Table 3. *Z_s Atomic coordinates perpendicular to the layers and lattice constants of clay minerals*

	Mica(a)(b)		Montmorillonite(c)		Kaolinite(d) Diocta-hedral		Kaolinite(d) Triocta-hedral		Chlorite(e)	
	(Å)		(Å)		(Å)				(Å)	
Octahedral	0·00		0·00		3·27				0·00	
O, OH	1·12		1·09		4·37				1·05	
Tetrahedral	2·70		2·70		0·60				2·71	
O	3·28		3·24		0·00				3·26	
Interlayer	5·00		7·70							
OH									6·00	
Mg									7·05	
	(Å)	(°)	(Å)	(°)	(Å)	(°)	(Å)	(°)	(Å)	(°)
a	5·189		5·21		5·14		5·55		5·33	
b	8·995		9·02		8·93		9·61		9·24	
$c \sin \beta$	20·014		14·40		7·13		7·20		14·10	
α		90		90		91·6		90		90
β		95·18		97		104·8		90		97
γ		90		90		89·9		90		90

(*a*) Atomic parameters from Jackson & West (1933).
(*b*) Lattice parameters from Radoslovich (1960).
(*c*) From MacEwan, Ruiz Amil & Brown (1961).
(*d*) From Brindley (1961*a*).
(*e*) From Brindley (1961*b*).

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Th_3N_4 crystal structure and comparison with that of Th_2N_2O.*

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The existence of Th_3N_4 has been reported (Matignon & Delépine, 1907) and later substantiated (Neumann, Kroeger & Haebler, 1932) by a different method of chemical analysis. The results reported in what follows were obtained with Th_3N_4 prepared by equilibrating ThN powder contained in an induction-heated tungsten crucible with 0·13 atm. nitrogen at 1320°. The composition of the product was determined both by weight gain as well as by ignition to ThO_2. The N:Th ratio was thus found to be $1\cdot33\pm0\cdot03$. Thorium sesquioxynitride, Th_2N_2O, was prepared by equilibration of the compacted mixture $3ThN+ThO_2$ with 2 atm. nitrogen at 1700°C. The Th content of this product was determined by ignition to ThO_2; the O:Th ratio was taken to be the same as that of the initial mixture, and nitrogen was computed by difference. The final composition thus obtained was $Th_2N_{2\cdot04\pm0\cdot06}O$. An X-ray diffraction powder pattern of a sample was found to be indistinguishable from that reported earlier (Zachariasen, 1949) for Th_2N_3 with the hexagonal lattice parameters $a_0=3\cdot8833\pm0\cdot0002$, $c_0=6\cdot1870\pm0\cdot0003$ Å. We did not succeed in obtaining N:Th ratios in excess of $1\cdot33\pm0\cdot03$ by reacting thorium or ThN with nitrogen at pressures up to 2 atm.; therefore, the Th_2N_3 phase was not obtained. Although we did not investigate sufficiently high nitrogen pressures to confirm or exclude the existence of the Th_2N_3 phase, all the experimental results suggest the material previously described as Th_2N_3 was the same as the Th_2N_2O phase described above.

The X-ray diffraction data obtained from a powder pattern of Th_3N_4 are shown in Table 1. The observed intensities are given for two samples I and II. In sample I, the intensities are modified by an appreciable preferential orientation.

The observed values of $\sin^2\theta$ correspond to a rhombohedral lattice with $a_0=9\cdot398\pm0\cdot002$ Å, $\alpha=23\cdot78\pm0\cdot01°$. The dimensions of the corresponding hexagonal cell are $a_0=3\cdot871\pm0\cdot001$, $c_0=27\cdot385\pm0\cdot005$ Å.

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Table 1. *X-ray diffraction data for* Th_3N_4 (Cu $K\alpha$; $\lambda = 1{\cdot}5405$ Å) *

Table 1 (*cont.*)

h k l	$\sin^2\theta \times 10^4$ calcd.	obs.	Relative Intensities obs. I.	obs. II.	calcd.
0 0 3	71				1.4
0 0 6	285				0.0
1 0 1	536	545	w	w+	33.8
0 1 2	560	567	vw-	vw-	14.2
0 0 9	641	649	vs	w	45.3
1 0 4	654	666	m	s	77.7
0 1 5	726	735	m	m	100
1 0 7	916	927	vw-	vw-	4.9
0 1 8	1034	1047	w	w	18.2
0 0 12	1139				0.1
1 0 10	1319	1334	w-	w-	6.7
0 1 11	1485	1492	vvw	vvw	2.4
1 1 0	1584	1600	m	s	16.7
1 1 3	1655				0.0
0 0 15	1780				0.0
1 0 13	1865	1834	m	m-	4.7
1 1 6	1869				0.0
0 1 14	2078	2088	w+	w	4.9
0 2 1	2120	2144	vw	vw	1.4
2 0 2	2143				0.6
1 1 9	2225	2246	s	s	13.2
0 2 4	2238				4.0
2 0 5	2309	2325	w+	wm	5.7
0 2 7	2499				0.5
1 0 16	2553	2574	m	vw+	0.5
0 0 18	2563				2.4
2 0 8	2618	2647	vw	vw+	1.9
1 1 12	2723				0.1
0 1 17	2814	2847	vw	vw-	0.9
0 2 10	2903	2911	vvw	vw-	1.3
2 0 11	3069	3087	trace		0.6
1 1 15	3364	3397	vw-	vvw	0.1
1 0 19	3384				0.7
0 2 13	3449	3476	w	w+	3.3
0 0 21	3489				0.0
2 0 14	3662	3676	w	w	2.5
0 1 20	3692	3713	w	w	0.3
2 1 1	3703				1.4
1 2 2	3727				0.6
2 1 4	3822	3841	m	ms	3.6
1 2 5	3893	3908	m	m	4.5
2 1 7	4083				0.3
0 2 16	4137	4158	s	ms	0.2
1 1 18	4147				4.9
1 2 8	4202	4201	trace	vw-	1.2
1 0 22	4357	4373	m	w	1.5
2 0 17	4398				0.3
2 1 10	4487	4503	vw	vw	0.8
0 0 24	4557				0.0
1 2 11	4653				0.4
0 1 23	4713	4712	wm	w	1.4
3 0 0	4751	4756	wm	wm	1.9
3 0 3	4822				0.0
0 2 19	4968				0.2
2 1 13	5032	5052	m	m	2.2
3 0 6	5036				0.1
1 1 21	5073				0.0
2 1 14	5246	5262	wm	w	1.9
2 0 20	5276				0.1
3 0 9	5392	5418	m	m	2.3
1 0 25	5472				0.1
2 1 16	5721				0.2
0 0 27	5767	5777	w+	vw	0.3
1 0 26	5876				0.2
3 0 12	5890				0.0
2 0 22	5941	5975	w+	w	0.6
2 1 17	5982				0.3
1 1 24	6141				0.0
2 0 23	6297	6328	wm	wm	0.4
2 2 0	6335				0.5
2 2 3	6406				0.0
3 0 15	6531				0.0
2 1 19	6551	6562	vw	vw	0.1
2 2 6	6620				0.0
1 0 28	6730	6746	vw	-	0.0
2 1 20	6860				0.0
3 1 1	6871	6893	vvw	vw	0.1
3 1 2	6895				0.0
2 2 9	6976	6986	s	s	0.6
3 1 4	6990				0.4
2 0 25	7056	7069	wm	m	0.0
3 1 5	7061				0.6
0 0 30	7120				0.0
1 0 29	7181				0.0
3 1 7	7251				0.1
3 0 18	7314	7347	s	s	1.4
1 1 27	7351				1.3
3 1 8	7369				0.4
2 0 26	7460				0.1
2 2 12	7474				0.0
2 1 22	7524	7533	m	m	1.2
3 1 10	7654				0.3
3 1 11	7820				0.1
2 1 23	7880	7885	wm	w	0.7
2 2 15	8115	8133	m	w-	0.0
1 0 31	8131				0.1
1 3 13	8200	8190	w	m	0.0
3 0 21	8240				0.0
0 2 28	8314				0.1
3 1 14	8414	8419	w+	m	0.6
4 0 1	8455				0.1
0 4 2	8478				0.0
4 0 4	8573	8587	w	w	0.5
0 0 33	8615				0.0
0 1 32	8629	8639	m	w	0.6
2 1 25	8640				0.2
0 4 5	8644				0.7
1 1 30	8704				0.0
2 0 29	8765				0.1
4 0 7	8834				0.1
1 3 16	8888	8904	m	m+	0.2
2 2 18	8898				3.1
0 4 8	8953				0.4
1 2 26	9043	9055	vvw	-	0.6
3 1 17	9149	9169	vvw	vw	0.6
4 0 10	9238				0.5
3 0 24	9308				0.0
0 4 11	9404				0.3
1 0 34	9673				0.6
0 2 31	9714	9716	w	w	4.5
1 3 19	9719				2.1
4 0 13	9784	9785	w	w	4.7
2 2 21	9824				0.0

Both the cell volume and the observed intensities require one stoichiometric molecule per rhombohedral cell, and the calculated density is accordingly $\varrho = 10{\cdot}55$ g.cm^{-3}.

The observed intensities demand that the three metal atoms per rhombohedral cell be in positions (000) and $\pm(zzz)$ with $z = 2/9$. Thus, the thorium atoms have the close-packed configuration *ABABCACACA*--- observed in the samarium metal structure.

The nitrogen atoms have too small an effect on the intensities to permit a direct determination of their positions. However, on the basis of chemical stoichiometry and assuming an ordered structure, spatial considerations require that they lie on the threefold axis with one set occupying

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* Calc. relative intensities proportional to

$$\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}\,p|F|^2$$

where p = multiplicity and F = structure factor.

octahedral and the other tetrahedral holes of the close-packed metal configuration.

The structure thus arrived at is

Space group $R\bar{3}m$

Hexagonal Description	Rhombohedral Description
$(000)(\frac{1}{3}\frac{2}{3}\frac{1}{3})(\frac{2}{3}\frac{1}{3}\frac{2}{3})^+$	
3 Th (I) (000)	1 Th (I) (000)
6 Th (II) $\pm(00z_1)$	2 Th (II) $\pm(z_1z_1z_1)$
6 N (I) $\pm(00z_2)$	2 N (I) $\pm(z_2z_2z_2)$
6 N (II) $\pm(00z_3)$	2 N (II) $\pm(z_3z_3z_3)$

with $z_1=0{\cdot}222\pm0{\cdot}003$, $z_2\simeq0{\cdot}137$, $z_3\simeq0{\cdot}389$.

The interatomic distances for this assumed structure are

Th (I)–6 N (II)	2·70 Å	Th (II)–4 N (I)	2·34 Å
–6 Th (II)	3·77	–3 N (II)	2·70
–6 Th (I)	3·87	–3 Th (I)	3·77
		–3 Th (II)	3·77
		–6 Th (II)	3·87

The Th_3N_4 structure is closely related to that of Th_2N_2O previously reported (Zachariasen, 1949) as Th_2N_3. In the latter structure the metal atoms are in simple hexagonal close-packing so that the *c* axis is twice the separation of hexagonal layers, whereas the *c* axis is nine times the layer distance in the Th_3N_4 structure. As shown below, the hexagonal *a* axis and the layer separation are slightly smaller for the Th_3N_4 phase:

Th_2N_2O	Th_3N_4
$a_0=3{\cdot}8833$ Å	$a_0=3{\cdot}871$ Å
$c_0=6{\cdot}1870=2\times3{\cdot}0935$ Å	$c_0=27{\cdot}385=9\times3{\cdot}043$ Å

The atomic positions of the Th_2N_2O structure are

2 Th in $\pm(\frac{1}{3}\frac{2}{3}z_1)$ with $z_1=0{\cdot}250\pm0{\cdot}006$
2 N in $\pm(\frac{1}{3}\frac{2}{3}z_2)$ with $z_2\simeq0{\cdot}631$
1 O in (000).

The N atoms occupy tetrahedral and the O atoms octahedral holes of the close-packed metal structure. The interatomic distances are

Th–4 N	2·35 Å
–3 O	2·72
–6 Th	3·81
–6 Th	3·88

Thus, the configuration about the Th (II) atoms of the Th_3N_4 structure is almost identical with that of the Th_2N_2O phase. However, the Th (I) atoms form only six bonds to nitrogen atoms, all occupying octahedral holes.

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X-ray examination of some rare-earth-containing binary alloy systems.

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Despite the intensive efforts which have been expended on the study of rare earth intermetallic compounds in recent years, there remains a large number of binary alloy systems yet to be investigated. Upon reviewing compendia by Gschneidner (1961) and McMasters & Gschneidner (1964), certain patterns of omission were observed, these usually occurring where one or both of the component elements are difficult to handle with ordinary melting techniques. In particular, most investigators seem to have avoided lanthanides with: high vapor pressures, high oxygen affinity, high melting points, divalent character, and those which are relatively scarce. The general approach followed during the present study was that described in earlier work by Moriarty (1960). Structural data for compounds formed in similar systems with gadolinium and dysprosium, and holmium and erbium can be found in reports by Baenziger & Moriarty (1961) and Moriarty, Gordon & Humphreys (1965) respectively.

Alloys were prepared by blending stoichiometric proportions of the components and either arc-melting them on a water cooled copper hearth or encapsulating them in tantalum crucibles and heating these in a tube or induction furnace. All procedures employed a protective atmosphere of dry argon gas. Each specimen was repeatedly remelted to improve homogeneity. Final weights differed from initial weights by less than 1·0 %. Purities of the metals used were: rare earths, at least 99·8 %; all others greater than 98·5 %.

In all cases the phases herein reported were identified by indexing the X-ray diffraction powder patterns. Diffraction equipment included a basic Norelco X-ray unit, using either filtered copper $K\alpha$ (Cu $K\alpha_1=1{\cdot}54051$, Cu $K\alpha_2=1{\cdot}54433$ Å) or iron $K\alpha$ (Fe $K\alpha_1=1{\cdot}93597$, Fe $K\alpha_2=1{\cdot}93991$ Å) radiation, 114·6 mm Debye–Scherrer cameras, and either Ansco Superay C or Kodak Type KK film. Suitable photographs were made at 20 to 25 °C of the alloy specimens in an annealed condition. Filings were annealed in Vycor capillaries previously 'gettered' with zirconium wire to minimize oxidation. Some alloys were 'bulk' annealed in small sealed Vycor tubes and then crushed.

Results of this study are given in Tables 1 through 4. The lattice constants were calculated under the direction of one of us (N.C.B.) with an IBM 7044 computer from back-reflection data, with the use of an analytical least-squares program written by Miss Carol Valley at State University of Iowa.

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