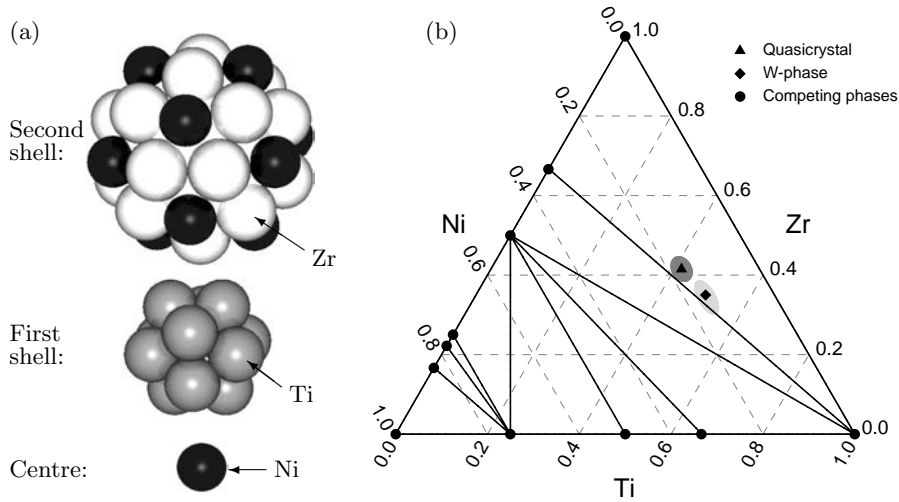
The ab-initio relaxations are performed using the VASP code [15], which is a density-functional method using a plane-wave basis and ultrasoft pseudopotentials. Atomic-level forces are calculated and relaxations with a conjugate gradient method are performed. In the ab-initio calculations the chemical disorder is idealised by only placing the majority component on each site.

The resulting structural model reproduced the x-ray and neutron diffraction data with a reduced  $\chi^2 = 1.4$  and the approximants were mechanically stable under ab-initio relaxations. The decoration model exhibits only small amounts of occupational disorder. The main features of the decoration model are shown in Fig. 27.1 using the decomposition of the canonical cells into the smaller Amman tiles, which are the prolate and oblate rhombohedron (PR and OR) as well as the rhombic dodecahedron (RD). The corners of the Amman tiles are occupied by Ni and the edge centres by Ti. Zr is found on all interior sites, i.e. the body diagonal of the PR and a group of sites forming a hexagonal bipyramid inside of the RD. Details of this work will be published elsewhere.

### 27.3 Ground-State Phase Diagram of Ti-Zr-Ni

To investigate the energetic stability of the quasicrystal phase, and to test the significance of detailed features of our atomic structure model, a ternary Ti-Zr-Ni ground state phase diagram was calculated using the VASP code. This involved the calculation of the relaxed crystalline structures of 9 elemental phases, 17 binary phases and 11 ternary phases. Furthermore, 16 structural models of approximants to the quasicrystal with 4 to 123 atoms per primitive cell were relaxed.

For all but one of the phases, our prediction as to their stability agrees with experimental facts [16]. The agreement of the relaxed lattice parameters with available experimental values was in all cases better than 2% [17]. Out



**Fig. 27.2.** Panel (a) depicts the two shell structure of the Bergman cluster consisting of a central Ni atom, a small icosahedron of Ti atoms and a large icosahedron of Ni atoms with Zr atoms on the face centres. In (b) the ground state phase diagram of Ti-Zr-Ni shows the creases (solid lines) of the minimum energy surface of the competing binary phases. The shaded regions represent the experimental composition of the quasicrystal and the approximant phase

of the set of ternary phases investigated here, only the large approximant structures of the  $i$ -TiZrNi quasicrystal (containing complete Bergman clusters) were found to be energetically stable against phase segregation into a mixture of competing phases (see Fig. 27.2b). The energy difference ranged from 14 meV/atom to 28 meV/atom. The large approximants all have similar compositions and structures, and are nearly degenerate in energy: thus, it is likely that the decoration model would be energetically stable for larger approximant structures or the TiZrNi quasicrystal.

The basic features of the decoration model of the quasicrystal can be understood by the energetics of the bonds between the constituents. Ti and Zr atoms are completely miscible and exhibit a zero heat of mixing. Ti and Ni as well as Zr and Ni, on the other hand, have a large negative heat of mixing, indicating strong attractive interactions between these pairs. Thus, it is energetically favourable for all the Ni atoms to be surrounded by Ti or Zr. This explains why, in the structure of the 1/1 approximant and the quasicrystal, hardly any Ni pairs occur. Since Zr is slightly larger than Ti it is no surprise that Zr occupies the more open sites of the structure given by the interior of the PR and RD.

## 27.4 Conclusion

The structure of *i*-TiZrNi was investigated by a least squares refinement of diffraction data combined with ab-initio relaxations. The refined decoration model is energetically stable for approximant structures. While it seems likely that the same holds for bigger approximants or the *i*-TiZrNi quasicrystal, calculations for larger systems have not been performed yet. The calculations, furthermore, indicate that the presence of complete Bergman clusters stabilises the structures.

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