The Intermetallic Compounds GdRe\(_2\)Al\(_{10}\) and TbRe\(_2\)Al\(_{10}\), Crystallizing with a Stacking Variant of the YbFe\(_2\)Al\(_{10}\) Type Structure

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Dedicated to Prof. Dr. Reginald Gruehn on the occasion of his 70th birthday

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Intermetallic Compounds, Crystal Structure, Close Packed Layers

The new compounds GdRe\(_2\)Al\(_{10}\) and TbRe\(_2\)Al\(_{10}\) were obtained in well-crystallized form by reaction of the elemental components with an excess of aluminum after dissolving the matrix in hydrochloric acid. They crystallize with a new structure type which has been determined for TbRe\(_2\)Al\(_{10}\) from single-crystal X-ray data: \(\text{Ccmm}, a = 932.2(1)\), \(b = 1030.4(1)\), \(c = 1803.2(3)\) pm, \(Z = 8, R = 0.031\) for 1159 structure factors and 77 variable parameters. Of the two terbium sites, one does not have full occupancy with terbium, however, it may have mixed Tb/Al occupancy. The resulting compositions are Tb\(_0.948\)Re\(_2\)Al\(_{10}\) or Tb\(_{0.936}\)Re\(_2\)Al\(_{10.046}\), respectively. The terbium atoms are coordinated by 4 Re and 16 Al atoms. The rhenium atoms are situated in distorted icosahedra formed by 2 Tb and 10 Al atoms. The nine different aluminum atoms have between 12 and 14 neighbors (1 or 2 Tb, 2 Re, and between 8 and 11 Al atoms). The structure may be viewed as consisting of two kinds of alternating layers. One of these is puckered, hexagonal close packed, with a mesh content of 4ReAl\(_3\); the other is planar and less densely packed. It has the mesh content 2TbAl\(_4\). The same kinds of atomic layers have been found in the structures of YbFe\(_2\)Al\(_{10}\) and LuRe\(_2\)Al\(_{10}\). Thus, the three structure types may be considered as stacking variants of each other. The tetragonal CaCr\(_2\)Al\(_{10}\) (ordered ThMn\(_{12}\)) type structure also belongs to this structural family, although the CaAl\(_4\) layers somewhat differ from the layers TbAl\(_4\), YbAl\(_4\), and LuAl\(_4\).

Introduction

We have recently reported on a series of ternary lanthanoid (\(Ln\)) palladium and platinum aluminides with the compositions \(Ln_2\)Pd\(_3\)Al\(_{12}\) and \(Ln_2\)Pt\(_3\)Al\(_{12}\) [1]. The structure of these intermetallic compounds was determined for Er\(_2\)Pt\(_3\)Al\(_{12}\). It may be considered as consisting of atomic layers \(A\) and \(B\) with the compositions Pt\(_3\)Al\(_6\) and Er\(_2\)Al\(_3\), respectively. These layers have the stacking sequence \(BAABA, BAABA\). Hence, the compound may be represented by the formula \(3\text{Pt}_3\text{Al}_6\cdot2\text{Er}_2\text{Al}_3\). In this structure the layers Pt\(_3\)Al\(_6\) are puckered hexagonal close packed. Puckered hexagonal close packed layers have also been observed in the structure of LuRe\(_2\)Al\(_{10}\). There the close packed layers \(A\) and the less densely packed planar layers \(B\) have the compositions Re\(_2\)Al\(_6\) and LuAl\(_4\), respectively [2]. The layers alternate, and a total of twelve layers is needed to complete one stacking sequence of LuRe\(_2\)Al\(_{10}\). The same types of layers exist in the structure of YbFe\(_2\)Al\(_{10}\) [3], where the stacking is \(ABA\), \(ABA\) [2]. In the present communication, we report on another structure for the composition \(1:2:10\), consisting of practically the same kinds of layers. The have the stacking sequence \(ABABABAB, ABABABAB\). Preliminary results of this work were published in the form of a conference abstract [4].

Sample Preparation and Lattice Constants

All elements were purchased with nominal purities > 99.9%. Filings of gadolinium and terbium were prepared under dried (Na) paraffin oil. The paraffin was removed with dry hexane, which was evaporated under vacuum prior to the reactions. Rhenium was purchased in the form of powder, and aluminum turnings were prepared from ingots. The elements were mixed in the ratio \(Ln:Re:Al = 1:2:22\), placed in alumina crucibles and slightly compacted. The alumina crucibles in turn were sealed in silica tubes under argon, annealed for 3 weeks at 850 °C, and slowly cooled to room temperature (5 °C/h).
Table I. Atomic parameters of TbRe$_2$Al$_{10}$. The last column contains the equivalent isotropic $B$ values of the anisotropic displacement parameters of all atoms (in units of $10^{-4}$ pm$^2$). The occupancy parameters were determined in a separate series of least-squares cycles. In the final cycles the ideal occupancy values were used, with the Tb(2)/Al site as the only exception, where the occupancy 0.872/0.128(6) was obtained. If this position is assumed to be occupied only by terbium atoms, its occupancy is 0.896(5).

<table>
<thead>
<tr>
<th>Atom</th>
<th>$Cmcm$</th>
<th>Occupancy</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
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<tr>
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<td>0</td>
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<tr>
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<td>1</td>
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<td>0.12172(4)</td>
<td>0.12050(2)</td>
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<tr>
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</table>

The aluminum-rich matrix was dissolved by diluted hydrochloric acid which leaves the crystals of the ternary aluminides essentially unattacked.

The crystals of the ternary aluminides LnRe$_2$Al$_{10}$ were obtained in the form of silvery shiny, brittle crystals, occasionally with the shape of square prisms. They are stable on air for long periods of time, and they are easily ground to powders which are dark grey. Energy-dispersive X-ray fluorescence analyses of the samples in a scanning electron microscope did not reveal any impurity elements heavier than sodium.

The compounds were characterized by their Guinier powder patterns, using CuK$_\alpha_1$ radiation and $\alpha$-quartz ($a = 491.30$, $c = 540.46$ pm) as an internal standard. The following orthorhombic lattice constants were obtained by least-squares fits of these data. GdRe$_2$Al$_{10}$: $a = 932.3(1)$, $b = 1031.9(1)$, $c = 1806.1(2)$ pm, $V = 1.7376$ nm$^3$. TbRe$_2$Al$_{10}$: $a = 932.2(1)$, $b = 1030.4(2)$, $c = 1803.2(3)$ pm, $V = 1.7320$ nm$^3$. They were considered to be more accurate than those obtained from the four-circle diffractometer, because the latter are affected by systematic errors due to absorption. Considering this effect, the lattice constants obtained from the single crystal of TbRe$_2$Al$_{10}$ ($a = 931.3(2)$, $b = 1030.4(3)$, $c = 1801.8(2)$ pm) are in good agreement with those of the Guinier powder data.

**Structure Determination of TbRe$_2$Al$_{10}$**

Single-crystal intensity data of TbRe$_2$Al$_{10}$ were recorded on an automated Enraf-Nonius CAD4 diffractometer with graphite-monochromated MoK$_\alpha$ radiation, a scintillation counter with pulse-height discriminator, and background counts at both sides of each $\theta/2\theta$ scan. The crystal had the dimensions 20-25-40 $\mu$m$^3$, and an absorption correction was made on the basis of psi scan data; the ratio of the highest to the lowest transmission was 1.39. All reflections within one half of the reciprocal sphere were collected up to $2\theta = 65^\circ$, resulting in a total of 8215 intensity values. After averaging equivalent reflections (internal residual on $F^2$: $R_I = 0.091$) 2040 reflections remained which were used for the structure determination and refinement. The systematic extinctions led to the space groups Cmcm, Cmcm, and C$_2$cm, of which the group with the highest symmetry – Cmcm (No. 63) – was found to be correct during the structure refinements. There are $Z = 8$ formula units in the $C$ centered orthorhombic cell and the calculated density is $\rho = 6.08$ g/cm$^3$ for the formula Tb$_{0.936(3)}$Re$_2$Al$_{10.064(3)}$.

The structure was solved and refined with the programme package SHELX-97 [5] using the atomic scattering factors as provided by the program. The first solution of the structure was in space group Cmcm, using some atomic positions as suggested by the Patterson synthesis of the program and others from recognizing the similarity of this structure with that of LuRe$_2$Al$_{10}$ [2]. The final refinements of the structure were in space group Cmcm. The positional parameters were standardized by the program STRUCTURE TIDY [6]. As a check for the composition, we refined occupancy parameters to-
Table II. Interatomic distances in the structure of TbRe₂Al₁₀. All distances shorter than 400 pm are listed. For the calculation of these distances the lattice constants obtained from the Guinier powder pattern were used. Standard deviations computed from those of the positional parameters and the lattice constants are given in parentheses.

<table>
<thead>
<tr>
<th>Tb(1):</th>
<th>Tb(2):</th>
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</table>


tb(1):
- 2Al(6): 316.5(4) Re 259.9(4) 2Re 270.4(2) 2Re 268.8(2)
- 4Re: 351.1(1) Al(1) 282.2(4) Tb(2): 315.6(4) Tb(1): 328.8(5) 2Al(2) 355(0.5)
- 2Al(8): 384.9(5) Al(7): 290.1(3) Tb(1): 297.1(2) 2Al(6) 271.4(2)
- 4Re: 343.9(1) Al(2): 271.7(9) 2Al(1): 292.4(6) 2Al(6): 297.1(2)
- 4Re: 347.4(1) 2Re: 279.7(2) 2Al(1): 292.4(6) 2Al(6): 297.1(2)
- Re: 254.3(1) Al(9): 283.2(4) Tb(2): 305.4(5) Tb(2): 327.6(6)
- Al(1): 259.7(4) 2Al(4): 288.0(5) 2Al(2): 315.6(4) 2Al(5): 338.7(5)
- Al(1): 259.9(4) 2Al(3): 289.6(6) 2Al(8): 338.7(5) Al(9): 254.3(1)
- Al(3): 269.9(2) 2Al(5): 315.6(4) Al(7): 261.5(6) 2Al(1): 269.5(3)
- Al(6): 264.5(2) Tb(1): 327.6(4) 2Re: 264.5(2) 2Al(6): 271.4(2)
- Al(8): 267.4(2) 2Al(7): 355(0.5) 2Al(9): 271.4(2) 2Al(8): 274.4(2)
- Al(7): 268.6(2) 2Al(3): 280.9(5) 2Al(1): 278.6(4) 2Al(5): 286.9(3)
- Al(4): 270.4(2) 2Al(2): 264.7(6) 2Al(8): 296.8(5) 2Al(2): 347.4(1)
- Al(5): 273.3(2) 2Al(7): 265.3(4) 2Al(5): 304.7(6) 2Al(2): 347.4(1)
- Al(2): 279.7(2) 2Al(7): 279.2(5) Tb(1): 315.6(4) Tb(2): 320.2(4)
- Tb(2): 299.3(5) 2Al(8): 299.3(5) Al(4): 299.3(5) Al(7): 304.7(6)
- Tb(1): 351.1(1) Tb(1): 384.9(5)

Fig. 1. Cell volumes per formula unit of the lanthanoid rhenium aluminides LnRe₂Al₁₀ with CaCr₂Al₁₀, TbRe₂Al₁₀ and LuRe₂Al₁₀ type structures.

Together with the displacement parameters. The results of this refinement are shown in the third column of Table I. For most positions no significant deviations from the ideal occupancy values were observed, and therefore the ideal occupancy values were used during the final refinement cycles. The only exception was the Tb(2) position. This position showed an occupancy value of 89.6(5)%, corresponding to the formula Tb₀.₉₄₈₄Re₂Al₁₀. We cannot exclude the possibility that this position is not really fully occupied. However, since the crystal was obtained from a sample with an excess of aluminum, we preferred to refine this position with mixed Tb/Al occupancy. This resulted in an occupancy of 87.2/12.8(6)%, corresponding to the formula Tb₀.₉₃₆₃Re₂Al₁₀. In any case, the deviations from the ideal composition are small and it seems possible that the ideal composition TbRe₂Al₁₀ is within the homogeneity range of the compound. For these reasons we use the ideal formula for most purposes. The final conventional residual is R = 0.031 for 77 variable parameters and 1159 structure factors greater than two standard deviations. The corresponding weighted residual (on F²) is R_w = 0.077. The highest and lowest residual electron densities...
The crystal structure of the new aluminides GdRe$_2$Al$_{10}$ and TbRe$_2$Al$_{10}$, determined for the terbium compound represents a new structure type which, however, is closely related to the structures of YbFe$_2$Al$_{10}$ [3], LuRe$_2$Al$_{10}$ [2], and to a lesser extent also to the CaCr$_2$Al$_{10}$ type structure [8] of the compounds LnRe$_2$Al$_{10}$ (Ln = Ce-Nd, Sm [2, 9]).

In Fig. 1 we have plotted the cell volume per formula unit of these rhenium containing compounds. It can be seen that the cell volumes of the CaCr$_2$Al$_{10}$ type compounds are relatively small, considering the expected lanthanoid contraction. This has to do with the fact that on close inspection the aluminum positions of the CaCr$_2$Al$_{10}$ type compounds (three structures were refined, resulting in the exact compositions CeRe$_2$Al$_{0.52(8)}$ [9], SmRe$_2$Al$_{0.16(9)}$ [9] and NdRe$_2$Al$_{0.86(10)}$ [2]) are not fully occupied, whereas in the present structure determination of TbRe$_2$Al$_{10}$ and in the determination and refinements of the structures of YbRe$_2$Al$_{10}$ [2] and LuRe$_2$Al$_{10}$ [2] essentially full occupancy of all aluminum sites was observed. Before we consider the structural relationships of these structures, we briefly want to discuss the near-neighbor environments in the structure of TbRe$_2$Al$_{10}$.

The terbium atoms in TbRe$_2$Al$_{10}$ occupy two different sites (Fig. 2), both with 4 rhenium and 16 aluminum neighbors (coordination number, CN 20). Even though the four rhenium neighbors of the two terbium sites have different Tb-Re distances (351.1 and 343.9 pm, Table II), and the Tb-Al distances cover a wide range, extending from 305.4 to 384.9 pm, the average distance for the 20 neighbors of a Tb(1) atom (334.1 pm) is very similar to the corresponding average distance of a Tb(2) atom (333.2 pm).

The rhenium atoms occupy only one site. It has CN 12 with 2 terbium and 10 aluminum atoms in a stretched icosahedral arrangement. The ten different Re-Al distances extend from 254.3 to 279.7 pm. However, the average Re-Al distance of 265.9 pm is very similar to the weighted average Re-Al distances of 265.1 pm in LuRe$_2$Al$_{10}$, 265.3 pm in YbRe$_2$Al$_{10}$, and 266.9 pm in NdRe$_2$Al$_{10}$ [2], where the rhenium atoms have a corresponding distorted icosahedral coordination.
The aluminum atoms occupy nine different sites with between 12 and 14 neighbors. Of these, two are always rhenium atoms, one or two are terbium atoms, and between 8 and 11 are aluminum atoms. The Al-Al distances almost continuously cover the wide range between 261.5 and 386.3 pm. It is reassuring that the average Al-Al distances (listed in parentheses in pm units) reflect the total coordination numbers of the aluminum atoms. The Al(1) (282.0), Al(3) (280.2), and Al(9) (275.6) atoms have CN 12, the Al(4) (292.6) and Al(6) (292.1) atoms have CN 13, and the Al(2) (301.2), Al(5) (301.8), Al(7) (304.6), and Al(8) (297.9) atoms have CN 14. The average distance of all Al-Al interactions in TbRe$_2$Al$_{10}$ listed in Table II is 292.0 pm, slightly greater than the Al-Al distance of 286.3 pm in elemental aluminum (fcc, CN 12) [10]. This distance is again very similar to the average Al-Al distances of 292.2 pm in LuRe$_2$Al$_{10}$ and 292.6 pm in YbRe$_2$Al$_{10}$ [2].

During the past six years we have published the structures of some 20 intermetallic compounds with high aluminum content. We have recently compared the average occupancy factors for all of these aluminides for all "fully" occupied atomic positions, i.e. excluding positions which have serious deviations from the ideal occupancy values, as for instance the Tb(2) position of TbRe$_2$Al$_{10}$. It turned out [2] that in comparison to the occupancy values of the rare earth and transition metal sites, which were assumed to be fully occupied (100.0%), the average aluminum site had always deficiencies. The scattering power of the average aluminum position was found to be about 2 to 3% lower. This is also the case for the occupancy values of TbRe$_2$Al$_{10}$ (Table I). Assuming 100% occupancy for the Tb(1) and the Re position, the average occupancy value of the nine aluminum positions in TbRe$_2$Al$_{10}$ is 98.4%. These deviations from the ideal occupancy values were ascribed to the differing electron dis-
tributions in the free and in the bonded aluminum atoms [2].

In Fig. 3 we show projections of the TbRe$_2$Al$_{10}$ structure. The layers designated (from top to bottom) with the letters $B$, $A$, $B$, $A$, etc. on the left-hand side are shown in projections perpendicular to the layers on the right-hand side. The layers $A$ contain only rhenium and aluminum atoms with the ratio $Re:Al = 1:3$. This type of layer is rectangular and is known to occur in the close-packed structure of TiAl$_3$ [11, 12]. However, in contrast to the layers of TiAl$_3$ which are flat, the layers $A$ of TbRe$_2$Al$_{10}$ are puckered. The layers $B$ of TbRe$_2$Al$_{10}$ contain all of the terbium atoms with additional aluminum atoms in the ratio $Tb:Al = 1:4$. These layers are less densely packed and exactly flat. The mesh contents of the layers $A$ and $B$ are $4ReAl_3$ and $2TbAl_4$, respectively, and the content of the $C$ centered cell is $8TbAl_4\cdot 16ReAl_3$.

Recently, the series of compounds $Lu^2T_2Al_{10}$ ($T = Fe, Ru, Os$) was published [13]. These aluminumides crystallize with a structure first determined for YbFe$_2$Al$_{10}$ [3]. As is demonstrated in the lower part of Fig. 4, the YbFe$_2$Al$_{10}$ type structure is composed of the same type of atomic layers $A$ and $B$ as found here for TbRe$_2$Al$_{10}$. In YbFe$_2$Al$_{10}$ the stacking is $ABAB$ and only four layers are needed to complete one translation period, in contrast to the eight layers of TbRe$_2$Al$_{10}$. The same type of layers were recently found also for LuRe$_2$Al$_{10}$ [2], where one translation period contains twelve layers.

The structure of YbFe$_2$Al$_{10}$ has been described as a combined substitution and stacking variant of the tetragonal ThMn$_{12}$ type structure [3]. A pure substitution variant of ThMn$_{12}$, with a $\sqrt{2}$ times larger $a$ axis, is the tetragonal structure of CaCr$_2$Al$_{10}$ found for the series $LnRe_2Al_{10}$ ($Ln = Ce$-Nd, Sm) [2, 9]. We have now looked again at the structure of CaCr$_2$Al$_{10}$ and searched for similarities to the layered structures of TbRe$_2$Al$_{10}$, YbFe$_2$Al$_{10}$, and LuRe$_2$Al$_{10}$. As is shown in the upper part of Fig. 4, the structure of CaCr$_2$Al$_{10}$ can indeed be decomposed to atomic layers which are similar to the layers of the structures just mentioned. The layers $A$ of CaCr$_2$Al$_{10}$ are again close-packed and puckered with the composition CrAl$_3$. However, in contrast to the layers $A$ of TbRe$_2$Al$_{10}$, YbFe$_2$Al$_{10}$, and LuRe$_2$Al$_{10}$ which are rectangular, the layers $A$ of CaCr$_2$Al$_{10}$ are hexagonal, as they are known from the layers in the well-known close-packed structure of Cu$_3$Au [11, 12]. The layers $B$ of CaCr$_2$Al$_{10}$ contain again the large electropositive (Ca) atoms and additional aluminum atoms in the ratio $Ca:Al = 1:4$, however in an arrangement which is different from that found in the structures of TbRe$_2$Al$_{10}$, YbFe$_2$Al$_{10}$, and LuRe$_2$Al$_{10}$, and the International Centre for Diffraction Data.

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