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Triclinic ReAl₄, a Periodic Domain Structure Variant of the Monoclinic WAl₄ Type

BY JULIUS C. SCHUSTER* AND ERWIN PARTHÉ

Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 quai Ernest Ansermet, CH-1211, Genève 4, Switzerland

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Dedicated to Professor Kurt Komarek, University of Vienna, on the occasion of his 60th birthday

Abstract. Re₁₄Al_{57-x} with $x = 2.25$, $M_r = 4145.08$ (for 14/57), triclinic, $aP71$ (for 14/57), $P\bar{1}$, $a = 5.159$ (1), $b = 9.106$ (1), $c = 23.755$ (2) Å, $\alpha = 100.94$ (1), $\beta = 90.30$ (1), $\gamma = 93.00$ (1)°, $V = 1094.0$ (3) Å³, $Z = 1$ (for 14/57), $D_x = 6.291$ Mg m⁻³ (for 14/57), $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 43$ mm⁻¹, $F(000) = 1791$ (for 14/57), $T = 293$ K, $R = 0.086$ for 2141 contributing independent reflections. Re₁₄Al_{57-x} can be described as a stacking of two slabs, both about 11.6 Å thick, one cut parallel to (110) and the second cut parallel to ($\bar{1}$ 10) from the monoclinic WAl₄ structure. In one unit cell of Re₁₄Al_{57-x} two WAl₄-type slabs, one of each kind, are stacked parallel to (001). Two kinds of antidomain boundary are found, one with perfect match and a second with less perfect match which provides space for an extra Al site. However, since all Al atom sites at or close to the second antidomain boundary are only partially occupied, the overall composition, despite the extra Al site, has fewer Al atoms than expected for 1:4 stoichiometry.

Introduction. The binary system Re–Al, recently investigated by Schuster (1984), is characterized by the formation of six binary compounds which all decompose before melting. The structures of two compounds tentatively labelled ReAl₃ and ReAl₄ are unknown. We report here on the structure of the latter for which d'Alte da Veiga (1963) assumed a triclinic unit cell with $a = 9.13$, $b = 13.8$, $c = 5.16$ Å, $\alpha = 99.5$, $\beta = 94$ and

$\gamma = 103.5$ °. The cited author expected a close structural relationship between the triclinic ReAl₄ structure and the monoclinic WAl₄ type (Bland & Clark, 1958) [found also with MoAl₄ (Leake, 1964)] based simply on the presence of axes about 5.2 Å along in both structure types, and he made a proposal how the ReAl₄ cell could be fitted to the WAl₄ cell. We shall see from our complete structure determination that there is really a close geometrical relationship between both structure types; however, the unit-cell relationship between ReAl₄ and WAl₄ proposed by d'Alte da Veiga (1963) does not hold. Only two unit-cell vectors of his proposed cell for ReAl₄ are correct.

Experimental. A cold pressed powder mixture Re_{0.1}-Al_{0.9} (Re 99.99%, Al 99.999%) was arc melted under argon atmosphere. The particular composition was chosen to allow the growth of ReAl₄ crystals at 1273 K. From the phase diagram ReAl₄ is in equilibrium with liquid aluminium at this temperature. The heat treatment of the sample was made in an alumina crucible which was placed inside an evacuated quartz tube. After 48 h the sample was water quenched and the unreacted Al dissolved in HCl. The residue consisted of needle-shaped metallic crystals containing 20.5–20.7 at.% Re (by atomic absorption analysis). The only major impurity found by spectrographic analysis was silicon. The rather complex powder diffraction pattern indicated this phase to be related to, but not isotypic with, the WAl₄ type. A needle with mean diameter of 0.015 mm and of 0.1 mm length (volume equal to that of a sphere of 0.0175 mm radius) was chosen.

* On leave from the Institute for Physical Chemistry, University of Vienna, Austria.

Automatic four-circle diffractometer (Enraf-Nonius CAD-4), lattice parameters from θ values of 25 reflections ($5 \leq \theta \leq 17^\circ$, Mo $K\alpha$, $\lambda = 0.71073 \text{ \AA}$). Data collection: $0.0767 < (\sin\theta)/\lambda < 0.6161 \text{ \AA}^{-1}$, 4269 unique reflections measured ($0 \leq h \leq +6$, $-10 \leq k \leq +10$, $-29 \leq l \leq +28$); two standard reflections ($02\bar{4}$, $1, \bar{1}, \bar{1}0$), ± 1.14 and $\pm 0.94\%$ variation respectively; ω - 2θ scan mode. 2141 observed reflections with $I > 3\sigma$, absorption correction using *CAMEL JOCKEY* (Flack, 1975) (min. 1.00, max. 3.18). 548 reflections with $|E| \geq 1.40$. The $|E|$ statistics indicated centrosymmetric space group $P\bar{1}$. The structure was solved by direct methods. The structure was refined based on $|F|$ values. Initial refinement of only positional and displacement parameters led to excessively large values for the displacement factors for the atoms Al(2), Al(3), Al(18), Al(21) and Al(29). Simultaneous refinement of positional, displacement and Al occupation parameters resulted in reasonable displacement factors for all atoms; however, the occupation parameters for the above mentioned Al atoms (and only for these) were found to be significantly less than unity (average uncertainty less than 0.1 atoms/site). When these occupational parameters were restricted in consecutive refinement cycles the final refinement of the 142 positional, displacement and scale factors resulted in a non-weighted $R = 0.086$ for 2141 contributing reflections, final max. shift/e.s.d. ≤ 0.207 . The difference electron density map was empty without significant peaks or holes, $|\Delta\rho| \leq 10 \text{ e \AA}^{-3}$. The value of R is not so good because of the problem with the occupation of the Al sites at one interface. No weighting scheme has been used; however, the information obtained was considered sufficient to interpret the essential features of the structure. Atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974). All programs used for structure determination and refinement from *XRAY76* system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). The final values of positional, displacement and occupational parameters are given in Table 1.* The overall composition calculated from the occupational parameters is $\text{Re}_{14}\text{Al}_{57-x}$ where $x = 2.25$.

Discussion. A projection of two unit cells of triclinic $\text{Re}_{14}\text{Al}_{57-x}$ along [100], the direction of the shortest axis, is shown in Fig. 1(a). Only the Re atom sites are numbered with, however, not the x coordinates but the relative heights of the atoms above the plane of projection. As a consequence of the non-orthogonal

Table 1. Atomic positional, atomic displacement parameters and occupation factors for $\text{Re}_{14}\text{Al}_{57-x}$ with $x = 2.25$, space group $P\bar{1}$

All atoms on Wyckoff position $2i$ except for Al(29) which is on $1a$. Isotropic displacement factors are expressed as $T = \exp[-2\pi^2 U(2\sin\theta/\lambda)^2]$. E.s.d.'s are given in parentheses.

| | x | y | z | $100U(\text{\AA}^2)$ | Occupation factor |
|--------|------------|------------|------------|----------------------|-------------------|
| Re(1) | 0.0122 (7) | 0.7376 (4) | 0.4716 (2) | 0.57 (7) | |
| Al(1) | 0.042 (5) | 0.443 (3) | 0.832 (1) | 1.0 (5) | |
| Al(2) | 0.047 (8) | 0.282 (4) | 0.973 (2) | 2.2 (8) | 0.71 (9) |
| Al(3) | 0.064 (9) | 0.475 (5) | 0.057 (2) | 1.9 (9) | 0.64 (10) |
| Al(4) | 0.075 (5) | 0.031 (3) | 0.124 (1) | 0.8 (6) | |
| Al(5) | 0.083 (5) | 0.711 (3) | 0.668 (1) | 0.7 (6) | |
| Re(2) | 0.1045 (7) | 0.0023 (4) | 0.3213 (2) | 0.62 (8) | |
| Al(6) | 0.111 (5) | 0.162 (3) | 0.424 (1) | 1.3 (6) | |
| Al(7) | 0.114 (6) | 0.261 (3) | 0.732 (1) | 1.7 (6) | |
| Re(3) | 0.1478 (7) | 0.4771 (4) | 0.2630 (2) | 0.53 (7) | |
| Al(8) | 0.166 (5) | 0.580 (3) | 0.374 (1) | 0.6 (5) | |
| Al(9) | 0.175 (5) | 0.454 (3) | 0.462 (1) | 0.8 (5) | |
| Al(10) | 0.183 (5) | 0.178 (3) | 0.619 (1) | 0.7 (5) | |
| Al(11) | 0.244 (5) | 0.197 (3) | 0.863 (1) | 1.3 (5) | |
| Re(4) | 0.2517 (7) | 0.7485 (4) | 0.1134 (2) | 0.87 (8) | |
| Al(12) | 0.253 (5) | 0.014 (3) | 0.520 (1) | 0.3 (5) | |
| Al(13) | 0.291 (5) | 0.907 (3) | 0.216 (1) | 0.6 (5) | |
| Re(5) | 0.2933 (7) | 0.2026 (4) | 0.0550 (2) | 0.63 (7) | |
| Al(14) | 0.336 (5) | 0.200 (3) | 0.260 (1) | 0.5 (5) | |
| Al(15) | 0.337 (5) | 0.324 (3) | 0.162 (1) | 1.0 (5) | |
| Al(16) | 0.351 (4) | 0.443 (2) | 0.572 (1) | 1.0 (4) | |
| Al(17) | 0.382 (4) | 0.755 (3) | 0.302 (1) | 0.4 (5) | |
| Re(6) | 0.4142 (6) | 0.3293 (3) | 0.3651 (1) | 0.52 (7) | |
| Al(18) | 0.443 (8) | 0.644 (4) | 0.010 (2) | 2.2 (9) | 0.81 (9) |
| Al(19) | 0.458 (5) | 0.623 (3) | 0.196 (1) | 1.1 (6) | |
| Al(20) | 0.492 (6) | 0.938 (3) | 0.046 (1) | 1.5 (6) | |
| Re(7) | 0.5667 (7) | 0.0710 (4) | 0.1565 (2) | 0.58 (8) | |
| Al(21) | 0.572 (7) | 0.500 (4) | 0.092 (2) | 1.8 (8) | 0.88 (8) |
| Al(22) | 0.592 (4) | 0.283 (3) | 0.465 (1) | 1.2 (5) | |
| Al(23) | 0.607 (4) | 0.067 (3) | 0.353 (1) | 0.6 (4) | |
| Al(24) | 0.642 (5) | 0.496 (3) | 0.300 (1) | 0.9 (5) | |
| Al(25) | 0.681 (6) | 0.117 (3) | 0.588 (1) | 1.7 (6) | |
| Al(26) | 0.794 (5) | 0.235 (3) | 0.085 (1) | 1.4 (6) | |
| Al(27) | 0.808 (5) | 0.021 (3) | 0.241 (1) | 1.8 (5) | |
| Al(28) | 0.832 (5) | 0.295 (3) | 0.205 (1) | 1.7 (5) | |
| Al(29) | 0 | 0 | 0 | 1.7 (11) | 0.67 (13) |

lattice, only atom sites related by the b translation have different numerical values (along b from left to right the relative height decreases by 0.09 for one b translation).

The chosen projection is very convenient for demonstrating the structural relationship with the monoclinic WAl_4 structure ($mS30$, Cm , $a = 5.272$, $b = 17.771$, $c = 5.218 \text{ \AA}$, $\beta = 100^\circ 12'$). One unit cell of WAl_4 is presented in Fig. 1(b) in a projection along [001], the direction of the shortest axis, which corresponds in length to the shortest axis in $\text{Re}_{14}\text{Al}_{57-x}$. Only W atom sites are numbered, not with the z coordinates but with the relative heights of the atoms above the plane of projection, with 0.53 added as a constant (along a the relative height decreases by 0.18 for one a translation). One notes good agreement between the heights of the W sites in WAl_4 and the heights of the Re sites in the shaded segment of $\text{Re}_{14}\text{Al}_{57-x}$. It can be shown that there is also good agreement between the Al sites of WAl_4 and the Al sites in the shaded $\text{Re}_{14}\text{Al}_{57-x}$ segment.

The area of structural analogy between $\text{Re}_{14}\text{Al}_{57-x}$ and WAl_4 is however much larger than the marked

* Lists of structure factors arranged in a standard crystallographic data file (Brown, 1983, 1985) and a list of interatomic distances up to 3.8 \AA have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43491 (76 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

segment. As shown in Fig. 2 the structure of $\text{Re}_{14}\text{Al}_{57-x}$ can be described as a periodic domain structure variant of WAl_4 consisting of two WAl_4 slabs, both 11.6 Å thick and limited in Fig. 2 by solid lines. The slab labelled II in Fig. 2 is cut parallel to the (110) plane of the monoclinic WAl_4 structure, while slab I is cut parallel to the $(\bar{1}10)$ plane. In Figs. 1(b) and 2 the (110) and $(\bar{1}10)$ planes are perpendicular to the plane of projection. Slab I and slab II are alternately stacked parallel to the (001) plane of the triclinic unit cell of $\text{Re}_{14}\text{Al}_{57-x}$ which is perpendicular (within half a degree) to the plane of projection of Figs. 1(a) and 2. It can be seen from Fig. 2 that slab I is inverted with respect to slab II. In the first slab the direction perpendicular to the plane of projection and pointing toward the viewer is labelled $[00\bar{1}]$, as referred to the WAl_4 structure, while in slab II it is $[001]$. As a consequence an a_w vector which originates in the plane of projection has its end in slab I above the plane of projection, while in slab II it is below the plane of projection.

Owing to the low symmetry of the parent structure the slabs also have low symmetry, resulting in two structurally different interfaces at the domain bound-

aries. In the $\text{Re}_{14}\text{Al}_{57-x}$ structure in the plane parallel to (001) at $z = \frac{1}{2}$ the atomic arrangement of the WAl_4 -type structural building units permits intergrowth between both WAl_4 -type slabs without misfit. In Fig. 2 this is the interface with slab II on top and slab I below. At the other domain boundary, which coincides with the (001) plane of $\text{Re}_{14}\text{Al}_{57-x}$ at $z = 0$, the intergrowth misfit provides sufficient space for an extra Al site [Al(29)]. However, all Al sites at and close to this interface [Al(2), Al(3), Al(18), Al(21) and Al(29)] are only partially occupied, apparently to reduce the strain caused by the mismatch. The compound contains less Al than expected for stoichiometric ReAl_4 despite the additional Al site at the origin of the $\text{Re}_{14}\text{Al}_{57-x}$ unit cell.

The interatomic distances within the slabs compare well with those in MoAl_4 or WAl_4 . The shortest Re–Al distances of 2.48 Å are found with Re(2)–Al(27), Re(7)–Al(27), Re(3)–Al(28) and Re(7)–Al(28), all five atoms being inside a slab and not close to its interface. Al(29) on the extra site (symmetry centre) has as closest neighbours two Re(5) atoms at 2.484 Å. Unusually short Al–Al distances occur only between

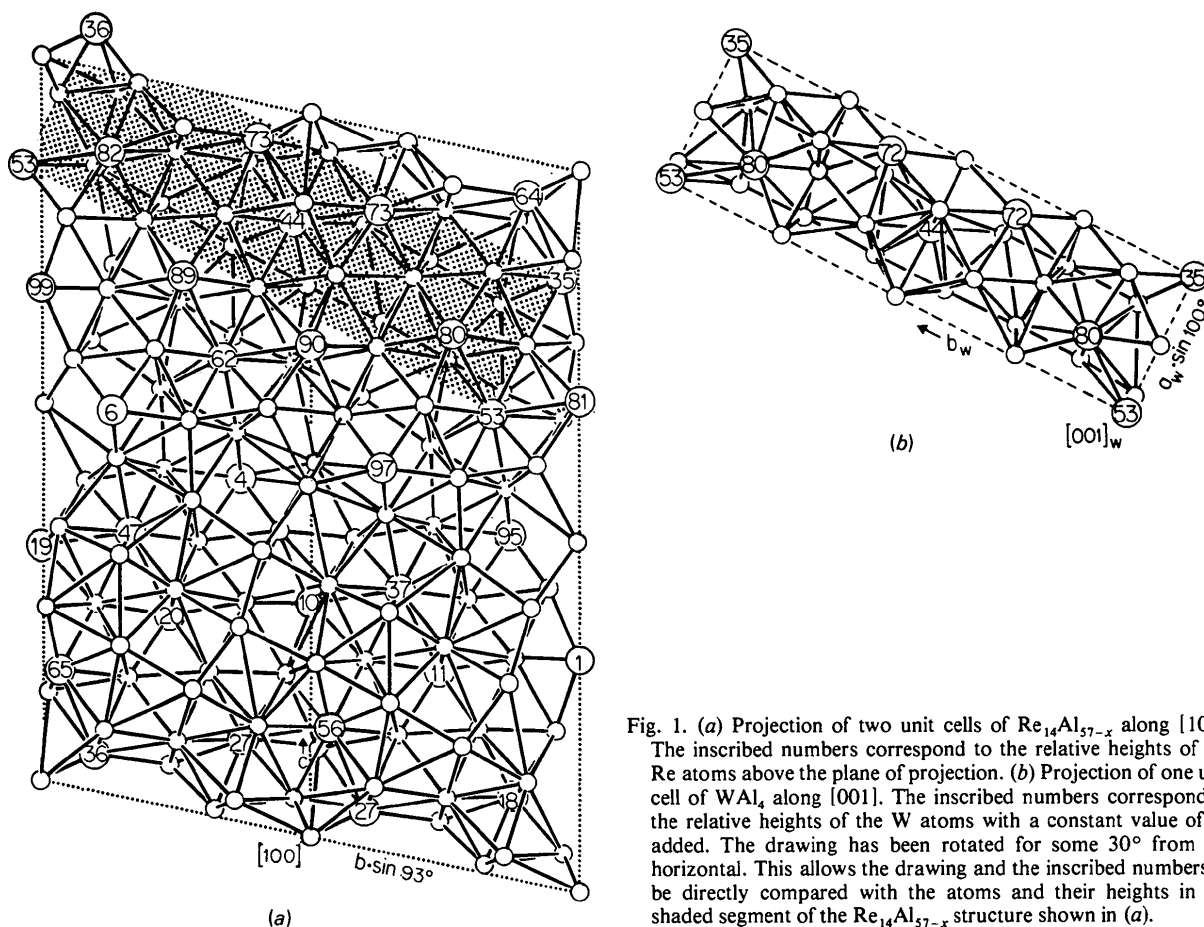


Fig. 1. (a) Projection of two unit cells of $\text{Re}_{14}\text{Al}_{57-x}$ along $[100]$. The inscribed numbers correspond to the relative heights of the Re atoms above the plane of projection. (b) Projection of one unit cell of WAl_4 along $[001]$. The inscribed numbers correspond to the relative heights of the W atoms with a constant value of 53 added. The drawing has been rotated for some 30° from the horizontal. This allows the drawing and the inscribed numbers to be directly compared with the atoms and their heights in the shaded segment of the $\text{Re}_{14}\text{Al}_{57-x}$ structure shown in (a).

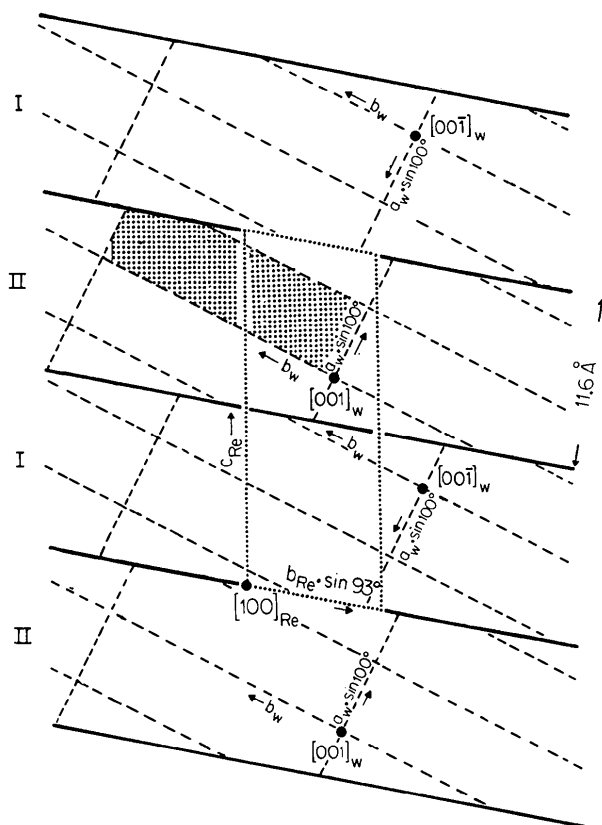


Fig. 2. The construction of the $\text{Re}_{14}\text{Al}_{57-x}$ structure with inverted WAl_4 -type slabs. The domain boundaries have been indicated with solid lines. The outlines of the WAl_4 unit cells within the slab are dashed and those of $\text{Re}_{14}\text{Al}_{57-x}$ are dotted in correspondence with the chosen outlines of the unit cells presented in Figs. 1(b) and 1(a). The shaded segment corresponds to the shaded segment of Fig. 1(a).

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Structures of Holmium Bromate Enneahydrate at 168 and 294 K and their Implications for the Isomorphic Series of Rare-Earth Bromate Enneahydrates

BY ROGER E. GERKIN AND WILLIAM J. REPPART*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA

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Abstract. $\text{Ho}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$, $M_r = 710.77$, orthorhombic, $Cmcm$, $Z = 4$, $F(000) = 1336$, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $T = 168 \text{ K}$: $a = 11.670 (1)$, $b = \sqrt{3}a = 20.213 (2)$, $c = 6.611 (1) \text{ \AA}$, $V = 1559.4 (3) \text{ \AA}^3$, D_x

the partially occupied Al sites near the interface [Al(2)–Al(3) 2.39; Al(18)–Al(21) 2.53 Å].

In connection with the interpretation of the $\text{Re}_{14}\text{Al}_{57-x}$ structure as a periodic domain structure one should mention the defect structure of Al-rich Mo–Al alloys studied by Van Tendeloo, Van Landuyt & Amelinckx (1975), who found by electron diffraction a pattern characteristic of inversion domains for MoAl_4 .

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* Present address: Shell Development Company, Houston, Texas 77001, USA.

$= 3.03 \text{ g cm}^{-3}$, $\mu = 128.32 \text{ cm}^{-1}$, $R = 0.041$ for 1565 unique reflections with $I > 0$; $T = 294 \text{ K}$: $a = 11.699 (1)$, $b = \sqrt{3}a = 20.263 (2)$, $c = 6.671 (1) \text{ \AA}$, $V = 1581.4 \text{ \AA}^3$, $D_x = 2.98 \text{ g cm}^{-3}$, $\mu = 126.53 \text{ cm}^{-1}$, $R = 0.041$ for 1304 unique reflections with $I > 0$. Examination of crystals of twelve (La, Pr, Nd, Sm–Lu) rare-earth bromate enneahydrates revealed that these