

Fig. 1. Projection de l'enchaînement des polyèdres de  $\text{LiBUO}_5$  selon [100].

Dans l'ensemble, la structure est tout à fait semblable à celle de  $\text{NaBUO}_5$ : les ions  $\text{U}^{6+}$  sont entourés d'une bipyramide pentagonale qui forme une liaison uranyle  $\text{O}(2)\text{—U—O}(4)$  et dont les bases sont liées par les arêtes  $\text{O}(3)\text{—O}(3)$  et  $\text{O}(1)\text{—O}(1)$  dans la direction  $c$ . Ces files de polyèdres sont reliées dans la direction  $b$  par les triangles  $\text{BO}_3$ . Cet assemblage  $(\text{BUO}_5)^-$ , situé en moyenne dans le plan  $bc$  autour de  $x = 0$ , est fixé dans le plan perpendiculaire par l'alcalin au voisinage de  $x = 0,5$ . La différence entre les deux structures réside dans le fait que l'ion  $\text{Li}^+$ , plus petit que  $\text{Na}^+$ , se déplace légèrement du centre de l'octaèdre que ce dernier occupe dans  $\text{NaBUO}_5$  pour se mettre au centre d'un tétraèdre  $\text{O}(2)\text{—O}(4)\text{—O}(5)\text{—O}(5)$  avec une distance moyenne  $\text{Li—O}$  de 2,05 Å. Il en résulte qu'une fois sur deux, une liaison alcalin—oxygène de la liaison uranyle est rompue, ce qui favorise le glissement des feuillets les

uns sur les autres. On comprend donc pourquoi le remplacement du sodium par le lithium a tellement fragilisé le composé, rendant très difficile le choix d'un cristal apte à une mesure diffractométrique. L'emplacement schématisé d'un des atomes de sodium tel qu'il se trouve dans  $\text{NaBUO}_5$  est indiqué en pointillés sur la Fig. 1, avec ses six liaisons.

L'abaissement de la coordinence de l'alcalin rend nécessaire une compensation de la balance des charges. Elle s'effectue à travers la déformation de la bipyramide pentagonale entourant l'uranium dont l'axe — la liaison uranyle  $\text{O}(2)\text{—U—O}(4)$  — est moins rectiligne que dans  $\text{NaBUO}_5$  ( $176^\circ$  au lieu de  $179^\circ$ ).

Signalons enfin que ce composé présente, à la simple lumière d'une lampe UV, une forte luminescence qui mérite d'être étudiée.

En conclusion, ce deux borouranates ne sont pas vraiment isotopes en raison des deux coordinences différentes prises par Na et Li. Ils sont néanmoins très proches, le moins symétrique,  $\text{LiBUO}_5$ , cristallisant dans un sous-groupe ( $P2_1/c$ ) du plus symétrique,  $\text{NaBUO}_5$  ( $Pbcm$  avec  $bc$ ).

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## Structure of $\omega\text{-Ti}_3\text{Al}_{2.25}\text{Nb}_{0.75}$

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**Abstract.**  $\omega$  phases form by cooling from high-temperature  $A2$  or  $B2$  phases as a result of displacement of some of the atoms in the direction of a body diagonal of the parent phase, accompanied by

ordering. The apparent cubic symmetry is caused by quadruple twinning of trigonal cells with their  $c$  axes in the directions of the body diagonals of the parent phase. The structure of one of the twin variants of an

$\omega$  phase in the Ti–Al–Nb system was determined from intensity data collected by X-ray diffractometer with Mo  $K\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ).  $\text{Ti}_3\text{Al}_{2.25}\text{Nb}_{0.75}$ ,  $M_r = 274.1$ , trigonal,  $P\bar{3}m1$ ,  $a = 4.5554 (10)$ ,  $c = 5.5415 (14) \text{ \AA}$ ,  $V = 99.59 (7) \text{ \AA}^3$ , atoms/cell = 6,  $D_x = 4.57 \text{ g cm}^{-3}$ ,  $\mu = 83.2 \text{ cm}^{-1}$ ,  $F(000) = 126$ ,  $T = 296 \text{ K}$ , final  $R = 0.032$  for 251 (single) reflections with  $I > 3\sigma$ . Ten parameters were refined: two  $z$  parameters, four occupancies, and four isotropic temperature factors. The atoms are partially ordered: the Ti atoms on  $1(a)$  (with some Nb mixed in) and  $2(d)$  together occupy the  $A$  positions of the  $B2$  substructure; the Nb atoms on  $1(b)$  (with some Al mixed in) together with the Al atoms on  $2(d)$  occupy the  $B$  positions. The atom displacements result in some short Al–Ti distances of 2.650 (1)  $\text{\AA}$ , and long Al–Al and Ti–Ti near-neighbor distances of 3.620 (3) and 3.567 (2)  $\text{\AA}$  respectively. Analysis of the twin reflections indicates that some untransformed cubic material is present.

**Introduction.** The  $\omega$  phase is a metastable phase formed in many alloy systems during cooling of a high-temperature disordered b.c.c. ( $A2$ ) or ordered CsCl ( $B2$ ) phase resulting in hardening of the alloys. The phase occurring in the Ti–Cr system at 8.1 wt% Cr was originally described as b.c.c.,  $I\bar{4}3m$  with  $a = 9.80 \text{ \AA}$ , equal to three times the  $a$  of the parent b.c.c. phase (Austin & Doig, 1957). Bagariatskii & Nosova (1958) determined that the apparent cubic symmetry was a result of quadruple twinning of trigonal cells with  $c$  axes in the directions of the body diagonals of the b.c.c. cell. These authors described the  $\omega$  phase with the trigonal  $c$  axis equal to one half of the body diagonal of the cubic cell;  $a = 4.62$ ,  $c = 2.83 \text{ \AA}$ , space group  $P\bar{3}m1$  (No. 164); random occupancy of positions:  $1(a)$  (0,0,0) and  $2(d)$  ( $\frac{1}{3}, \frac{2}{3}, z; \frac{2}{3}, \frac{1}{3}, \bar{z}$ ) with  $z = 0.480 \pm 0.003$  determined by X-ray diffraction of a single crystal with Ti–5%Cr. Silcock (1958) concluded from single-crystal X-ray diffraction of  $\omega$  phases in TiV, TiZr, TiMo and TiCr systems that  $z$  is not significantly different from  $\frac{1}{2}$ , which makes the structure of the  $\text{AlB}_2$  or  $C32$  type ( $hP3$ ) with random occupancy of the sites. Prasetyo, Reynaud & Warlimont (1976) studied the quenched CuZn  $\beta$  brass ( $B2$ ) system by electron microscopy and diffraction and observed an ordered  $\omega$  phase (also called  $\omega'$  phase), again with four trigonal variants in the cubic  $B2$  matrix. The  $c$  axis of this trigonal phase equals the body diagonal of the parent cubic phase; space group  $P\bar{3}m1$ , Cu at  $1(a)$  (0,0,0) and  $2(d)$  ( $\frac{1}{3}, \frac{2}{3}, z$ ) with  $z = \frac{3}{4}$ , Zn at  $1(b)$  (0,0, $\frac{1}{2}$ ) and  $2(d)$  with  $z = \frac{1}{4}$ . These positions correspond to the positions of the atoms in the  $B8_2$  or  $\text{Ni}_2\text{In}$  type ( $hP6$ ), which however has space group  $P6_3/mmc$  (No. 194) with Ni occupying the Cu positions and the Zn position at  $0,0,\frac{1}{2}$ . The  $\omega$ -phase model described by Georgopolous & Cohen

(1981) in the Ni–Al system (which we will call  $\omega''$  phase) is similar to the CuZn model, but allows for a variable  $z$  parameter:  $P\bar{3}m1$ , Ni at  $1(a)$  and  $2(d)$  ( $\frac{1}{3}, \frac{2}{3}, \frac{2}{3} + u$ ), Al at  $1(b)$  and  $2(d)$  ( $\frac{1}{3}, \frac{2}{3}, \frac{1}{6} + u$ ). In this description the positions correspond for  $u = 0$  with the CsCl structure and for  $u = \frac{1}{2}$  with  $\text{Ni}_2\text{In}$ .

Bendersky & Boettinger (1988) studied the Ti–Al–Nb system where an alloy of composition  $\text{Ti}_3\text{Al}_{2.25}\text{Nb}_{0.75}$  forms large grains (a few millimeters in size) of b.c.c. or  $B2$  phase at high temperature (1373–1673 K) which transform to  $\omega$ -phase twins upon cooling. One of these grains cut out from the specimen was used in this X-ray diffraction study. The  $c/a$  ratio of the twins (see below) is very close to the value of  $\sqrt{3}/\sqrt{2}$  for cubic symmetry and there are therefore reflections approximately in the positions of the cubic reflections to which all four variants contribute as well as other reflections each caused by only one of the variants.

**Experimental.** Intensity data were collected from a black, cube-shaped crystal, edge length approximately 0.4 mm, with a Rigaku AFC6 diffractometer with Mo  $K\alpha$  graphite-monochromated radiation. The  $\omega$ -scan technique was used, scan rate  $16.0^\circ \text{ min}^{-1}$ , scan width  $(1.60 + 0.30 \tan \theta)^\circ$ ,  $2\theta_{\text{max}} = 100^\circ$ . The lattice parameters were determined with eight reflections from one twin only in the  $31\text{--}45^\circ 2\theta$  range [ $c/a = 1.216 (1)$ , to be compared to  $\sqrt{3}/\sqrt{2} = 1.225$ ]. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. Three standard reflections had an average intensity drift of 0.5%. The intensities of the twin reflections and the single reflections, originating from one variant only, were measured for  $h - 9$  to 9,  $k - 9$  to 9,  $l$  0 to 11. The number of reflections measured was 2213, the number of unique reflections 433,  $R$  factor for averaged reflections (based on  $F^2$ ) 0.065. 293 single reflections (251 with  $I > 3\sigma$ ) were used to determine the structure of the corresponding variant. There were no systematic absences; the symmetry of the diffraction data indicated space group  $P\bar{3}m1$  (No. 164).

The structure model was essentially the  $\omega''$  structure described by Georgopolous & Cohen (1981), but with variable occupancies of the  $1(a)$ ,  $1(b)$ , and  $2(d)$  sites and different  $z$  parameters for the two  $2(d)$  sites. This model was refined by the full-matrix least-squares program contained in the *TEXRAY* system of programs (Molecular Structure Corporation, 1985). In the final cycles the scale factor was kept constant to correspond to the stated composition. The ten variables were two  $z$  coordinates, four isotropic temperature parameters, and four occupancies. An experimental absorption correction (Walker & Stuart, 1983) was applied, which reduced  $R$  from

Table 1. Positional parameters, isotropic *B* values and occupancies (see text) for  $\omega$ -Ti<sub>3</sub>Al<sub>2.25</sub>Nb<sub>0.75</sub>

$f_0$  is the scattering factor for the atom in column 1 at  $2\theta = 0^\circ$  multiplied by the occupancy factor from the refinement.

Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )	$f_0$	No. of atoms		
						Ti	Al	Nb
Ti(1)	1( <i>a</i> )	0	0	0.492 (20)	24.30 (37)	0.88 (2)		0.12 (2)
Nb	1( <i>b</i> )	0	0	0.368 (14)	30.73 (31)		0.32 (2)	0.68 (2)
Al	2( <i>d</i> )	$\frac{1}{2}$	$\frac{1}{2}$	0.22449 (30)	0.669 (33)	13.34 (22)	0.06 (4)	1.94 (4)
Ti(2)	2( <i>d</i> )	$\frac{1}{2}$	$\frac{1}{2}$	0.590 (16)	22.39 (22)	2.00 (2)		

Table 2. Interatomic distances (Å) in  $\omega$ -Ti<sub>3</sub>Al<sub>2.25</sub>Nb<sub>0.75</sub>

Distances in the parent *B2* phase are *A*—*A* (or *B*—*B*) = 3.203 Å and *A*—*B* = 2.774 Å.

	<i>N</i>		Distance	Distance in <i>B2</i>
Ti(1)	2	Nb	2.771 (1)	8 <i>A</i> — <i>B</i>
	6	Al	2.909 (1)	
	6	Ti(2)	3.061 (1)	
Nb	2	Ti(1)	2.771 (1)	8 <i>B</i> — <i>A</i>
	6	Ti(2)	2.893 (1)	
	6	Al	3.041 (2)	
Al	3	Ti(2)	2.650 (1)	8 <i>B</i> — <i>A</i>
	1	Ti(2)	2.732 (3)	
	1	Ti(2)	2.810 (3)	
	3	Ti(1)	2.909 (1)	6 <i>B</i> — <i>B</i>
	3	Nb	3.041 (2)	
	3	Al	3.620 (3)	
Ti(2)	3	Al	2.650 (1)	8 <i>A</i> — <i>B</i>
	1	Al	2.732 (3)	
	1	Al	2.810 (3)	
	3	Nb	2.893 (1)	6 <i>A</i> — <i>A</i>
	3	Ti(1)	3.061 (1)	
	3	Ti(2)	3.567 (2)	

0.062 to 0.058; correction factors on *I*: 0.770 to 1.073. Final  $R = 0.032$ ,  $wR = 0.059$ ,  $S = 1.88$ , 251 reflections with  $I > 3\sigma$ . For all 293 reflections  $R = 0.038$ ,  $wR = 0.062$ . Quantity minimized was  $\sum w(F_o - F_c)^2$  with  $w^{-1} = \sigma^2(F)$ , based on  $\sigma^2(F^2)$  as determined by counting statistics plus a contribution of  $(0.05 F^2)^2$ .  $(\Delta/\sigma)_{\max} = 0.002$ . Final  $\Delta\rho$  excursions  $-1.46$  to  $2.41 e \text{ \AA}^{-3}$ . The scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). The final parameters are listed in Table 1 and the interatomic distances in Table 2.\*

**Discussion.** The  $\omega''$  phase forms from the *B2* phase by ordering of the atoms and small displacements of the atoms in the 2(*d*) positions. The occupancy of the sites given in Table 1 is calculated assuming that the alloy has the stated composition and that no more than two kinds of atoms occupy a site. The Ti atoms

\* A list of structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52378 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

on 1(*a*) and 2(*d*) together occupy the positions of the *A* atoms of the *B2*-type structure [with some Nb mixed in on site 1(*a*)]; the Nb atoms on 1(*b*) (with some Al mixed in) together with the Al atoms on 2(*d*) correspond to the *B* atoms of *B2*. The Al-atom *z* parameter has increased by 0.0578 (3) from the ideal value of  $\frac{1}{6}$  for *B2* and has moved towards the value of  $\frac{1}{4}$  for the Ni<sub>2</sub>In structure. Similarly the *z* parameter for Ti(2) has increased by 0.0508 (2) from the ideal value of  $\frac{2}{3}$  for *B2* in the direction of the value of  $\frac{3}{4}$  for Ni<sub>2</sub>In (see Fig. 1).

Table 2 shows that the distance range in the  $\omega$  phase is not very different from that in the *B2* phase. For Ti(1) and Nb six of the eight distances corresponding to the *A*—*B* distances in *B2* have increased by about 0.12 Å and the six distances corresponding to *A*—*A* and *B*—*B* in *B2* have decreased by about 0.15 Å. The largest changes occur for the atoms in the 2(*d*) positions. The distances between Al and Ti(2) are the shortest in the structure: 2.650 (1) Å, down 0.12 Å from the *A*—*B* distance in *B2*. The Al—Al and Ti(2)—Ti(2) distances have increased to about 3.6 Å, giving these atoms a coordination number of 8 + 3 instead of 8 + 6 in the *B2* structure.

#### Twin reflections

Since the twin domains are microscopic (about 0.2 μm) it was presumed that the contributions of the four orientational variants are approximately equal. In an attempt to confirm this presumption the Miller indices of the four contributions to each of the cubic subcell reflections were identified and the relative amounts of the four contributing variants were estimated by least squares. (Because of intensity

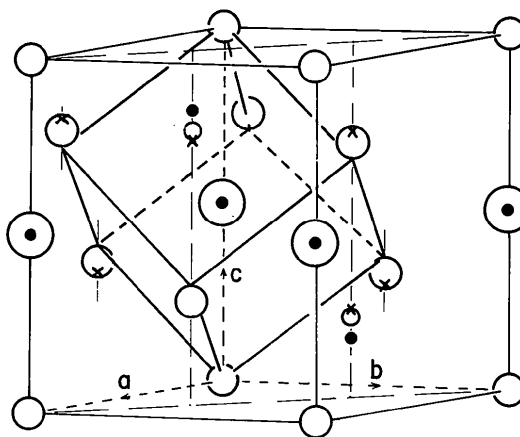


Fig. 1. Trigonal cell for  $\omega$ -Ti<sub>3</sub>Al<sub>2.25</sub>Nb<sub>0.75</sub>. Large open circles: mainly Nb; intermediate open circles: mainly Ti; small open circles: mainly Al (see Table 1). The cube outlines the framework of the *A* atoms in the parent *B2* structure; the filled circles correspond to the *B* atoms of that structure. The crosses indicate the positions of the atoms in the Ni<sub>2</sub>In structure at  $z = \frac{1}{4}$  and  $\frac{3}{4}$ .

considerations, the fit was limited to 62 data with even  $l_{\text{hex}}$ . It was found necessary to include also in the least-squares fit some amount of untransformed cubic material. The resulting percentages of the five contributors together with their e.s.d.'s were:

	Twin (1)	Twin (2)	Twin (3)	Twin (4)	Untransformed
	23.9	18.3	19.1	10.5	28.1
E.s.d.	1.3	1.4	1.3	3.3	3.5

Of the four variants, only twin (4) differs significantly in amount from the average of the others; the reason for the deviation is not apparent. If in the least-squares fit the amounts for all the twin variants are constrained to be equal the fit is significantly less good (at the 99% confidence level according to the  $F$  test), and the amount of untransformed cubic material is indicated to be 17.5% with an e.s.d. of 1.4%. For the untransformed material the temperature factor  $B$  (on  $F$ ) is apparently  $1.53 \text{ \AA}^2$ , about twice the value found for the single twin variant, indicating atomic positional displacements presumably resulting from occupational disorder in the untransformed cubic phase.

*Note added in proof:* We have found that on annealing at 923 K  $\omega''$  transforms into the  $B8_2$  or  $\text{Ni}_2\text{In}$  structure: the  $z$  parameter of Al becomes  $\frac{1}{4}$  and that of Ti(2) becomes  $\frac{3}{4}$ , and the occupancies of 1(a)

and 1(b) become identical mixtures of Ti, Nb, and Al. The intensities of the twin reflections can be accounted for by (unequal) contributions of the four twins without any untransformed cubic material being left over.

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## Structure of Bis(acetato)bis(*meso*-1,2-diphenyl-1,2-ethanediamine)nickel(II) Trihydrate, $[\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{C}_{14}\text{H}_{16}\text{N}_2)_2] \cdot 3\text{H}_2\text{O}$

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**Abstract.**  $[\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{C}_{14}\text{H}_{16}\text{N}_2)_2] \cdot 3\text{H}_2\text{O}$ ,  $M_r = 655.43$ , monoclinic,  $C2/c$ ,  $a = 30.7007$  (3),  $b = 7.1898$  (4),  $c = 22.7114$  (7) Å,  $\beta = 138.513$  (2)°,  $V = 3321.0$  (3) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.28 \text{ Mg m}^{-3}$ . Mo  $K\alpha$  radiation (graphite crystal monochromator,  $\lambda = 0.71073$  Å),  $\mu(\text{Mo } K\alpha) = 0.630 \text{ mm}^{-1}$ ,  $F(000) = 1392$ ,  $T = 293 \text{ K}$ . Final conventional  $R$  factor = 0.035 for 4842 unique reflections. Distances Ni—N(1) and Ni—N(2) are 2.082 (4) and 2.127 (4) Å respectively and the N(1)—Ni—N(2) bite angle is 79.8 (1)°. The nickel coordination is pseudo-octahedral, with two diamine ligands on a plane and two acetates in *trans* position.

**Introduction.** The crystal and molecular structure of the title compound was determined as part of our work on nickel complexes and C-substituted 1,2-ethanediamines. In a previous communication we reported a square-planar complex of nickel(II) with *meso*-stien (García-Granda & Gómez-Beltrán, 1984b). As far as we know no crystal structure of a blue complex of nickel(II) and *meso*-1,2-diphenyl-1,2-ethanediamine (*meso*-stien), has been reported, with the exception of a paper by Nyburg & Wood (1964) where a crystal structure containing yellow and blue forms of bis(*meso*-stien)nickel(II) bis(dichloroacetate) was described. The present paper