

Rietveld refinement and *ab initio* calculations of a C14-like Laves phase in Ti–Zr–Ni

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ABSTRACT

Ternary Ti–Zr–Ni alloys form icosahedral and other complex phases near the composition $\text{Ti}_{41.5}\text{Zr}_{41.5}\text{Ni}_{17}$. Among these is a C14-like Laves phase, λ -(Ti–Zr–Ni), which forms at a composition $\text{Ti}_{37}\text{Zr}_{33}\text{Ni}_{30}$. The crystal structure of this phase is determined by a Rietveld analysis. *Ab initio* calculations are used to confirm the structural details and to investigate the energetic stability of the structure. We show that λ -(Ti–Zr–Ni) is a high-temperature phase, with a MgZn_2 -type structure with Zr occupying primarily the Mg sites and Ti and Ni randomly occupying the Zn sites.

§ 1. INTRODUCTION

Studies on Ti–Zr–Ni ternary alloys, which form a quasicrystal near the composition $\text{Ti}_{41.5}\text{Zr}_{41.5}\text{Ni}_{17}$, demonstrate the formation of a wide variety of complex crystal phases (Davis *et al.* 2000) including a tetrahedrally coordinated phase, λ -(Ti–Zr–Ni), which forms in a phase field roughly between 0.30–0.40 (Ni) and 0.30–0.60 (Zr). Early studies identified the structure of this phase as a MgZn_2 -type Laves phase (Teslyuk 1969, Molokanov *et al.* 1989). The Laves phases are one of three polytetrahedral intermetallic phases denoted in the Strukturbericht system as C14, C15 and C36. Their general formula is AB_2 where A is the larger of the two elements which, for a maximum filling of space, requires that $r_A/r_B = 1.225$ for hard spheres. The C14 or MgZn_2 -type phase, observed in the Ti–Zr–Ni alloys, is hexagonal with B atoms forming tetrahedra that are stacked base to base and tip to tip along the *c*-axis (Barrett and Masalski 1980). The lattice parameters, at 30 at.% Zr, determined by Teslyuk (1969) and Molokanov *et al.* (1989) are $a = 5.23 \text{ \AA}$, $c = 8.53 \text{ \AA}$, and $a = 5.191 \text{ \AA}$, $c = 8.520 \text{ \AA}$, respectively.

The formation and structure of this C14 phase can provide important clues about why a stable icosahedral phase forms in these alloys. The structure of this phase was investigated using a Rietveld refinement of both X-ray and neutron diffraction data to determine the atomic positions and occupancies of the constituent

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elements. To confirm the structural details and to investigate the energetics of the formation of the Laves phase, *ab initio* calculations were performed for different models of the Laves phase based on the Rietveld refinement. The results of these investigations are reported here.

§ 2. EXPERIMENTAL METHODS

Sample materials were purchased from Alpha Aesar[®], with O concentrations of 166, 70, and 66 ppm for Ti, Zr and Ni respectively. Alloy ingots of the desired composition were made by arc melting mixtures of the pure elements on a water-cooled Cu hearth in a high-purity Ar gas atmosphere. The ingot was melted, flipped and remelted. This cycle was repeated three times to maximize sample homogeneity. The ingot was placed in a graphite crucible and sealed in a fused silica tube under a dynamic vacuum of 10^{-4} – 10^{-5} Pa. The graphite crucible prevented possible O and Si contamination from the fused silica tube, which was known to promote the formation of a Ti₂Ni-type phase (Davis *et al.* 2000) and an amorphous phase (Zhang *et al.* 1994). A Ti–Zr getter, located at some distance from the sample, was sealed in the same silica tube. Prior to sample annealing, the Ti–Zr getter was first heated to approximately 1000°C for 10 min, keeping the alloy ingot and the graphite crucible near room temperature. This resulted in a dramatic decrease in the residual O in the silica tube.

A sample of composition Ti₃₇Zr₃₃Ni₃₀ was the most Laves phase pure, containing less than 5% of other phases. The volume fraction of impurities was determined by the peak areas in X-ray powder diffraction which could not be indexed to the Laves phase. No further attempt was made to investigate the impurities. The composition of the sample was determined from the mass of its elemental constituents prior to arc melting. The as-cast sample prepared at this composition was annealed at 800°C for 5 days to maximize the amount of Laves phase present. The sample was ground under ethanol in an agate mortar to a particle size of around 10 µm prior to diffraction analysis.

X-ray diffraction studies were made using a Rigaku Geigerflex powder diffractometer in the Bragg–Bretano geometry, with Cu K_α radiation, and graphite exit monochromator. A powder sample of mass about 100 mg was adhered to a Rigaku glass slide by a thin smear of Vaseline petroleum jelly, applied with a cotton swab. The count time for each step of $0.05^\circ(2\theta)$ was 3 s.

Neutron diffraction data were obtained at the Missouri University Research Reactor. A powdered sample of mass 1 g was contained in a V tube of about 0.3 cm diameter. The diffractometer used a bent Si monochromator, resulting in neutrons with a wavelength of 1.4875 Å. The data were collected using a $20^\circ(2\theta)$ linear position-sensitive detector and binned into $0.05^\circ(2\theta)$ increments. Each $20^\circ(2\theta)$ section of data were counted up to a monitor count of eight million.

§ 3. RIETVELD REFINEMENT

A Rietveld refinement of the neutron and X-ray powder diffraction data was performed to determine the crystal structure of the phase. The quality of a structural analysis is characterized by the residual R and the weighted residual R_w , as well as the reduced χ^2 , providing a standard measure of how well the calculated data matches the observed data. The refinement was performed using the *general structural analysis system* (GSAS) (Larson and Dreele 2000). In GSAS the residuals are defined as

$$R = \frac{\sum_q |I_o(q) - I_c(q)|}{\sum_q I_o(q)},$$

$$R_w = \left(\frac{\sum_q w(q) [I_o(q) - I_c(q)]^2}{\sum_q w(q) I_o(q)^2} \right)^{1/2}. \quad (1)$$

The reduced χ^2 is given by

$$\chi^2 = \frac{\sum_q w(q) [I_o(q) - I_c(q)]^2}{N_{\text{obs}} - N_{\text{var}}}, \quad (2)$$

where $I_o(q)$ and $I_c(q)$ are the observed and calculated intensities respectively. N_{obs} and N_{var} are the number of data points and the number of fitting parameters respectively. The weighting factor w is given by $w = 1/\sigma^2$, where σ is the estimated statistical error of the intensity. Ideally the reduced χ^2 for refinement is one, indicating a statistically perfect fit. A refinement usually has crystallographic significance if the reduced χ^2 has a value that is less than four. For the thermal correction of the structure factors, a Debye–Waller factor

$$f_{\text{DW}} = \exp\left(-\frac{B_{\text{iso}}}{8\pi^2} q^2\right) \quad (3)$$

was used with isotropic thermal parameters B_{iso} for each of the three types of atom on every site.

The refinement results for the C14 structure from X-ray and neutron data are shown in figure 1 and table 1. The resulting residual R of the structure factors is

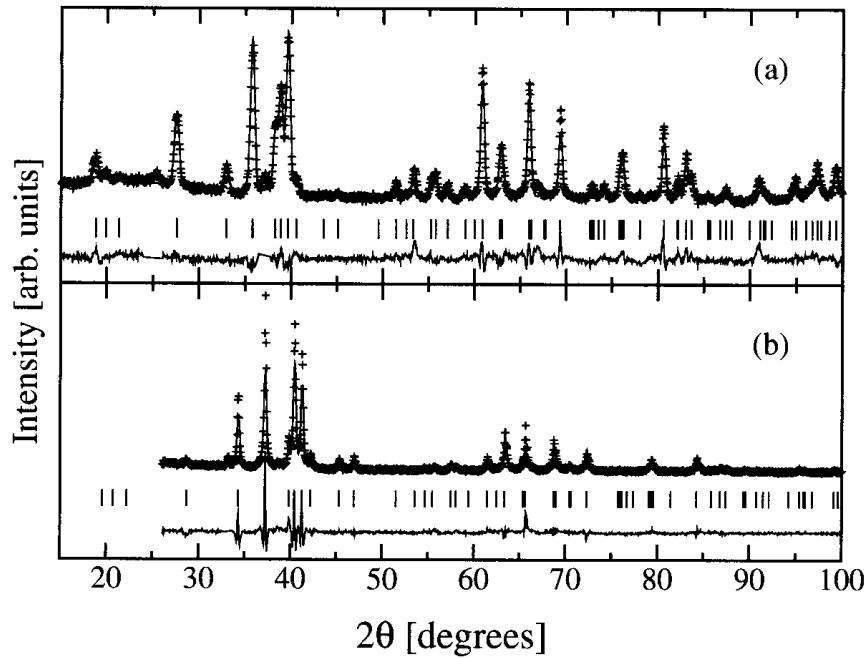


Figure 1. Rietveld refinement of Laves-type Ti–Zr–Ni: (a) neutron scattering and (b) X-ray diffraction data: (+), experimental data; (—), fit data. The vertical bars indicate the calculated reflection positions. The difference curves are shown at the bottom of (a) and (b). The shoulder at 67° in the neutron diffraction data is due to the V sample holder.

Table 1. Results of the combined X-ray and neutron diffraction Rietveld refinement of the Laves phase in $\text{Ti}_{37}\text{Zr}_{33}\text{Ni}_{30}$. The numbers in parentheses are standard deviations.

Space group	$P6_3/mmc$				
a	5.222 10(15) Å				
c	8.558 5(4) Å				
χ^2	1.27				
X-ray					
R	11.2%				
R_w	14.6%				
Neutron					
R	3.6%				
R_w	4.7%				
Combined					
R	5.2%				
R_w	7.9%				
					B_{iso} (Å ²)
Site	x	y	z	Occupancy	
2(a) Ti	0	0	0	0.804(3)	3.07(32)
2(a) Ni	0	0	0	0.196(3)	2.55(48)
4(f) Zr	$\frac{1}{3}$	$\frac{2}{3}$	0.066 33(28)	0.850(2)	2.16(5)
4(f) Ti	$\frac{1}{3}$	$\frac{2}{3}$	0.066 33(28)	0.150(2)	0.77(52)
6(h) Ti	0.837 1(4)	0.674 3(7)	$\frac{1}{4}$	0.463(2)	2.53(26)
6(h) Ni	0.837 1(4)	0.674 3(7)	$\frac{1}{4}$	0.537(2)	2.34(9)

5.2%, and the weighted residual R_w is 8%. The reduced χ^2 is 1.27, indicating crystallographic significance for the fit. The thermal parameters are listed for each site in table 1.

The refined atomic decoration of the sites shows chemical disorder on all sites, mostly between Ti and Ni. The 4(f) site corresponds to the A atom and the 2(a) and 6(h) sites to the B atom in the formula AB_2 . The ratio of the atomic radii of the Zr to the Ti atoms is about 1.28 (Kittel 1953), suggesting that Zr should occupy the A site; the refinement places Zr on the A site, in agreement with this size argument. The refined composition of $\text{Ti}_{41}\text{Zr}_{29}\text{Ni}_{30}$ agrees with the nominal composition of $\text{Ti}_{37}\text{Zr}_{33}\text{Ni}_{30}$ to within 4 at.%. The composition of the refined structure is low in Zr. Forcing a sole occupancy of the 4(f) site with Zr, to improve the chemical order and to increase the amount of Zr, increases the value of χ^2 from 1.29 to 2.62 and increases R_w to 11.3%. This indicates that chemical disorder occurs also between Zr and Ti on the 4(f) sites.

§ 4. *AB INITIO* ENERGY CALCULATIONS

The Rietveld refinement of the Laves phase shows that chemical disorder is abundant on all three Wyckoff sites. Furthermore, it is known that the λ phase forms at high temperatures, around 800°C. Altogether, the experimental results indicate that the λ phase is a high-temperature phase, stabilized by entropy. *Ab initio* relaxations were performed to confirm the structural details of the Rietveld analysis and to provide information about the total energy of this phase.

4.1. Method and structural models

The *ab initio* calculations were performed with the Vienna *ab initio* simulation package (VASP) (Kresse and Hafner 1993, Kresse and Furthmüller 1996a,b), a density functional code using a plane-wave basis and ultrasoft Vanderbilt (1990) type pseudopotentials (Kresse and Hafner 1994). The generalized-gradient approximation by Perdew and Wang (1992) was used for the exchange–correlation energy. The core states described by the pseudopotentials consist of the [Ne] 3s² states for Ti, the [Ar] 3d¹⁰4s² states for Zr and the [Ar] states for Ni. It is noted that for Ti and Zr the 3p and 4p states respectively are treated as semicore states, which was found to be necessary to avoid unphysical short distances between the atoms. For the plane-wave cut-off energy a value of 302 eV was used to ensure convergence to better than 2 meV atom^{−1}.

Atomic-level forces were calculated and relaxations of the atomic position and the cell parameters with a conjugate gradient method were performed until the energy changed by less than 1 meV, corresponding to forces smaller than 0.02 eV Å^{−1}. The size of the *k*-point mesh was chosen to give the same accuracy for the energy and forces. The Brillouin-zone integration was performed using the method of Methfessel and Paxton (1989), using an 8 × 8 × 8 *k*-point mesh and a smearing of 0.1 eV. These parameters yield an overall accuracy of the calculated energies to be better than 5 meV atom^{−1}.

To investigate the structure of the λ phase, *ab initio* relaxations for the six possible structures resulting from distributing the three species Ti, Zr and Ni over the three Wyckoff sites 2(a), 4(f) and 6(h), are performed (see table 2). To investigate possible disorder, three further structural models were investigated; the details will be given below.

The energies of the competing binary phases were calculated using the same method. The results of that work have been published elsewhere (Hennig 2000, Hennig *et al.* 2002).

4.2. Results

The calculated energies and lattice parameters of the models of the λ-(Ti–Zr–Ni) phase are shown in table 2. The energies Δ*E* of formation from the competing binary phases of the ordered structural models 1–6 for the λ phase range from −11 meV atom^{−1} for model 1 to +786 meV atom^{−1} for model 3. The only λ-phase model which is stable against the binary phases is given by model 1, λ-Ti₆Zr₄Ni₂. However, this composition is very close to the composition of two other ternary Ti–Zr–Ni phases, namely the W phase and the quasicrystal, which are even lower in energy (Hennig 2000, Hennig *et al.* 2002). Also in experiments the composition of the λ phase is found to be around Zr(Ti + Ni)₂ with at least 20 at.% Ni. Thus, it can be concluded that the ordered λ phase cannot be a ground-state structure.

The lattice parameters and *c/a* ratios calculated for the models 1–6 of the λ phase differ significantly from the experimental values. Of these models the lattice parameters of model 6 are closest to the experimental values. Although, this structure is unstable against the binary phases, the energy difference Δ*E* = +66 meV atom^{−1} is small enough that the structure could be stabilized by entropy. This is in contrast with the other four models 2–5, which have a very high formation energy of over +210 meV atom^{−1}.

The results presented so far indicate that the structure of the λ phase might be understood as a mixture of structure models 1 and 6, corresponding to chemical

disorder of Ti and Ni on sites 2(a) and 6(h), while the 4(f) sites are occupied by Zr. In order to investigate the effects of disorder between Ti and Ni on the 2(a) and 6(h) sites, *ab initio* relaxations for three further structural models were performed. In all three models, the 4(f) sites are occupied by Zr and the 6(h) sites are occupied by three Ti atoms and three Ni atoms, such that the structure retains its threefold symmetry axis but not the inversion symmetry, lowering the space group of the structure from $P6_3/mmc$ to $P3m1$. The 2(a) sites are occupied by Ti in model 7 and by Ni in model 8. In model 9 Ni is placed on one of the 2(a) sites and Ti on the other (see table 2).

It is first noted that the lattice constants for the structural models containing site disorder are closer to the experimental values than for the models without disorder. The electronic energies for the disordered structures are unfavourable by 114–143 meV atom⁻¹ against decomposition into the competing binary phases, indicating that these structures are not ground-state structures either but could possibly be stabilized by entropy at higher temperatures. To investigate a possible entropic stabilization of the λ phase, the entropy of mixing due to the random occupation of the sites 2(a) and 6(h) by Ti and Ni is estimated by

$$S_M = -Nk_B(\nu_{\text{Ti}} \ln \nu_{\text{Ti}} + \nu_{\text{Ni}} \ln \nu_{\text{Ni}}). \quad (4)$$

Assuming an equal number of Ti and Ni atoms, that is $\nu_{\text{Ti}} = \nu_{\text{Ni}} = 0.5$, yields for the entropy of mixing $S_M \approx 0.5k_B \text{ atom}^{-1}$. The λ phase forms at temperatures near 1000 K. The entropic stabilization by the random mixing of Ti and Zr at this temperature is approximately 40 meV atom⁻¹. Thus, the entropy of mixing alone cannot explain the stability of the λ phase; however, it already accounts for about a third of the necessary value. A large vibrational or electronic entropy appears to be crucial for the stability of the λ phase. The vibrational entropy can be calculated in the quasiharmonic approximation from the phonon density of states. However, the calculation of the phonon spectrum of complex metallic phases is computationally extremely demanding and beyond the scope of this letter.

Table 2. Structures and electronic energies of possible λ -(Ti–Zr–Ni) phases. The experimental values of the lattice constants for $\text{Zr}(\text{Ti} + \text{Ni})_2$ have been given by Stroud (1996).

Model	Atoms in following sites			a (Å)	c (Å)	c/a	E (eV atom ⁻¹)	ΔE (meV atom ⁻¹)
	2(a)	4(f)	6(h)					
1	Ni	Zr	Ti	5.638	7.901	1.40	-7.767	-11
2	Ni	Ti	Zr	6.008	7.636	1.27	-7.653	+210
3	Ti	Ni	Zr	6.533	6.352	0.97	-6.855	+786
4	Zr	Ni	Ti	4.961	9.209	1.86	-6.715	+689
5	Zr	Ti	Ni	5.128	7.897	1.54	-6.952	+210
6	Ti	Zr	Ni	5.176	7.996	1.55	-7.219	+66
7	Ti	Zr	Ti/Ni	5.239	8.780	1.68	-7.524	+114
8	Ni	Zr	Ti/Ni	5.205	8.242	1.59	-7.262	+143
9	Ti/Ni	Zr	Ti/Ni	5.268	8.400	1.59	-7.387	+135
Experimental: $\text{Zr}(\text{Ti} + \text{Ni})_2$				5.23	8.55	1.63		
Experimental: $\text{Ti}_{37}\text{Zr}_{33}\text{Ni}_{30}$				5.22	8.56	1.64		
Rietveld: 2(a), Ti(0.8), Ni(0.2); 4(f), Zr(0.9), Ti(0.1); 6(h), Ti(0.5), Ni(0.5)								

Altogether, the results of the calculations confirm the experimental observation that the λ phase is a high-temperature phase, which can form over a wide range of compositions. The structure of the λ phase is given by the C14 structure, with Zr occupying the 4(f) sites and Ni and Ti randomly occupying the 2(a) and 6(h) sites. Interestingly, the disorder in the λ phase occurs between Ti and Ni, while for other phases in the Ti–Zr–Ni phase diagram such as the W phase and the quasicrystal the disorder seems to occur mostly between Ti and Zr (Hennig *et al.* 2000). This indicates that in the λ phase the size of the atoms is more important than the chemistry.

§ 5. CONCLUSION

The first Rietveld refinement of the structure of the C14-like phase, λ -(Ti–Zr–Ni), was reported. *Ab initio* relaxations confirmed the structural details. The calculated energies indicate, in agreement with experimental results, that the λ phase is a high-temperature phase. Random site occupation seems to occur between Ni and Ti on the 2(a) and 6(h) sites of the structure. The entropy of mixing alone, however, is not enough to explain the stability of this phase at high temperatures. It is conjectured that the structure is stabilized by additional vibrational or electronic entropy.

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REFERENCES

- BARRETT, C., and MASSALSKI, T. B., 1980, *Structure of Metals*, third edition (Oxford: Pergamon), chapter 10, pp. 256–259.
- DAVIS, J. P., MAJZOUB, E. H., SIMMONS, J. M., and KELTON, K. F., 2000, *Mater. Sci. Engng*, **A294–A296**, 104.
- HENNIG, R. G., 2000, PhD Thesis, Washington University, Saint Louis, Missouri, USA.
- HENNIG, R. G., KELTON, K. F., and HENLY, C. L., 2002, *Studies in Condensed-Matter Physics*, Springer Proceedings in Physics, Vol. 89, edited by D. P. Landau, S. P. Lewis and H.-B. Schüttler (Berlin: Springer), pp. 27–31.
- HENNIG, R. G., MAJZOUB, E. H., CARLSSON, A. E., KELTON, K. F., HENLEY, C. L., YELON, W. B., and MISTURE, S., 2000, *Mater. Sci. Engng*, **A294–A296**, 361.
- KITTEL, C., 1953, *Introduction to Solid State Physics* (New York: Wiley).
- KRESSE, G., and HAFNER, J., 1993, *Phys. Rev. B*, **47**, 558; 1994, *J. Phys.: condens. Matter*, **6**, 8245.
- KRESSE, G., and FURTHMÜLLER, J., 1996a, *Comput. Mater. Sci.*, **6**, 15; 1996b, *Phys. Rev. B*, **54**, 11 169.
- LARSON, A. C., and VON DREELE, R. B., 2000, Report LAUR 86-748, Los Alamos National Laboratory.
- METHFESSEL, M., and PAXTON, A. T., 1989, *Phys. Rev. B*, **40**, 3616.
- MOLOKANOV, V. V., CHEBOTNIKOV, V. N., and KOVNERISTYI, Y. K., 1989, *Inorg. Mater.* **25**, 46.
- PERDEW, J. P., and WANG, Y. 1992, *Phys. Rev. B*, **45**, 13 244.
- STROUD, R. M., 1996, PhD Thesis, Washington University, St. Louis, Missouri, USA.
- TESLYUK, M. Y., 1969, *Metallic Compounds with Laves Phase Structure* (Moscow: Nauka).
- VANDEBILT, D., 1990, *Phys. Rev. B*, **41**, 7892.
- ZHANG, X., STROUD, R. M., LIBBERT, J. L., and KELTON, K. E., 1994, *Phil. Mag. B*, **70**, 927.

