Structural modelling of the Ti–Zr–Ni quasicrystal

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Abstract

The atomic structure of the icosahedral Ti–Zr–Ni quasicrystal is studied using a canonical cell tiling approach. An investigation of the previously proposed structure for W-Ti–Zr–Ni, the 1/1 crystal approximant to the Ti–Zr–Ni icosahedral quasicrystal, has revealed improbable occupation of sites in the region between the Bergman clusters and at the cluster centre. The 1/1 structure is refined for a better-ordered sample of the approximant, using X-ray and neutron diffraction measurements and ab initio relaxation studies. Based on this refined structure, an atomic decoration model for large canonical cell tilings is developed. Calculated diffraction patterns from the generated structures are in reasonable agreement with those measured for the icosahedral quasicrystal. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since the discovery of quasicrystals by Shechtman et al. [1], much effort has been spent in investigating their physical properties, and in particular, exploring the conditions under which nature prefers quasiperiodic to periodic order. Most work has concentrated on aluminium-based quasicrystals.

Here, we consider Ti–Zr-based quasicrystals. As early as 1990, Molokanov and Chebotnikov [2] discovered a metastable icosahedral phase in Ti–Zr–Ni. In the following years further icosahedral phases in the alloys Ti–Zr–Fe [3] and Ti–Zr–Co [4] were found. In the Ti–Zr–Ni system, a thermodynamically stable phase has been discovered [5]. The icosahedral phases in these alloys are disordered with coherence lengths of less than 200 Å. Furthermore, the Ti–Zr-based quasicrystals are formed by rapid quenching or solid state reactions at temperatures of $\approx 600°$C, generally leading to a fine microstructure of quasicrystal and crystal phases. Therefore, an atomic structure determination by diffraction experiments is hardly possible. Consequently little is known about their atomic structure.

There is a hope of obtaining information on the atomic arrangement in Ti–Zr-based quasicrystals by studying the structure of related periodic approximants. In the approximants one is also confronted with the problem of random site occupation, but in these systems the distribution probabilities for the different atoms on the various sites may be determined by diffraction experiments.

In this investigation, we consider the experimentally well-studied Ti–Zr–Ni system. There are several competing periodic phases known in the Ti–Zr–Ni phase diagram. Besides the binary phases α-Ti–Zr, Ti_2Ni and Zr_2Ni, there are two ternary phases; a cubic Frank–Kasper type structure (W-phase) and a hexagonal Laves type phase. The addition of very small amounts of Pd to the W-phase and of Pb to the quasicrystal stabilises these structures [6]. Kim et al. [7] used X-ray and neutron powder diffractions to determine the structure of the W-Ti–Zr–Ni phase, which can be interpreted as a Fibonacci 1/1 approximant of i-Ti–Zr–Ni. The chemical occupation of several sites of the determined structure seems problematic. The cluster centre is only partially occupied and Ni and Ti, despite their chemical differences, share sites.

The experimental investigations raise three questions which will be considered in this work: (a) What is the atomic structure of the 1/1 approximant Ti–Zr–Ni? (b) How does Pd stabilise the 1/1 structure? (c) What are the structural details of the quasicrystal? In this paper, we present a new structural analysis of the 1/1 approximant phase in

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Ti–Zr–Ni, combining powder diffraction data and information from ab initio calculations. The total electronic energies of different atomic configurations of the 1/1 approximant are determined in order to illuminate the questions of partially vacant sites and chemical disorder in these structures. The influence of Pd on the total energy will be investigated. Based on these results a first decoration model for the canonical cell tiling [9] is proposed and compared to the diffraction data.

2. Structural analysis and ab initio calculations for the Frank–Kasper phase

A Rietveld analysis of X-ray and neutron powder diffractions from W-Ti–Zr–Ni data was made to determine its atomic structure. The small number of measurable structural factors makes it difficult to extract information about the site occupation from diffraction data alone. Results from ab initio calculations are used to confirm the structural details.

The refinement of the neutron and X-ray diffraction data originated with the model proposed by Kim et al. [7] by analogy with the structure of $Al_{56}Li_{32}Cu_{12}$ [10]. The atomic positions, site occupancies and thermal parameters converged to a model with $R = 0.043$ and $R_w = 0.060$ (see Fig. 1 and Table 1). Due to the small number of measurable structural factors, the unambiguous determination of the site occupancies is difficult and the refined decoration has to be checked. The composition of the derived structure $Ti_{51}Zr_{33}Ni_{16}$ agrees with the nominal composition $Ti_{50}Zr_{35}Ni_{15}$ within 2%.

Table 1
Refined structure of W-Ti–Zr–Ni showing the sites and the chemical decoration, cI162, space group $Im\bar{3}$, $a_0 = 14.30$ Å, $R_{wp} = 6.0\%$, $R_p = 4.3\%$, $\chi^2 = 1.05$

	Site	x	y	z	Occupancy
1	2(a)	0	0	0	Ni (1.0)
2	24(g)	0	0.103	0.165	Ti (1.0)
3	24(g)	0	0.193	0.310	Ni (1.0)
4	16(f)	0.186	0.186	0.186	Zr (1.0)
5	24(g)	0	0.307	0.114	Zr (1.0)
6	12(e)	0.204	0	0.5	Zr (0.6),Ti (0.4)
7	48(h)	0.145	0.187	0.401	Ti (1.0)
8	12(e)	0.412	0	0.5	Zr (0.5), Ti (0.5)

The atomic positions obtained for the W-phase are similar to the Frank–Kasper phases $Al_{56}Li_{32}Cu_{12}$ [10] and $Al_{40}Mg_{40}Zn_{20}$ [11], consisting of a body centred cubic packing of Bergman clusters connected by a few "glue" sites (see Table 1). The W-Ti–Zr–Ni structure differs from these in (i) the occupation of the central site of the Bergman cluster, which is empty in the cases of Al–Li–Cu and Al–Mg–Zn, and (ii) the chemical disorder, which occurs between the smaller components Al and Cu or Zn in Al–Li–Cu and Al–Mg–Zn, respectively, and between the larger components Ti and Zr in the case of Ti–Zr–Ni. Furthermore, the analysis indicates chemical ordering on the sites of the Bergman cluster and Ti/Zr disorder in the glue sites.

The refined structure differs from that suggested by Kim et al. [7] in the atomic decoration of the sites. Firstly, the centre of the Bergman cluster is found to be fully occupied. Secondly, the first icosahedral shell of the cluster is occupied by Ti only. Thirdly, the chemical disorder on the glue sites
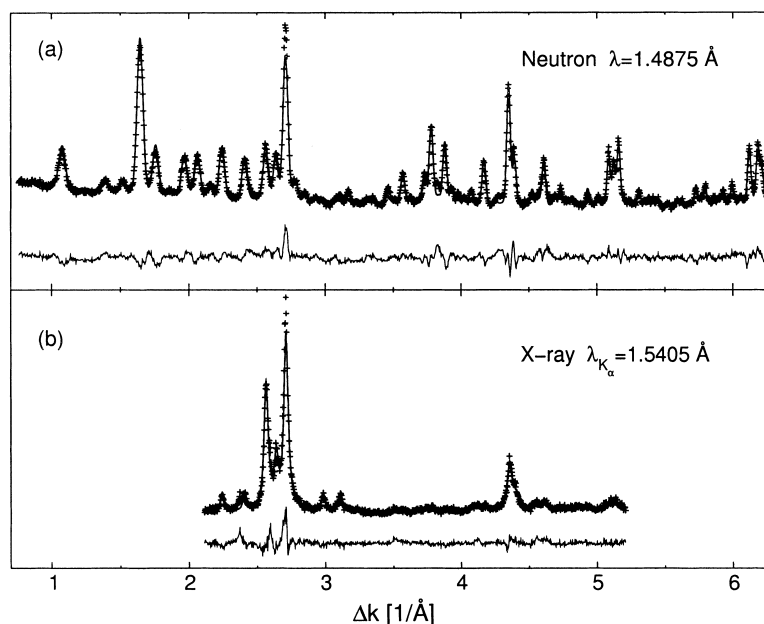

Fig. 1. Rietveld refinement of W-Ti–Zr–Ni: (a) neutron scattering and (b) X-ray diffraction data. The measured data are indicated by "+" and the fit is shown by the solid line. The differences between the fit and the data are given by the thin line at the bottom of each panel.

is solely between Ti and Zr and not between Ti and Ni. Furthermore, the residuals of the refinement ($R_w = 0.06$) are smaller than the ones obtained by Kim et al. [7] ($R_w = 0.10$).

To check the results of the Rietveld analysis, ab initio relaxations are performed. The ab initio calculations were done using the VASP code [8,16,17], 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. As a starting configuration the results from the analysis of the diffraction data are used, where chemical disorder is neglected. The calculations were done at the Γ-point using medium precision which corresponds to a plane-wave kinetic energy cut-off of $E_{cut} = 241.7$ eV. The pseudopotentials for Ti and Zr contain the 3p and 4p states, respectively, as semi-core states.

The atoms are relaxed until the total electronic energy change is smaller than 10^{-3} eV. This corresponds to atomic-level forces $F_{max} \leq 0.01$ eV/Å. For the 1/1 approximant the lattice constant shrank from 14.3 to 13.9 Å which is consistent with typical errors in density functional theory. The atomic positions after the ab initio relaxation are remarkably close to the atomic positions of the refined structure with displacements smaller than 0.06 Å and also

Table 2
Displacement of the atoms (Å) in the model 1/1 structure ($a = 14.3$ Å) between the relaxed and refined as well as between the relaxed and ideal structures

	Site	Rietveld/ab initio	Ideal/ab initio
1	2(a)	0.00	0.00
2	24(g)	0.05	0.20
3	24(g)	0.02	0.04
4	16(f)	0.05	0.07
5	24(g)	0.06	0.02
6	12(e)	0.06	0.13
7	48(h)	0.06	0.13
8	12(e)	0.01	0.10

close to the structure of an ideal 1/1 approximant with displacements smaller than 0.20 Å (see Table 2).

The structural refinement indicated a fully occupied cluster centre, which is scrutinised by calculating the vacancy formation energy for that site

$$Ti_{42}Zr_{26}Ni_{13} \rightleftharpoons Ti_{42}Zr_{26}Ni_{12} + Ni_{f.c.c.} \quad (\Delta E = +3 \text{ eV})$$
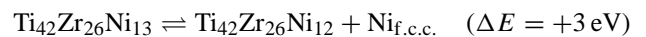
Furthermore chemical disorder seems to be abundant on the "glue" but not on the cluster sites. To check this, the energies of Ti–Zr anti-site defects in the "glue" and cluster regions
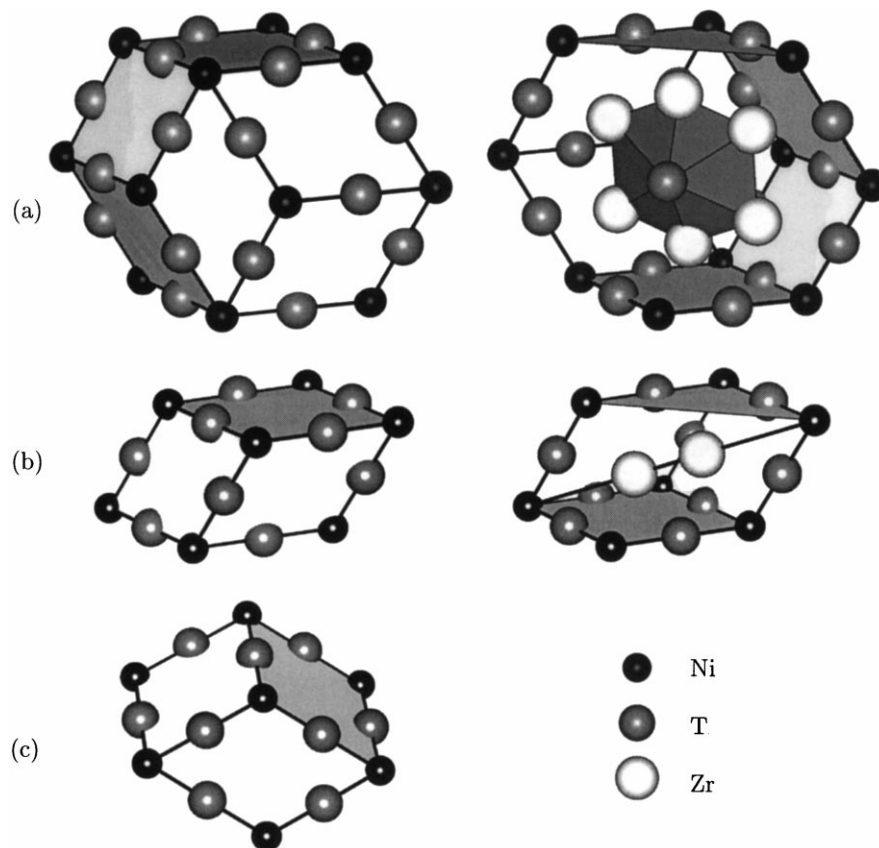

Fig. 2. Decoration of: (a) the rhombic dodecahedron; (b) the prolate rhombohedron; (c) the oblate rhombohedron. The right-hand side pictures show the same decorations with interiors visible.

are calculated. For the "glue" region, two neighbouring Ti and Zr atoms on sites 6 and 8 are exchanged, and for the cluster atoms on sites 2 and 4. The change in energy after relaxation is $-0.6\,\text{eV}$ for the glue defect and $0.06\,\text{eV}$ for the cluster defect, which is consistent with the refinement.

Experiments show that small amounts of Pd stabilise and order the 1/1 approximant. A possible site for these small amounts of Pd is the centre of the Bergman clusters. To check this assumption, the energy gain due to the substitution of Ni with Pd on this site is calculated. Ni and Pd on this site have 12 Ti neighbours. To avoid the inclusion of the difference in the heat of formation into the energy difference, it is assumed that the exchanged Ni and Pd are taken out of a Ti_3Ni and $Ti_3Pd\,L1_2$ structure, respectively, where Ni and Pd have the same coordination. The results of the calculation are

$$Ti_{42}Zr_{26}Ni_{13} + Ti_3Pd \rightleftharpoons Ti_{42}Zr_{26}Ni_{12}Pd_1 + Ti_3Ni$$

$$(\Delta E = -0.5\,\text{eV})$$
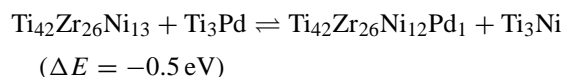
Due to the larger size of Pd compared to Ni, the first shell of the cluster expands by $0.03\,\text{Å}$, the second shell expands by $0.02\,\text{Å}$ and the lattice constant increases by $0.02\,\text{Å}$. The small size of the relaxation effects indicates that the main part of the stabilisation is electronic in nature.

3. Decoration model

In modelling the quasicrystal structure the canonical cell tiling (CCT) model is used [9]. The packing rules permit periodic, random and, in principle, quasiperiodic tilings, although no rule for a quasiperiodic tiling is yet known [9,12]. CCTs consist of four kinds of cells, such that their nodes are joined by two types of linkages, b and c bonds, which run in twofold and threefold directions, respectively. CCTs can be decomposed into smaller tiles with edges along fivefold directions, the prolate and oblate rhombohedra, as well as the rhombic dodecahedron [9].

The atomic decoration of the rhombic dodecahedron and the prolate rhombohedron is determined by the atomic structure of the 1/1 approximant. As for the oblate rhombohedron, its face decoration is forced by the need to adjoin with the other tiles (see Fig. 2), and it has no space for additional interior atoms. The decoration is similar to the Henley–Elser decoration of Al–Mg–Zn [13].

4. Diffraction

As a good approximation of the quasiperiodic tiling, a cubic 8/5 CCT approximant with 576 nodes forming 1320 A, 576 BC and 136 D cells is used [14]. The structure factor of the icosahedral reflections is approximated by averaging
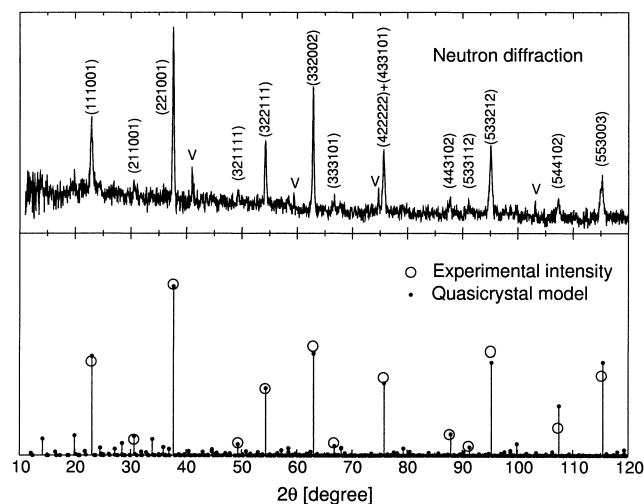

Fig. 3. Comparison of the experimental neutron scattering data to the simulated neutron scattering of the icosahedral structure.

Table 3
Results of the refined chemical disorder on the glue sites for the quasicrystal

Site	Decoration
Cluster	
Corner	Ni (1.0)
Mid-edge	Ti (1.0)
Body diagonal of PR	Zr (1.0)
Glue	
Corner	Ni (1.0)
Mid-edge	Ti (0.7), Zr (0.3)
Body diagonal of PR	Zr (0.6), Ti (0.4)
Distant sites inside RD	Zr (0.7), Ti (0.3)
Close sites inside RD	Zr (0.5), Ti (0.5)

over the amplitudes of all the Bragg peaks in the approximant, which map onto a single orbit of icosahedral peaks.

The chemical decoration of the ideal atomic sites is refined with respect to the integrated intensity of 13 neutron diffraction structure factors for i-Ti–Zr–Ni (see Fig. 3 and Table 3). The results show a strong disorder on "glue" sites and a chemically ordered cluster, which is consistent with the results for the 1/1 approximant and helps to explain the good agreement of the simulated diffraction of an icosahedral glass model for these alloys [15].

The composition of the derived structure $Ti_{42}Zr_{42}Ni_{16}$ agrees with the nominal composition $Ti_{41.5}Zr_{41.5}Ni_{17}$ within 1%.

5. Summary

We presented the refinement of the atomic structure of the 1/1 approximant W-Ti–Zr–Ni to X-ray and neutron diffraction data using results of ab initio calculations to verify

structural features. The information from the 1/1 approximant was used to derive the atomic sites of a decoration model for the quasicrystal i-Ti–Zr–Ni based on the CCT. The chemical decoration was derived by refining simulated neutron scattering to measured structure factors. The results indicate a chemically ordered cluster and Ti/Zr disorder on the "glue" sites.

Acknowledgements

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