

Ternary Aluminides $A_6T_4Al_{43}$ ($A = Y, Nd, Sm, Gd-Lu, \text{ and } U; T = Ti, V, Nb, \text{ and } Ta$) with $Ho_6Mo_4Al_{43}$ Type Structure

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Forty-four new ternary aluminides, which crystallize with the hexagonal $Ho_6Mo_4Al_{43}$ type structure, were prepared by arc-melting of the elemental components and subsequent annealing. The crystal structure of $Dy_6Ti_4Al_{43}$ was refined from single-crystal X-ray data: $P6_3/mcm$, $a = 1104.6(3)$ pm, $c = 1787.7(4)$ pm, $Z = 2$, and $R = 0.014$ for 793 structure factors and 53 variable parameters. In contrast to the structures of $Ho_6Mo_{4+x}Al_{43-x}$ ($x = 0.11$) and $Yb_6Cr_{4+x}Al_{43-x}$ ($x = 1.15$) no significant deviation from the ideal composition could be observed for $Dy_6Ti_4Al_{43}$. © 1995 Academic Press, Inc.

SAMPLE PREPARATION, PROPERTIES, AND LATTICE CONSTANTS

Starting materials were the elemental metals, all with purities >99.9%. Powders of the transition metals (V: ABCR; Ti, Ta: Ventron; Nb: Serva) were used as purchased. The rare earth elements and aluminum (KCL Koch Chemicals LTD) were in the form of ingots. Filings of the light lanthanoids (Rhône-Poulenc Co.) were prepared under dried (Na) paraffin oil. After the paraffin was removed with dried *n*-hexane and the hexane was evaporated under vacuum, the filings were only briefly exposed to air prior to the reactions. The other lanthanoids (Kelpin) and aluminum were used in the form of turnings. Platelets of uranium (Merck) were treated with nitric acid to remove the oxide coating.

The title compounds were obtained by arc-melting cold-pressed pellets (~0.4 g) with the ideal atomic ratio of the elemental components under argon. After the arc-melting the samples were wrapped in steel foil, sealed in silica tubes under an atmosphere of dried argon, and annealed for 3 weeks at 800°C.

Single crystals of $Dy_6Ti_4Al_{43}$ were prepared by reaction of the elements in the atomic ratio 5 : 5 : 90 in an alumina crucible under argon, which was sealed in a silica tube, annealed for 3 weeks at 800°C, and subsequently were cooled to room temperature at a rate of 5°C/hr. The aluminum matrix was dissolved in diluted hydrochloric acid, which attacks the crystals of the ternary aluminides at a much slower rate.

Energy dispersive X-ray fluorescence analyses of the aluminides in a scanning electron microscope did not show any impurity elements heavier than sodium. The compounds are stable in air and show metallic luster with a color similar to elemental aluminum. The samples are easily ground to gray powders. They are strongly attacked by concentrated solutions of HCl and NaOH, but

INTRODUCTION

The binary systems of metals with aluminum contain a remarkable variety of compounds with high aluminum content. About 30 binary aluminides are known in which the minority component is equal to or less than 20%. These compounds crystallize in about a dozen crystal structure types, of which the types $BaAl_4$, $LaAl_4$, UAl_4 , WAl_4 , Co_2Al_9 , $MnAl_6$, and WAl_{12} have three or more representatives (1). We recently started to investigate ternary systems with high aluminum content and have already reported about 30 isotypic aluminides with $CeCr_2Al_{20}$ type structure (2). We found about 40 isotypic compounds with a somewhat lower content of aluminum with the ideal composition $A_6T_4Al_{43}$ ($A = \text{lanthanoids or actinoids}, T = Cr, Mo, W$). Their crystal structure was determined for $Ho_6Mo_{4+x}Al_{43-x}$ ($x = 0.11$) and $Yb_6Cr_{4+x}Al_{43-x}$ ($x = 1.15$) (3). Here we report the isotypic aluminides with titanium, vanadium, niobium, and tantalum as the transition metal components. Such compounds may occur in commercial aluminum alloys, since small additions of rare earth and transition metals are reported to increase the hardness and extend the service temperatures of these alloys (4).

they are—similar to elemental aluminum—passivated by concentrated nitric acid.

The samples were characterized by Guinier powder patterns with α -quartz ($a = 491.30$ pm, $c = 540.46$ pm) as a standard. The lattice constants (Table 1) were refined by least-squares fits. The rather small standard deviations do not reflect possible homogeneity ranges. The cell volumes of these compounds are plotted in Fig. 1 to-

TABLE 1
Lattice Parameters of the Compounds $A_6T_4Al_{13}$
($T = Ti, V, Nb, Ta$)^a

Compound	a (pm)	c (pm)	c/a	V (nm ³)
Y ₆ Ti ₄ Al ₁₃	1105.8(2)	1790.5(3)	1.619	1.896
Nd ₆ Ti ₄ Al ₁₃	1112.4(2)	1806.9(3)	1.624	1.936
Sm ₆ Ti ₄ Al ₁₃	1109.3(1)	1799.3(2)	1.622	1.917
Gd ₆ Ti ₄ Al ₁₃	1107.2(2)	1794.2(3)	1.620	1.905
Tb ₆ Ti ₄ Al ₁₃	1105.1(1)	1789.4(1)	1.619	1.892
Dy ₆ Ti ₄ Al ₁₃	1104.6(3)	1787.7(4)	1.618	1.889
Ho ₆ Ti ₄ Al ₁₃	1103.5(1)	1783.9(2)	1.617	1.881
Er ₆ Ti ₄ Al ₁₃	1102.4(2)	1780.0(3)	1.615	1.873
Tm ₆ Ti ₄ Al ₁₃	1101.9(2)	1779.1(3)	1.615	1.870
Yb ₆ Ti ₄ Al ₁₃	1104.4(1)	1785.8(2)	1.617	1.886
Lu ₆ Ti ₄ Al ₁₃	1100.8(2)	1773.6(3)	1.611	1.861
Nd ₆ V ₄ Al ₁₃	1103.6(3)	1793.9(4)	1.625	1.893
Sm ₆ V ₄ Al ₁₃	1100.2(2)	1783.9(3)	1.621	1.870
Gd ₆ V ₄ Al ₁₃	1098.4(2)	1779.5(2)	1.620	1.859
Tb ₆ V ₄ Al ₁₃	1096.0(1)	1773.8(2)	1.618	1.845
Dy ₆ V ₄ Al ₁₃	1095.4(2)	1770.9(3)	1.617	1.840
Ho ₆ V ₄ Al ₁₃	1094.7(2)	1767.9(2)	1.615	1.835
Er ₆ V ₄ Al ₁₃	1093.5(2)	1762.7(3)	1.612	1.825
Tm ₆ V ₄ Al ₁₃	1093.1(2)	1761.0(2)	1.611	1.822
Yb ₆ V ₄ Al ₁₃	1094.8(2)	1770.9(3)	1.618	1.838
Lu ₆ V ₄ Al ₁₃	1092.1(2)	1756.2(3)	1.608	1.814
U ₆ V ₄ Al ₁₃	1092.2(2)	1769.1(3)	1.620	1.828
Nd ₆ Nb ₄ Al ₁₃	1115.7(2)	1802.9(3)	1.616	1.944
Sm ₆ Nb ₄ Al ₁₃	1113.0(2)	1797.2(4)	1.615	1.928
Gd ₆ Nb ₄ Al ₁₃	1110.4(4)	1791.7(5)	1.614	1.913
Tb ₆ Nb ₄ Al ₁₃	1108.2(2)	1784.6(3)	1.610	1.898
Dy ₆ Nb ₄ Al ₁₃	1108.7(3)	1782.7(5)	1.608	1.898
Ho ₆ Nb ₄ Al ₁₃	1107.9(3)	1781.5(5)	1.608	1.894
Er ₆ Nb ₄ Al ₁₃	1106.5(3)	1777.0(4)	1.606	1.884
Tm ₆ Nb ₄ Al ₁₃	1106.0(2)	1774.6(4)	1.605	1.880
Yb ₆ Nb ₄ Al ₁₃	1109.3(2)	1784.7(4)	1.609	1.902
Lu ₆ Nb ₄ Al ₁₃	1105.1(2)	1770.7(3)	1.602	1.873
U ₆ Nb ₄ Al ₁₃	1106.1(1)	1781.0(2)	1.610	1.887
Nd ₆ Ta ₄ Al ₁₃	1115.1(3)	1802.6(3)	1.617	1.941
Sm ₆ Ta ₄ Al ₁₃	1112.7(2)	1795.4(4)	1.614	1.925
Gd ₆ Ta ₄ Al ₁₃	1109.9(2)	1789.6(4)	1.612	1.909
Tb ₆ Ta ₄ Al ₁₃	1109.0(2)	1785.1(3)	1.610	1.901
Dy ₆ Ta ₄ Al ₁₃	1108.3(3)	1783.4(4)	1.609	1.897
Ho ₆ Ta ₄ Al ₁₃	1107.1(2)	1779.6(3)	1.607	1.889
Er ₆ Ta ₄ Al ₁₃	1105.7(3)	1775.6(6)	1.606	1.880
Tm ₆ Ta ₄ Al ₁₃	1105.1(1)	1773.3(2)	1.605	1.875
Yb ₆ Ta ₄ Al ₁₃	1108.1(1)	1782.5(2)	1.609	1.895
Lu ₆ Ta ₄ Al ₁₃	1104.3(2)	1769.0(3)	1.602	1.868
U ₆ Ta ₄ Al ₁₃	1105.2(1)	1778.6(2)	1.609	1.881

^a Standard deviations in the positions of the least significant digits are given in parentheses throughout the paper.

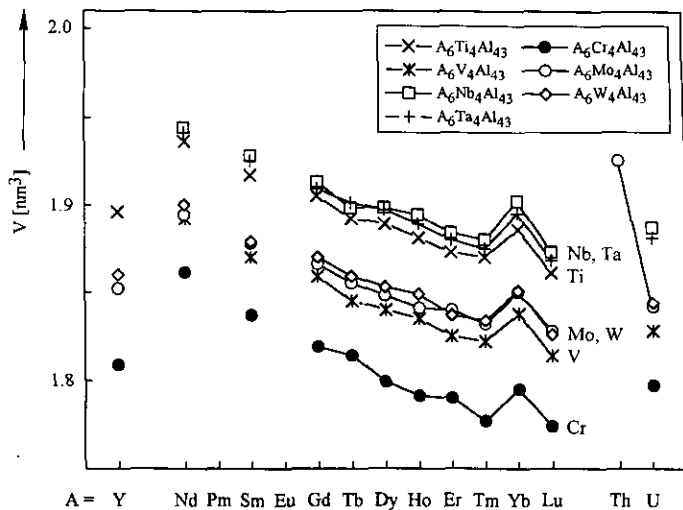


FIG. 1. Cell volumes of ternary aluminides with $Ho_6Mo_4Al_{13}$ type structure.

gether with the volumes of the earlier reported aluminides (3).

THE STRUCTURE OF $Dy_6Ti_4Al_{13}$

The crystal structure of $Dy_6Ti_4Al_{13}$ was refined from single-crystal X-ray diffractometer data collected with an automated four-circle diffractometer with graphite-monochromated $MoK\alpha$ radiation, a scintillation counter, a pulse-height discriminator, and with background counts at both ends of each $\theta/2\theta$ scan. The crystallographic data are summarized in Table 2.

TABLE 2
Crystal Data for $Dy_6Ti_4Al_{13}$

Lattice constants	(see Table 1)
Structure type	$Ho_6Mo_4Al_{13}$
Formula units/cell	$Z = 2$
Space group	$P6_3/mcm$ (No. 193)
Formula weight	2326.8
Calculated density (g/cm ³)	$\rho_c = 4.09$
Absorption coefficient (cm ⁻¹)	$\mu(MoK\alpha) = 136.4$
Crystal dimensions (μm^3)	$70 \times 70 \times 120$
$\theta/2\theta$ scans up to	$2\theta = 65^\circ$
Range in hkl	$\pm 13, \pm 13, 0+26$
Total number of reflections	13,479
Absorption correction	From psi scans
Highest/lowest transmission	1.16
Unique reflections	1424
Inner residual (on F values)	$R_i = 0.035$
Reflections with $I > 3\sigma(I)$	793
Number of variables	53
Conventional residual	$R = 0.014$
Weighted residual	$R_w = 0.015$

TABLE 3
Atomic Parameters of $Dy_6Ti_4Al_{43}$ ^a

	$P6_3/mcm$	Occupancy	x	y	z	B_{eq}
Dy	12k	1.000(1)	0.52866(2)	0	0.09601(1)	0.536(3)
Ti(1)	6g	0.987(3)	0.7276(1)	0	1/4	0.37(2)
Ti(2)	2b	1.007(5)	0	0	0	0.38(2)
Al(1)	24l	0.994(2)	0.15917(9)	0.39370(9)	0.16380(5)	0.75(2)
Al(2)	12k	0.980(4)	0.1566(1)	0	0.61640(8)	0.71(3)
Al(3)	12k	1.003(3)	0.2538(1)	0	0.02905(8)	0.73(3)
Al(4)	12j	0.984(3)	0.1489(1)	0.5956(1)	1/4	0.72(3)
Al(5)	12i	0.992(3)	0.24747(7)	2x	0	0.74(3)
Al(6)	8h	0.987(4)	1/3	2/3	0.12560(9)	0.70(2)
Al(7)	6g	0.980(5)	0.1466(2)	0	1/4	0.69(4)

^a The last column contains the equivalent isotropic B values (in units of 10^{-2} nm²). The occupancy parameters listed in the third column were obtained in previous least-squares cycles.

For the structure refinement by full-matrix least-squares cycles the positional parameters as obtained for $Ho_6Mo_4Al_{43}$ (3) were used as the starting atomic positions. The atomic scattering factors (5) were corrected for anomalous dispersion (6). The weighting schemes included a term which accounted for the counting statistics, and a parameter correcting for isotropic secondary extinction was optimized. All positions were refined with anisotropic thermal parameters. To check for deviations from the ideal composition, the occupancy factors were allowed to vary together with the thermal parameters during one series of least-squares cycles. The scale factor was fixed during these cycles. No serious deviations from the full occupancies were found and in the final cycles the ideal occupancy parameters were assumed again. In the structure refinement of $Yb_6Cr_{4+x}Al_{43-x}$ the Al(5) atoms were refined in the split position (24l) off the twofold axis (3). In the structure refinement of $Dy_6Ti_4Al_{43}$ this was not necessary: the displacement parameter U_{33} (120 pm²) was

TABLE 4
Interatomic Distances in the Structure of $Dy_6Ti_4Al_{43}$ ^a

Dy:	2Al(1) 306.7(1)	Al(1):	1Ti(1) 272.2(1)	Al(3):	2Al(5) 275.9(1)	Al(5):	2Al(3) 274.9(1)
	2Al(4) 310.1(1)		1Al(6) 273.1(1)		1Al(2) 281.3(1)		2Al(6) 278.2(1)
	2Al(5) 312.6(1)		1Al(2) 273.9(1)		1Ti(2) 285.2(1)		2Al(5) 284.5(1)
	2Al(6) 324.8(1)		1Al(4) 275.9(1)		2Al(2) 290.6(1)		2Al(1) 311.2(1)
	1Al(3) 326.3(1)		1Al(4) 283.7(1)		2Al(1) 292.7(1)		2Dy 312.6(1)
	1Al(3) 328.2(1)		1Al(7) 284.9(1)		2Al(3) 299.0(1)		2Dy 340.2(1)
	2Al(1) 333.7(1)		1Al(3) 292.7(1)		1Dy 326.3(1)	Al(6):	3Al(1) 273.1(1)
	2Al(5) 340.2(1)		1Al(1) 304.5(1)		1Dy 328.2(1)		3Al(5) 278.2(1)
	1Dy 349.1(1)		1Dy 306.7(1)	Al(4):	1Ti(1) 268.9(1)		3Al(4) 284.8(1)
	1Al(2) 349.6(1)		1Al(1) 308.2(1)		2Al(1) 275.9(1)		3Dy 324.8(1)
	1Ti(1) 352.3(1)		1Al(5) 311.2(1)		2Al(1) 283.7(1)	Al(7):	2Ti(1) 260.8(1)
Ti(1):	2Al(7) 260.8(2)		1Dy 333.7(1)		1Dy 333.7(1)		2Al(7) 280.6(3)
	2Al(4) 268.9(1)	Al(2):	1Ti(2) 270.6(1)		1Al(4) 284.9(1)		4Al(1) 284.9(2)
	2Al(2) 270.9(1)		1Ti(1) 270.9(1)		2Al(4) 308.3(2)		4Al(2) 291.9(1)
	4Al(1) 272.2(1)		2Al(1) 273.9(1)		2Dy 310.1(1)		
	2Dy 352.3(1)		1Al(3) 281.3(2)				
Ti(2):	6Al(2) 270.6(1)		2Al(3) 290.6(1)				
	6Al(3) 285.2(1)		2Al(7) 291.9(1)				
			2Al(2) 299.6(2)				
			1Dy 349.6(1)				

^a All distances shorter than 394 pm are listed.

only found to be less than two times as high as the values for U_{11} (87 pm²) and U_{22} (67 pm²). A final difference Fourier analysis showed no significant electron densities at sites suitable for additional atomic positions. The atomic parameters and the interatomic distances are listed in Tables 3 and 4. The structure factor table and the anisotropic displacement parameters are available from the authors. The structure and the near-neighbor coordinations are shown in Figs. 2 and 3.

DISCUSSION

With the presently reported 44 compounds the number of aluminides with $Ho_6Mo_4Al_{43}$ type structure has increased to 81. It should be possible to prepare even more compounds with this structure. We have not prepared

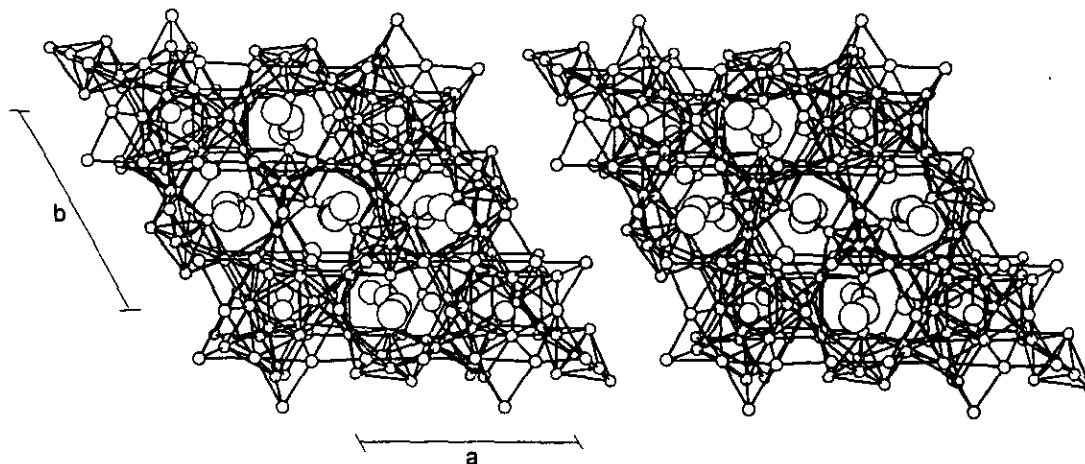


FIG. 2. Stereoplot of $Dy_6Ti_4Al_{43}$. The section between $z = -0.1$ and $z = 0.6$ is shown in a view along the b_3 axis. For clarity, only the Al-Al bonds are plotted. Large and medium sized spheres represent dysprosium and titanium atoms.

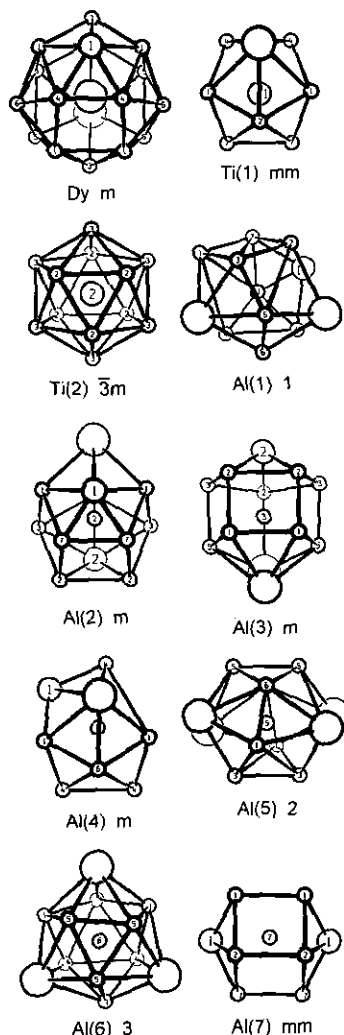


FIG. 3. Coordination polyhedra in the structure of $Dy_6Ti_4Al_{43}$ as viewed exactly along the sixfold axis. The site symmetries of the central atoms are indicated. The polyhedra around the Ti(1), Al(4), and Al(7) atoms have mirror planes, which are parallel to the plane of the paper.

any with the radioactive element promethium and obviously not all (Fig. 1) with yttrium and thorium. In samples with lanthanum, cerium, praseodymium, and europium we have not yet found such compounds. Instead we obtained the aluminides with the composition 1 : 2 : 20 (2). Nevertheless, it seems possible that one or the other of these aluminides with the composition 6 : 4 : 43 could also be obtained. With titanium we found both series, ATi_2Al_{20} (2) and $A_6Ti_4Al_{43}$, to extend to the heavier rare earth metals. So far we have not been successful in preparing corresponding compounds with zirconium as the transition metal component; however, preliminary results with manganese suggested the existence of such aluminides as $A_6Mn_4Al_{43}$ (7).

The cell volumes of the ternary ytterbium transition metal aluminides deviate somewhat from the smooth plot of the compounds with the typically trivalent lanthanoids (Fig. 1), suggesting an intermediate valency of ytterbium, since a larger deviation could be expected if this element were purely divalent. The nonexistence of the europium compounds may be rationalized with the higher tendency of europium (as compared to ytterbium) to be divalent. Divalent europium has a size similar to that of lanthanum and both form the 1 : 2 : 20 compounds, as already mentioned above. The cell volumes of the uranium compounds fit in between those of the holmium and the erbium compounds (with $T = V, Nb, Ta, W$) or between the dysprosium and the holmium compounds ($T = Cr, Mo$), while the cell volumes of the yttrium compounds are in between the compounds of gadolinium and terbium ($T = Ti, W$) or between terbium and dysprosium ($T = Cr, Mo$).

The near-neighbor coordinations in the 6 : 4 : 43 aluminides were discussed previously (3). The lanthanoid atoms have the coordination number (CN) 17 while all other atoms have the CN 12. The average Al–Al distances in the coordination polyhedra of the aluminum atoms are again remarkably similar: Al(1), 289.8 pm; Al(2), 288.1 pm; Al(3), 288.4 pm; Al(4), 287.8 pm; Al(5), 287.2 pm; and Al(7), 286.8 pm. The only exception is the average Al–Al distance of the Al(6) atom, which is considerably smaller: 278.7 pm. This was also the case for $Ho_6Mo_{4+x}Al_{43-x}$ with $x = 0.11(1)$ and $Yb_6Cr_{4+x}Al_{43-x}$ with $x = 1.15(3)$, and it was argued that this might be the reason for the mixed occupancy of the Al(6) site. Certainly the atomic radii (8) for CN 12 of chromium (128 pm) and molybdenum (140 pm) are smaller than that of aluminum (143 pm), while the radius of titanium (146 pm) is larger, and the refinement of the occupancy parameters (Table 3) suggested that the Al(6) site in $Dy_6Ti_4Al_{43}$ is occupied only by aluminum atoms. Nevertheless, the average Al–Al distance of the Al(6) site is again the smallest one. Thus, it seems possible that the coordination shell of the Al(6) atoms is somewhat smaller than those of the other aluminum atoms for "packing" effects and that this strain can somewhat be relieved by substituting the aluminum atoms of this site by transition metal atoms if they are smaller than the aluminum atoms.

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