

Ternary Aluminides AT_2Al_{20} ($A =$ Rare Earth Elements and Uranium; $T =$ Ti, Nb, Ta, Mo, and W) with $CeCr_2Al_{20}$ -Type Structure

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Of the title compounds 28 were prepared for the first time. They crystallize with a cubic structure (space group $Fd\bar{3}m$, $Z = 8$) similar to the structures of $Mg_3Cr_2Al_{18}$ and $ZrZn_{22}$ with an atom distribution first proposed for $CeCr_2Al_{20}$. Single-crystal X-ray data for $CeTi_2Al_{20}$ ($a = 1470.5(1)$ pm) and $CeMo_2Al_{20}$ ($a = 1457.5(1)$ pm) were refined to residuals of $R = 0.017$ and $R = 0.012$ for 17 variables from 302 and 289 structure factors, respectively. The atoms occupy five atomic sites, which are fully occupied in the titanium compound. For the molybdenum compound a considerable deviation from the ideal composition was observed for the crystal used for the structure refinement; nevertheless, it is argued that the homogeneity range might include the ideal composition. The cerium and the transition metal atoms are surrounded by 16 and 12 aluminum atoms, respectively, which correspond to Frank-Kasper polyhedra. In contrast, the aluminum atoms have coordination polyhedra formed by pentagonal and hexagonal prisms of aluminum atoms, which are capped by the cerium and the transition metal atoms. © 1995 Academic Press, Inc.

INTRODUCTION

We have recently reported (1) a new series of aluminides $A_nT_4Al_{43}$ ($A = Ln, Th, U$; $T = Cr, Mo, W$). While searching for isotopic compounds we found another series of aluminides with cubic symmetry and similar composition. Their structure turned out to be isotopic with $CeCr_2Al_{20}$ (2), which has the same atomic positions as $Mg_3Cr_2Al_{18}$ (3) and $ZrZn_{22}$ (4). Our structure determinations resulted in the compositions $CeTi_2Al_{20}$ and $CeMo_{1.474(4)}Al_{20.526(4)}$. Since these crystals were prepared from melts with a low transition metal content, it seems possible that the molybdenum compound can also be prepared with the ideal composition. Therefore we use the ideal formula $CeMo_2Al_{20}$ for most purposes.

SAMPLE PREPARATION AND PROPERTIES

Starting materials were the elemental metals, all with nominal purities $>99.9\%$. 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 paraffin oil. The paraffin was washed out with dried (Na) hexane, and the hexane was removed 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. The uranium platelets (Merck) were treated with nitric acid to remove the oxide coating. The transition metals (Ti, Ta, W, Ventron; Nb, Serva; Mo, Riedel de Haën) were in the form of powders and used as purchased.

The single crystals of $CeTi_2Al_{20}$ and $CeMo_2Al_{20}$ were prepared by reaction of the elements in the atomic ratio 5:5:90 in alumina crucibles under argon, which were sealed in silica tubes, annealed for 3 weeks at $800^\circ C$, and subsequently cooled to room temperature at a rate of $5^\circ C/hr$. The aluminum matrix was dissolved by diluted hydrochloric acid, which leaves the crystals of the ternary aluminides essentially unattacked.

The other compounds with titanium and molybdenum as transition metal components were prepared in the same way, except that the starting ratio of the elements was 4:8:88. The compounds with $T = Nb, Ta, \text{ or } W$ were prepared by arc-melting cold-pressed pellets (~ 0.4 g) of the elemental components under argon, using a starting ratio of $Ln:T:Al = 4:8:88$. 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 $800^\circ C$.

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

TABLE 1
Lattice Parameters of the
Compounds AT_2Al_{20} ^a

Compound	<i>a</i> (pm)	<i>V</i> (nm ³)
LaTi ₂ Al ₂₀	1476.4(1)	3.218(1)
CeTi ₂ Al ₂₀	1470.5(1)	3.180(1)
PrTi ₂ Al ₂₀	1472.4(1)	3.192(1)
NdTi ₂ Al ₂₀	1470.4(1)	3.179(1)
SmTi ₂ Al ₂₀	1469.8(1)	3.175(1)
EuTi ₂ Al ₂₀	1473.2(1)	3.198(1)
GdTi ₂ Al ₂₀	1468.4(1)	3.166(1)
TbTi ₂ Al ₂₀	1468.2(1)	3.165(1)
DyTi ₂ Al ₂₀	1467.2(1)	3.159(1)
HoTi ₂ Al ₂₀	1467.0(1)	3.157(1)
ErTi ₂ Al ₂₀	1466.2(1)	3.152(1)
TmTi ₂ Al ₂₀	1466.1(1)	3.151(1)
YbTi ₂ Al ₂₀	1468.1(1)	3.165(1)
UTi ₂ Al ₂₀	1461.9(1)	3.124(1)
UNb ₂ Al ₂₀	1466.2(1)	3.152(1)
UTa ₂ Al ₂₀	1466.1(1)	3.151(1)
LaMo ₂ Al ₂₀	1463.4(1)	3.134(1)
CeMo _{1.474(4)} Al _{20.526(4)}	1457.5(1)	3.096(1)
PrMo ₂ Al ₂₀	1460.1(1)	3.113(1)
NdMo ₂ Al ₂₀	1459.4(1)	3.108(1)
SmMo ₂ Al ₂₀	1459.7(1)	3.110(1)
EuMo ₂ Al ₂₀	1462.9(1)	3.130(1)
UMo ₂ Al ₂₀	1450.6(1)	3.053(1)
LaW ₂ Al ₂₀	1465.4(1)	3.147(1)
CeW ₂ Al ₂₀	1458.9(1)	3.105(1)
PrW ₂ Al ₂₀	1461.2(1)	3.120(1)
NdW ₂ Al ₂₀	1460.5(1)	3.115(1)
EuW ₂ Al ₂₀	1463.1(1)	3.132(1)
UW ₂ Al ₂₀	1450.5(1)	3.052(1)

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

LATTICE CONSTANTS

Guinier powder patterns of the samples were recorded 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 the homogeneity ranges. The cell volumes of these compounds are plotted in Fig. 1. The volumes of several cerium, europium, and ytterbium compounds deviate from the smooth functions, indicating mixed or intermediate valence (Ce^{3+}/Ce^{4+} , Eu^{2+}/Eu^{3+} , Yb^{2+}/Yb^{3+}) of the lanthanoid atoms in these aluminides.

STRUCTURE REFINEMENTS

Single crystals of $CeTi_2Al_{20}$ and $CeMo_2Al_{20}$ were investigated in a Buerger precession camera to establish their symmetry and suitability for intensity data collection. They showed cubic symmetry with the extinctions charac-

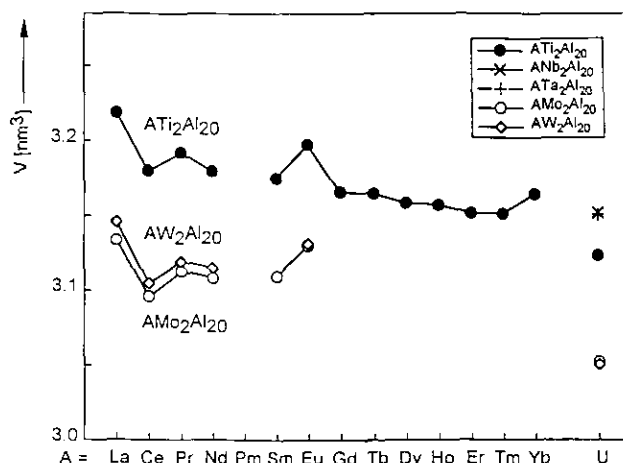


FIG. 1. Cell volumes of $CeCr_2Al_{20}$ -type compounds.

teristic of the face-centered space groups $Fd\bar{3}$ and $Fd\bar{3}m$, of which the one with the higher symmetry, $Fd\bar{3}m$ (No. 227), was found to be correct during the structure refinements. We point out that the crystals of $CeMo_2Al_{20}$ have a tendency to twin with one threefold axis of the cubic (c) crystals as the common axis of the twin domains. Thus the twinned crystals mimic hexagonal (h) symmetry with the lattice constants $a_h = a_c/\sqrt{2}$ and $c_h = a_c\sqrt{3}$. The single crystal of $CeMo_2Al_{20}$ used for the data collection, however, was a single domain.

Intensity data were measured on an automated four-circle diffractometer with graphite-monochromated $MoK\alpha$ radiation, a scintillation counter with a pulse-height discriminator, and background counts on both ends of each $\theta/2\theta$ scan. The crystallographic data are summarized in Table 2. The structures of $CeTi_2Al_{20}$ and $CeMo_2Al_{20}$ were assumed to be isotypic with $CeCr_2Al_{20}$ (2), which was confirmed during the full-matrix least-squares refinements with atomic scattering factors (5), 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.

To check for deviations from the ideal compositions, occupancy parameters were refined as least-squares parameters. For $CeTi_2Al_{20}$ no serious deviations from full occupancy were found. In contrast, the occupancy of the transition metal position in the crystal of $CeMo_2Al_{20}$ diverged considerably from the ideal value. Assuming this position to be occupied only by molybdenum atoms, an occupancy parameter of 81.8(1)% was obtained. However, as will be discussed further below, it seemed more likely to us that this position has mixed occupancy. Allowing for a mixed occupancy of the molybdenum position in $CeMo_2Al_{20}$, we obtained an occupancy of 73.7(2)% molybdenum and 26.3(2)% aluminum. This corresponds

TABLE 2
Crystal Data for CeTi₂Al₂₀ and CeMo_{1.474(4)}Al_{20.526(4)}

	CeTi ₂ Al ₂₀	CeMo _{1.474(4)} Al _{20.526(4)}
Lattice constants	Table 1	Table 1
Structure type	CeCr ₂ Al ₂₀	CeCr ₂ Al ₂₀
Formula units/cell	Z = 8	Z = 8
Space group	<i>Fd3m</i> (No. 227)	<i>Fd3m</i> (No. 227)
Formula weight (g/mol)	775.6	835.4
Calculated density (g/cm ³)	$\rho_c = 3.24$	$\rho_c = 3.58$
Absorption coefficient (cm ⁻¹)	$\mu(\text{MoK}\alpha) = 49.4$	$\mu(\text{MoK}\alpha) = 56.0$
Crystal dimensions (μm^3)	150 × 130 × 40	130 × 110 × 40
$\theta/2\theta$ scans up to	2 $\theta = 70^\circ$	2 $\theta = 70^\circ$
Range in <i>hkl</i>	-23 to 14, -23 to 14, -23 to 2	±23, ±23, -23 to 3
Total number of reflections	5754	9668
Absorption correction	From psi scans	From psi scans
Highest/lowest transmission	1.40	1.09
Unique reflections	403	399
Inner residual	$R_i = 0.030$	$R_i = 0.030$
Reflections with $I > 3\sigma(I)$	302	289
Number of variables	17	17
Conventional residual	$R = 0.017$	$R = 0.012$
Weighted residual	$R_w = 0.024$	$R_w = 0.014$

to the formula CeMo_{1.474(4)}Al_{20.526(4)}. All other positions of the two structures were refined with the ideal occupancies during the final least-squares cycles. These positions were refined with anisotropic thermal parameters, while the Mo/Al position of CeMo_{2-x}Al_{20+x} was refined with one isotropic thermal parameter. The residuals for the refinement with partial occupancy of the Mo site and with mixed Mo/Al occupancy were the same. Subsequent difference Fourier analyses showed no significant electron densities at sites suitable for additional atomic positions. The atomic parameters are listed in the standardized form

(7) in Table 3. The interatomic distances are given in Table 4. Listings of the anisotropic displacement parameters and the structure factors are available from the authors. The structure and the near-neighbor coordinations are shown in Figs. 2 and 3.

DISCUSSION

With the currently reported aluminides the number of CeCr₂Al₂₀-type compounds has increased to around 50.

TABLE 3
Atomic Parameters of CeTi₂Al₂₀ and CeMo_{2-x}Al_{20+x} ($x = 0.526(4)$)^a

	<i>Fd3m</i>	Occupancy	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
CeTi ₂ Al ₂₀						
Ce	8 <i>a</i>	0.994(1)	1/8	1/8	1/8	0.610(2)
Ti	16 <i>d</i>	1.038(2)	1/2	1/2	1/2	0.269(4)
Al(1)	96 <i>g</i>	0.977(2)	0.05938(4)	0.05938	0.32465(6)	0.900(9)
Al(2)	48 <i>f</i>	0.982(3)	0.48720(8)	1/8	1/8	0.73(1)
Al(3)	16 <i>c</i>	0.992(4)	0	0	0	1.36(1)
CeMo _{2-x} Al _{20+x}						
Ce	8 <i>a</i>	1.003(1)	1/8	1/8	1/8	0.614(1)
Mo(26.3(2)% Al)	16 <i>d</i>	1	1/2	1/2	1/2	0.440(5)
Al(1)	96 <i>g</i>	0.992(2)	0.05905(3)	0.05905	0.32503(4)	0.892(6)
Al(2)	48 <i>f</i>	0.994(2)	0.48767(6)	1/8	1/8	0.966(8)
Al(3)	16 <i>c</i>	1.004(5)	0	0	0	1.418(7)

^a The last column lists 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. During the last cycles the ideal occupancy parameters were used with the exception of the Mo position of CeMo_{2-x}Al_{20+x}, which was refined with one isotropic thermal parameter and mixed Mo/Al occupancy. This resulted in an occupancy of 73.7(2)% Mo and 26.3(2)% Al. Therefore the exact formula of the crystal used for the structure refinement corresponds to CeMo_{1.474(4)}Al_{20.526(4)}.

TABLE 4
Interatomic Distances (pm) in the Structures of
 $\text{CeTi}_2\text{Al}_{20}$ and $\text{CeMo}_{2-x}\text{Al}_{20+x}$ ^a

		$\text{CeTi}_2\text{Al}_{20}$	$\text{CeMo}_{2-x}\text{Al}_{20+x}$
Ce	4Al(3)	318.4	315.6
	12Al(1)	323.8	321.7
<i>T</i> ^b	6Al(2)	260.6	258.3
	6Al(1)	285.9	282.6
Al(1)	1Al(1)	272.9	271.9
	1Al(2)	275.2	273.3
	2Al(1)	278.7	276.4
	1 <i>T</i>	285.9	282.6
	2Al(2)	289.3	286.2
	2Al(1)	297.8	294.5
	2Al(3)	313.4	311.2
	1Ce	323.8	321.7
Al(2)	2 <i>T</i>	260.6	258.3
	2Al(1)	275.2	273.3
	4Al(2)	286.6	283.1
	4Al(1)	289.3	286.2
Al(3)	12Al(1)	313.4	311.2
	2Ce	318.4	315.6

^a All distances shorter than 400 pm are listed. The standard deviations are all equal to or less than 0.1 pm.

^b The *T* position of $\text{CeMo}_{2-x}\text{Al}_{20+x}$ was refined with mixed Mo/Al occupancy.

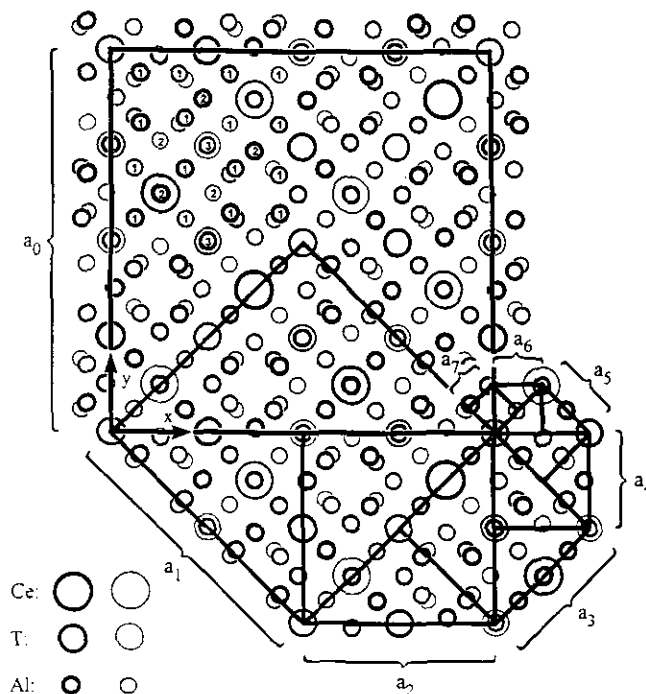


FIG. 2. Projection of the $\text{CeT}_2\text{Al}_{20}$ structure along the *c* axis. The heights of the atoms are indicated by the linewidths. Small atoms under large ones are not shown. Single-digit numbers correspond to the atom designations. It is remarkable that the structure is based on several nested cubic subcells. They are indicated in the lower part of the illustration.

The isotypic series $\text{RCr}_2\text{Al}_{20}$ ($R = \text{Ca}, \text{Y}, \text{La-Nd}, \text{Sm-Er}, \text{U}$) was reported earlier (2, 8–11). Corresponding aluminides with vanadium as the transition metal component are also known (2, 8–11). However, their exact composition was considered questionable (2), since these compounds may extend as solid solutions from the binary aluminide VAl_{10} (12), which crystallizes in the same space group and with similar positional parameters. Therefore the formula of the binary compound may be written $\square\text{V}_2\text{Al}_{20}$, where \square indicates a vacant site, which is occupied by large electropositive atoms in the “filled” ternary aluminides. More recently, precipitates of $\text{GdTi}_2\text{Al}_{20}$ were identified in aluminum alloys (13).

The currently reported structure refinements seem to be the first from single-crystal diffractometer data for a ternary aluminide with the composition 1:2:20. The atomic distribution of $\text{CeCr}_2\text{Al}_{20}$ was established from a comparison of powder data (2) assuming the positional parameters obtained for $\text{Mg}_3\text{Cr}_2\text{Al}_{18}$ (3) and ZrZn_{22} (4). As could be guessed from the high aluminum content of the $\text{AT}_2\text{Al}_{20}$ compounds, the coordination polyhedra of the *A* and *T* atoms consist exclusively of aluminum atoms (Fig. 3). The *A* atoms are situated in a perfect Friauf polyhedron (3, 4, 14–16) with the coordination number

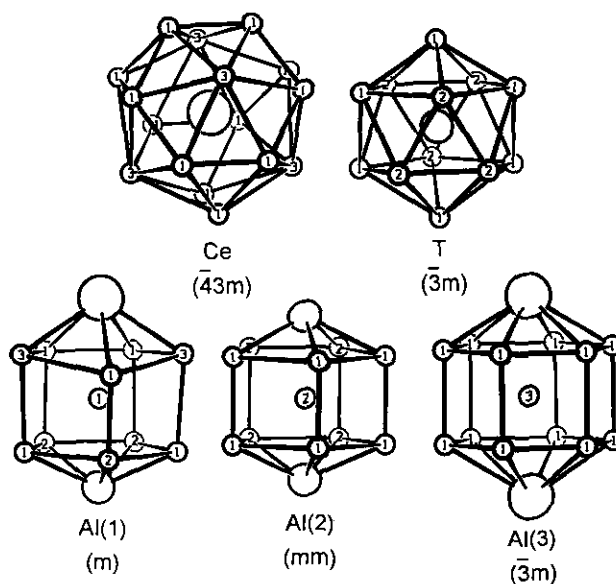


FIG. 3. Coordination polyhedra of $\text{CeT}_2\text{Al}_{20}$. The site symmetries are given in parentheses.

(CN) of 16 and a $\bar{4}3m$ site symmetry, while the T atoms have (only slightly distorted) icosahedral aluminum environments (CN 12). Both of these polyhedra are frequently also referred to as Frank–Kasper polyhedra. A common feature of these polyhedra is that they have only triangular faces. This is not the case for the polyhedra surrounding the three aluminum sites. The Al(1) and Al(2) atoms are coordinated by 10 aluminum atoms forming pentagonal prisms with two additional heteroatoms capping the pentagonal faces, thus increasing the CN to 12. The Al(3) atom is situated in a hexagonal prism of aluminum atoms, which is capped by two A atoms. It is this site with the higher CN of 14 which is believed to be occupied by magnesium atoms in the compounds $Mg_3T_2Al_{18}$ ($T = Ti, V, Ta, Cr, Mo, W, Mn$) (3, 17, 18).

The refinement of the occupancy parameters for the $CeTi_2Al_{20}$ structure showed only small deviations from the ideal values. The most significant one is the occupancy parameter of 1.038 with a standard deviation of 0.002. Since the occupancy parameters of the other four atomic sites are slightly less than one, and since the scale factor is variable, the occupancy factor of the titanium site might be as high as 1.05. This could mean that this site is occupied by as much as 3% cerium atoms. However, since the compound is expected to have a range of homogeneity, the ideal composition may well be within this range.

The reverse situation was observed during the refinement of the $CeMo_2Al_{20}$ data. Here the occupancy of the molybdenum site was found to be less than one. This could mean that there are some vacancies at this site or that some molybdenum atoms are substituted by aluminum atoms. Aluminum and molybdenum atoms have very similar metallic radii, and from size considerations a substitution seems quite possible. The compound contains mostly aluminum, and chemical bonding in the ternary aluminides AT_2Al_{20} and the elemental aluminum should have some similarity. Elemental aluminum is electron deficient: its melting point (660°C) is lower than that of silicon (1410°C) because it does not have enough electrons to optimally fill all bonding states. In other words, the Fermi level cuts through bands which are essentially bonding (as opposed to antibonding), and this should also be the case for the ternary aluminides AT_2Al_{20} . We therefore believe that the two extra electrons of the molybdenum atoms (compared to the titanium atoms in $CeTi_2Al_{20}$) could easily be accommodated in the band structure, and they are not the reason for the deviation from the ideal composition. The crystals were prepared from a melt of the composition $Ce : Mo : Al = 5 : 5 : 90$, which is deficient in molybdenum, and if there are not enough molybdenum atoms, then aluminum atoms will occupy that site. It seems likely to us that crystals with the ideal composition could be grown from melts with a higher molybdenum content.

The structure of the $CeCr_2Al_{20}$ -type compounds is not easy to visualize (some photographs showing cutouts of the $Mg_3Cr_2Al_{18}$ structure are given in Ref. (3)). We therefore limited our discussion to the coordination polyhedra, which all interpenetrate each other. The projection of the structure along an edge of the cubic cell (Fig. 2) shows a remarkable pattern. There is a consecutive series of cubic subcells, where each lattice constant is always smaller than the preceding one by a factor of $1/\sqrt{2}$. However, we point out that the smallest of these subcells, as they appear in the projection, has a cell edge of only $a_7 \sim 130$ pm; on average the cell with $a_5 \sim 260$ pm contains only one atom. The real structure contains $(4\sqrt{2})^3 \sim 181$ such cells with a cell edge a_5 , and there are 184 atoms in the real cell. The smaller of these nesting subcells are pronounced only in the projection of the structure. They are remarkable, but we do not ascribe great significance to them.

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