

Intermetallic 2-17 Stoichiometry: The Crystal Structure of $\text{Th}_2\text{Fe}_{17}$ and $\text{Th}_2\text{Co}_{17}$ *

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The monoclinic structure reported for $\text{Th}_2\text{Fe}_{17}$ and $\text{Th}_2\text{Co}_{17}$ has been found to be in error. The correct structure is rhombohedral, $R\bar{3}m$, with hexagonal cell constants of $a=8.565$, $c=12.469$ Å for $\text{Th}_2\text{Fe}_{17}$ and $a=8.438$, $c=12.254$ Å for $\text{Th}_2\text{Co}_{17}$. Calculated densities are 8.885 and 9.661 g.cm⁻³ for the iron and cobalt compounds respectively. These compounds are shown to be isostructural with $\text{Th}_2\text{Zn}_{17}$. Although literature surveys cite at least five A_2B_{17} structure types ($\text{Th}_2\text{Fe}_{17}$, $\text{Th}_2\text{Ni}_{17}$, $\text{Th}_2\text{Zn}_{17}$, U_2Zn_{17} , and $\text{Nb}_2\text{Be}_{17}$), only the $\text{Th}_2\text{Zn}_{17}$ structure type is both unique and compositionally correct. A remarkable feature of the $\text{Th}_2\text{Zn}_{17}$ structure type is the constancy of the c/a ratio. This ratio has been found to be 1.46 ± 0.01 for over 40 compounds with the $\text{Th}_2\text{Zn}_{17}$ structure.

Introduction

For binary intermetallic compounds AB_x with $x \geq 7$, few unique structure types are known – in contrast, for example, to the case for $x=1.0$. A recent compilation of intermetallic structures (Pearson, 1967) lists only 12 structure types for which this condition holds (disregarding oxides, nitrides, borides, and carbides). Another compilation (Schubert, 1964) lists 14 unique structure types satisfying these criteria. Since disparate-composition† structure types appear to be somewhat rare for intermetallics, it is surprising to discover that so many are reported to have the intuitively unusual composition A_2B_{17} . The A_2B_{17} structure types listed in these two compilations are shown in Table 1.

Table 1. Reported A_2B_{17} structure types

Prototype	Reference
$\text{Th}_2\text{Fe}_{17}$	Florio, Baenziger & Rundle (1956)
$\text{Th}_2\text{Ni}_{17}$	Florio, Baenziger & Rundle (1956)
$\text{Th}_2\text{Zn}_{17}$	Makarov & Vinogradov (1956)
U_2Zn_{17}	Marakov & Vinogradov (1956)
$\text{Nb}_2\text{Be}_{17}$	Zalkin, Sands & Krikorian (1959)

This list is too long by at least two entries, and probably by four. One of the incorrect types is that reported for the compound $\text{Th}_2\text{Fe}_{17}$ (Florio, Baenziger & Rundle, 1956). Johnson (1962) suggested that the reported structure was incorrect and that the correct structure would turn out to be identical to $\text{Th}_2\text{Zn}_{17}$. We have carried out single-crystal investigations on $\text{Th}_2\text{Fe}_{17}$ and its isostructural partner $\text{Th}_2\text{Co}_{17}$ which have confirmed this speculation.

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† There appears to be no name for the class of binary compounds in which one element is predominant compositionally. We propose this name, which implies that the two elements should be totally unequal in composition. We have arbitrarily chosen $x > 7$ to convey this gross inequality.

Experimental

The thorium used in these experiments is of unknown origin. A spectrographic analysis showed it to be greater than 99.99 wt. % pure, the major impurities being iron, chromium and silicon. Spectrographic analysis of the 'Armco' iron showed it to be 99.9 wt. % pure, the principal impurities being copper, manganese, nickel, and molybdenum. The cobalt was obtained several years ago from the Cobalt Information Center at Battelle Memorial Institute. The stated purity of this cobalt was 99.947%; however, no analysis was made because of the limited quantity of material available.

A button of $\text{Th}_2\text{Fe}_{17}$ was made by placing 0.4740 g of thorium (cleaned with silicon carbide paper) and 0.9698 g of clean iron on a massive polished copper hearth in an argon-filled drybox and melting with an arc from a tungsten electrode. The button was melted and turned four times. The final weight was 1.4400 g indicating a 3.8 mg loss during melting. This button was then wrapped in thin tantalum foil and sealed into a quartz ampoule with a partial atmosphere of argon. The heat treatment consisted of a gradual rise over a 24 hr period to 880°C where the temperature was maintained for 135 hr. At the end of this time, the capsule was removed from the furnace and cooled.

In like manner, 1.4798 g of thorium and 3.1942 g of cobalt were melted with a loss of 0.14 g during melting. The heat treatment was carried out in the same way except that the ampoule was placed into the hot furnace and held at 880°C for 90 hr. The microstructure showed a very small quantity of a second phase distributed in a coarse dendritic pattern.

The powder patterns of both compounds were found to be nearly identical with that of $\text{Pr}_2\text{Fe}_{17}$, a compound which has been shown to have the $\text{Th}_2\text{Zn}_{17}$ structure (Johnson, Wood, Smith & Ray, 1968). Weissenberg and precession photographs of single crystals established the rhombohedral symmetry. This symmetry was subsequently confirmed by diffractometric meas-

urement of the intensities of several equivalent reflections. Hexagonal cell constants were obtained by a least-squares fit of powder data from an Fe $K\alpha$ ($\lambda=1.9373 \text{ \AA}$) powder pattern. For $\text{Th}_2\text{Fe}_{17}$, these are $a=8.565 \pm 0.002$, $c=12.469 \pm 0.003 \text{ \AA}$, and for $\text{Th}_2\text{Co}_{17}$, $a=8.438 \pm 0.005$, $c=12.254 \pm 0.008 \text{ \AA}$. Calculated densities are 8.885 g.cm^{-3} for $\text{Th}_2\text{Fe}_{17}$ and 9.661 g.cm^{-3} for $\text{Th}_2\text{Co}_{17}$. The incorrect monoclinic cell is related to the correct cell in the hexagonal setting as follows: $\mathbf{a}_h = (\mathbf{a}_m - \mathbf{b}_m)/2 + \mathbf{c}_m$; $\mathbf{b}_h = \mathbf{b}_m$; $\mathbf{c}_h = -\mathbf{a}_m + \mathbf{c}_m$.

A single crystal of $\text{Th}_2\text{Fe}_{17}$ which was satisfactory for intensity measurements was easily obtained. All crystals of $\text{Th}_2\text{Co}_{17}$ investigated were twinned. Nevertheless, a small fragment of $\text{Th}_2\text{Co}_{17}$ was obtained for intensity measurements with the intention of applying a twinning correction to the data. $\text{Pr}_2\text{Fe}_{17}$ crystals were also twinned (Johnson *et al.*, 1968) but not to the same degree.

Intensities of all independent reflections were recorded up to $2\theta \leq 40^\circ$, using zirconium-filtered Mo $K\alpha$ radiation ($\lambda=0.7107 \text{ \AA}$) and a single-crystal orienter. A φ -dependent absorption correction was applied to the intensities; the maximum correction for $\text{Th}_2\text{Fe}_{17}$ was 35%, but for $\text{Th}_2\text{Co}_{17}$ it was 80%. Atomic parameters for $\text{Pr}_2\text{Fe}_{17}$ were used as a starting point for full-matrix, least-squares refinements. Atomic scattering factors were those for the neutral atoms listed in *International Tables for X-ray Crystallography* (1962), corrected for anomalous dispersion (Dauben & Templeton, 1955). The quantity minimized in the least-squares program is $\sum w(|F_o| - (1/k)|F_c|)^2$ where k is the scale factor relating $|F_o|$ and $|F_c|$ and the w 's are given by the following weighting scheme:

$w = F_o^{1/4}$, $F_o < A$; $w = A^{5/4}F_o^{-1}$, $F_o > A$, with $A = 151$ for $\text{Th}_2\text{Fe}_{17}$ and 142 for $\text{Th}_2\text{Co}_{17}$. For $\text{Th}_2\text{Co}_{17}$, a twinning correction was introduced by multiplying the intensities of affected reflections by a twin parameter. This parameter was adjusted to give the lowest $R[\sum (k|F_o| - |F_c|)/\sum k|F_o|]$ value and agreed well with the ratio obtained by measurement of intensities of several pairs of twin-related reflections. The parameter was 0.36. Changes in parameters for the last cycle of refinement were less than 0.01 times the estimated standard deviations. The R value including all data was 3.7% for $\text{Th}_2\text{Fe}_{17}$ and 6.8% for $\text{Th}_2\text{Co}_{17}$. The higher value for

Table 3. Observed and calculated structure factors

$\text{Th}_2\text{Fe}_{17}$ data are listed first.

H	K	L	F _O	/F _C	F _O	/F _C	H	K	L	F _O	/F _C	F _O	/F _C	H	K	L	F _O	/F _C	F _O	/F _C	
0	0	0	3	82	75	79	74	1	2	11	32	34		3	1	2	6	8	5	8	
0	0	0	6	352	353	366	362	1	3	1	11	8	20	6	3	1	5	14	14	5	8
0	0	0	9	86	85	102	95	1	3	4	70	69	70	68	3	1	8	15	11	18	7
0	0	0	12	241	228			1	3	7	82	79	88	83	3	2	1	72	75	65	73
0	1	2	2	28	26	21	27	1	3	10	26	28	34	27	3	2	4	133	133	135	139
0	1	5	35	34	37	27		1	4	7	85	86	94	86	3	2	7	131	136	135	137
0	1	8	3	1	12	7		1	4	3	137	134	133	139	3	3	0	130	127	141	128
0	1	11	66	65	82	78		1	4	6	19	23	25	20	3	3	3	175	169	166	172
0	2	1	79	75	58	72		1	4	9	114	111			3	3	6	64	62	68	60
0	2	4	183	177	198	192		1	5	2	70	69	76	71	3	4	2	32	31	37	35
0	2	7	111	104	107	103		1	5	5	75	75	78	75	3	4	5	8	12	6	12
0	2	10	118	116	132	123		1	6	1	15	17	7	15	3	5	1	43	43	49	42
0	3	0	203	207	202	213		1	6	4	62	64	71	68	4	0	1	44	42	48	52
0	3	3	254	256	258	264		2	0	2	63	62	42	55	4	0	4	50	52	44	57
0	3	6	116	110	113	112		2	0	5	130	125	145	148	4	0	7	14	13	23	9
0	3	9	207	192	193	192		2	0	8	14	16	46	39	4	1	3	133	132	137	135
0	4	2	54	50	63	65		2	0	11	27	32	46	50	4	1	6	23	25	16	25
0	4	5	16	13	42	25		2	1	1	70	70	61	73	4	1	9	104	107		
0	4	8	98	91	118	115		2	1	4	123	125	125	126	4	2	2	33	37	34	32
0	5	1	72	69	73	73		2	1	7	130	132	141	140	4	2	5	80	83	93	98
0	5	4	106	106	102	105		2	1	10	64	64	65	64	4	2	8	19	19		
0	5	7	120	119	118	125		2	2	0	272	288	277	302	4	3	1	20	19	20	19
0	6	0	248	257	257	267		2	2	3	85	79	96	92	4	4	4	25	20	6	20
0	6	3	16	11	24	14		2	2	5	171	170	179	170	4	4	0	225	237	263	249
0	6	6	175	173	170	173		2	2	9	34	30	38	24	5	0	2	51	54	49	51
0	7	2	27	33				2	3	2	85	82	87	89	5	0	5	69	70	73	71
1	0	1	20	22	18	23		2	3	5	75	73	72	69	5	0	8	22	26	17	27
1	0	4	96	100	101	93		2	3	8	46	47	57	55	5	1	1	76	77	81	79
1	0	7	110	105	114	113		2	4	1	46	47	46	46	5	1	4	115	117	112	120
1	0	10	39	42	46	43		2	4	4	122	120	135	130	5	1	7	114	123	117	129
1	1	0	70	70	80	65		2	4	7	74	75	73	74	5	2	3	105	105	104	110
1	1	3	136	138	144	137		2	5	0	61	66	67	67	5	3	2	41	42		
1	1	6	18	14	32	19		2	5	3	108	103	105	104	6	0	3	16	11	29	14
1	1	9	112	107	107	105		3	0	3	242	258	259	268	6	0	6	167	173	172	173
1	2	2	61	61	64	62		3	0	5	105	107	113	105	6	1	2	11	22	24	26
1	2	5	74	72	81	72		3	0	9	195	196	196	200	7	0	1	34	44	46	47
1	2	8	28	27	41	32															

the cobalt compound reflects the difficulties encountered with respect to both twinning and absorption.

Final parameters and estimated standard deviations are given in Table 2. Table 3 is the list of observed and calculated structure factors. Interatomic distances are presented in Table 4.

Discussion

These results conclusively show that the list in Table 1 should be shortened by one. It is possible to eliminate $\text{Nb}_2\text{Be}_{17}$ from the list also, as it is identical with $\text{Th}_2\text{Zn}_{17}$ but with the origin shifted by $0, 0, \frac{1}{2}$.

There are five single-crystal determinations of the atomic parameters in $\text{Th}_2\text{Zn}_{17}$ structures. The parameters are listed in Table 5 for comparison. In addition, parameters were obtained for at least three others, by powder methods. They are $\text{Th}_2\text{Zn}_{17}$ by Makarov & Vinogradov (1956); $\text{Gd}_2\text{Co}_{17}$ by Bouchet, Laforest, Lemaire & Schweizer (1966); and $\text{Ho}_2\text{Zn}_{17}$ by Landelli & Palenzona (1967). The parameters obtained from

Table 2. Hexagonal atomic parameters for $\text{Th}_2\text{Fe}_{17}$ and $\text{Th}_2\text{Co}_{17}$, space group $R\bar{3}m$ (e.s.d.'s in parentheses)

	Atom	Wyckoff notation	10^4x	10^4y	10^4z	$B (\text{\AA}^2)$
$\text{Th}_2\text{Fe}_{17}$	Th	6c	0	0	3428 (2)	0.39 (0.07)
	Fe (1)	6c	0	0	959 (7)	0.69 (0.18)
	Fe (2)	9d	$\frac{1}{2}$	0	$\frac{1}{2}$	0.70 (0.14)
	Fe (3)	18f	2860 (6)	0	0	0.50 (0.11)
	Fe (4)	18h	1686 (3)	8314	4899 (4)	0.68 (0.10)
$\text{Th}_2\text{Co}_{17}$	Th	6c	0	0	3431 (3)	0.21 (0.13)
	Co (1)	6c	0	0	958 (10)	0.37 (0.29)
	Co (2)	9d	$\frac{1}{2}$	0	$\frac{1}{2}$	0.36 (0.22)
	Co (3)	18f	2852 (10)	0	0	0.46 (0.19)
	Co (4)	18h	1694 (6)	8306	4858 (6)	0.52 (0.17)

Table 4. Interatomic distances in Th₂Fe₁₇ and Th₂Co₁₇

	Ligancy	Th ₂ Fe ₁₇		Th ₂ Co ₁₇	
		Distance	e.s.d.	Distance	e.s.d.
Th	1 B (1)	3.079	0.009	3.031	0.014
	6 B (3)	3.080	0.003	3.039	0.005
	3 B (4)	3.101	0.004	3.032	0.006
	3 B (4)	3.203	0.004	3.113	0.006
B(1)	3 B (4)	3.256	0.004	3.244	0.006
	3 B (2)	3.307	0.002	3.257	0.003
	1 B (1)	2.392	0.017	2.347	0.027
	3 B (2)	2.625	0.003	2.586	0.005
B(2)	3 B (4)	2.644	0.004	2.612	0.007
	6 B (3)	2.726	0.006	2.677	0.009
	1 Th	3.079	0.009	3.031	0.014
	4 B (3)	2.428	0.001	2.396	0.002
B(3)	4 B (4)	2.462	0.003	2.422	0.004
	2 B (1)	2.625	0.003	2.586	0.005
	2 Th	3.307	0.002	3.257	0.003
	2 B (2)	2.438	0.001	2.396	0.002
B(4)	2 B (3)	2.450	0.005	2.407	0.008
	2 B (4)	2.542	0.004	2.541	0.007
	2 B (4)	2.678	0.005	2.604	0.008
	2 B (1)	2.726	0.006	2.677	0.009
B(4)	2 Th	3.080	0.003	3.039	0.005
	2 B (2)	2.462	0.003	2.422	0.004
	2 B (4)	2.513	0.003	2.501	0.005
	2 B (3)	2.542	0.004	2.541	0.007
	1 B (1)	2.644	0.004	2.612	0.007
	2 B (3)	2.678	0.005	2.604	0.008
	1 Th	3.101	0.004	3.032	0.006
	1 Th	3.203	0.004	3.113	0.006
	1 Th	3.256	0.004	3.244	0.006

powder methods are not included as they are not considered to be of the same accuracy as the single-crystal parameters. It is not apparent just how much variation in the atomic parameters is significant. No clear-cut correlation is obvious between the atomic parameters and the individual atom radii or the radius

ratio; certain trends are apparent – for example, $z(A)$ becomes larger as r_A/r_B becomes larger.

At the time of writing, we know of 40 binary and three ternary intermetallic compounds having the Th₂Zn₁₇ structure. The current list is given in Table 6. Cell parameters are those of the first listed reference. Radius ratios have been computed from the radii of Teatum, Gschneidner, & Waber (1959). One fact to be noted from this list is that the radius ratio interval is small ($1.12 \leq r_A/r_B \leq 1.46$) and different for different B elements. This list also points out the fact that no nickel compound has yet been found. Size considerations alone cannot account for this. One interesting correlation is noted by observing that Be, Mg, Co, and Zn all have the close-packed hexagonal crystal structure under ordinary conditions, and that Fe assumes this structure at 130 kbar (Jamieson & Lawson, 1962; Clendenan & Drickamer, 1964). In the case of nickel, the hexagonal modification has not been observed, except perhaps in thin films (Trillat, Tertian & Terao, 1961). If a systematic effort were to be made to extend this list, it would therefore perhaps be well to choose B elements which have hexagonal crystal structures and a radius ratio satisfying $1.12 \leq r_A/r_B \leq 1.46$. Examples satisfying these conditions would be some of the rare earths for A and Ru, Re, or Os as B .

The feature of greatest significance to be noted from Table 6 is that although this list contains over 40 compounds comprising a wide range of elements and the cell constant variation exceeds 40%, the c/a ratio is remarkably constant at 1.46 ± 0.01 (or in terms of rhombohedral α , $82.9 \pm 0.2^\circ$). Viewing these compounds as close-packed structures of slightly impure B elements provides little in the way of enlightenment.

Table 5. Parameters reported for single crystal refinements of five compounds with the Th₂Zn₁₇ structure

Compounds	Nb ₂ Be ₁₇	Pr ₂ Fe ₁₇	Th ₂ Fe ₁₇	Th ₂ Co ₁₇	U ₂ Zn ₁₇
a	7.409	8.585	8.565	8.438	8.978
c	10.84	12.464	12.469	12.254	13.160
c/a	1.463	1.452	1.452	1.452	1.466
r_A	1.468	1.828	1.798	1.798	1.56
r_B	1.128	1.274	1.274	1.252	1.394
r_A/r_B	1.301	1.435	1.411	1.436	1.119
$z(A)$	0.3401	0.3436	0.3428	0.3431	0.337
$z(B_1)$	0.103	0.0960	0.0959	0.0958	0.099
$x(B_3)$	0.297	0.2868	0.2860	0.2852	0.294
$x(B_4)$	0.164	0.1696	0.1686	0.1694	0.162
$z(B_4)$	0.494	0.4897	0.4899	0.4858	0.482
$B(A)$	0.56	0.54	0.39	0.21	0.05
$B(B_1)$	0.5	0.55	0.69	0.37	0.81
$B(B_2)$	1.6	0.47	0.70	0.36	1.32
$B(B_3)$	1.5	0.66	0.50	0.46	0.74
$B(B_4)$	0.3	0.68	0.68	0.52	1.04
R factor	6.7%	3.9%	3.7%	6.8%	12.7%
Number of data	100	108	109	102	240
Type of data	Diffraction	Diffraction	Diffraction	Diffraction	Film data
Reference	(5)	(12)	(20)	(20)	(30)

(Numbers correspond to those of Table 6)

Close-packed B spheres require $a=4\sqrt{3}r_B$, $c=4\sqrt{6}r_B$ and $c/a=\sqrt{2}$. Cell constants computed from these relations do not predict the observed values better than about 5%. For the pure B metals the c/a ratios range from 1.57 to 1.86, a variation of 18% *versus* only about 1.5% for this much more complicated structure. The underlying cause of this constantancy is probably of considerable significance, but we are unable to advance ideas concerning it.

Thus far, the list of Table 1 has been shortened to three. One of those remaining $-U_2Zn_{17}-$ is questioned by Vold & Peterson (1961). In studies of U-Zn preparations they obtained single crystals of both the Th_2Zn_{17} and the Th_2Ni_{17} structure types. Some of their Weissenberg photographs led to a unit-cell consistent with that reported by Makarov & Vinogradov (1956).

Vold & Peterson point out, however, that these photographs can be explained by assuming that the crystal photographed is not a single crystal but rather a mixture of the two known phases. Indeed, the crystallographic experiments of Makarov & Vinogradov could not have distinguished between these two interpretations; thus until more detailed crystallographic, collaborated by metallographic, experiments reveal greater complexity than that found by Vold & Peterson, it is more reasonable to accept their simpler interpretation. Pearson (1967) cites two other compounds reported to have the ' U_2Zn_{17} ' structure. One of these, Pu_2Zn_{17} , (Cramer, Ellinger & Land, 1960) has been eliminated by more recent work (Cramer & Wood, 1967). The other, Hf_2Be_{17} , (Kripyakevich, Tylkina, & Savitskii, 1961) is based on powder patterns alone. Zalkin, Sands,

Table 6. *Compounds reported to have the Th_2Zn_{17} structure*

Cell constants are from first reference.

Compounds	a	c	c/a	r_A/r_B	References
Ti_2Be_{17}	7.392	10.79	1.460	1.296	(1); (2), (3)
Zr_2Be_{17}	7.548	10.997	1.457	1.420	(4)
Nb_2Be_{17}	7.409	10.84	1.463	1.301	(5)
Hf_2Be_{17}	7.494	10.93	1.459	1.401	(1); (3), (6)
Ta_2Be_{17}	7.388	10.74	1.454	1.301	(1); (3)
Ba_2Mg_{17}	10.664	15.593	1.462	1.400	(7); (8)
Y_2Fe_{17}	8.46	12.41	1.467	1.414	(9)
Ce_2Fe_{17}	8.488	12.402	1.461	1.432	(10); (9), (11)
Pr_2Fe_{17}	8.585	12.464	1.452	1.435	(12); (9), (10), (13)
Nd_2Fe_{17}	8.578	12.462	1.453	1.429	(10); (9), (11), (14), (15), (16)
Sm_2Fe_{17}	8.554	12.441	1.454	1.414	(10); (9)
Gd_2Fe_{17}	8.536	12.429	1.456	1.414	(17); (9), (14), (18), (19)
Tb_2Fe_{17}	8.54	12.43	1.456	1.399	(13); (9)
Th_2Fe_{17}	8.565	12.469	1.456	1.411	(20); (21)
Y_2Co_{17}	8.355	12.183	1.458	1.438	(22); (9), (23)
Ce_2Co_{17}	8.368	12.204	1.458	1.458	(22); (9), (24)
Pr_2Co_{17}	8.430	12.253	1.453	1.460	(22); (9), (24)
Nd_2Co_{17}	8.422	12.246	1.454	1.454	(22); (9), (24)
Sm_2Co_{17}	8.385	12.214	1.457	1.439	(22); (9), (24)
Gd_2Co_{17}	8.377	12.198	1.456	1.439	(22); (9), (24), (25)
Tb_2Co_{17}	8.357	12.186	1.458	1.423	(22); (9), (24)
Dy_2Co_{17}	8.346	12.180	1.459	1.416	(22); (9), (24)
Th_2Co_{17}	8.438	12.254	1.452	1.436	(20); (21)
Y_2Zn_{17}	9.13	13.40	1.468	1.292	(26)
La_2Zn_{17}	9.131	13.334	1.460	1.346	(27)
Ce_2Zn_{17}	9.0708	13.2844	1.465	1.309	(28); (27)
Pr_2Zn_{17}	9.066	13.274	1.464	1.311	(27)
Nd_2Zn_{17}	9.052	13.236	1.462	1.306	(27)
Sm_2Zn_{17}	9.017	13.211	1.465	1.293	(27)
Gd_2Zn_{17}	8.994	13.169	1.464	1.293	(27)
Tb_2Zn_{17}	8.997	13.161	1.466	1.278	(27)
Dy_2Zn_{17}	8.967	13.139	1.465	1.272	(27)
Ho_2Zn_{17}	8.956	13.133	1.466	1.267	(27)
Er_2Zn_{17}	8.942	13.118	1.467	1.260	(27)
Tm_2Zn_{17}	8.937	13.110	1.467	1.253	(27)
Yb_2Zn_{17}	9.040	13.216	1.462	1.392	(27)
Lu_2Zn_{17}	8.920	13.096	1.468	1.244	(27)
Th_2Zn_{17}	9.060	13.234	1.461	1.290	(27); (29)
U_2Zn_{17}	8.983	13.161	1.465	1.119	(27); (29), (30)
Pu_2Zn_{17}	8.95	13.1	1.464	1.133	(31); (32)
$Ce_2Mn_7Al_{10}$	8.85-9.07	12.95-13.19	1.463-1.454		(33)
$Ce_2Co_{15}Al_2$	8.44	12.30	1.457		(33)
$Ce_2Cu_{6.5-7.3}Al_{10.5-9.7}$	8.98-8.96	13.07-13.04	1.456-1.455		(33)

Table 6 (*cont.*)

1. Zalkin, Sands, Bedford & Krikorian (1961).
2. Gladyshevskii, Kripyakevich, Teslynk, Zarechnyuk & Kuz'ma (1961).
3. Paine & Carrabine (1960).
4. Zalkin, Bedford & Sands (1959).
5. Zalkin, Sands & Krikorian (1959).
6. Kripyakevich, Tykina & Savitskii (1961).
7. Kripyakevich & Evdokimenko (1962).
8. Wang, Kanda, Miskell & King (1963).
9. Buschow (1966).
10. Ray (1966).
11. Savitskii, Terekhova, Burov, Markova & Naumkin (1962).
12. Johnson, Wood, Smith & Ray (1968).
13. Kripyakevich & Frankevich (1964).
14. Kripyakevich, Terekhova, Zarechnyuk & Burov (1963).
15. Savitskii, Terekhova, Burov & Naumkin (1964).
16. Terekhova, Maslova & Savitskii (1965).
17. Savitskii, Terekhova, Burov & Chistyakov (1961).
18. Kripyakevich & Gladyshevskii (1961).
19. Savitskii, Terekhova & Burov (1960).
20. This work.
21. Florio, Baenziger & Rundle (1956).
22. Bouchet, Laforest, Lemaire & Schweizer (1966).
23. Ostertag (1965).
24. Ostertag & Strnat (1966).
25. Savitskii, Terekhova & Burov (1962).
26. Ryba & Gill (1962).
27. Iandelli & Palenzona (1967).
28. Lott & Chiotti (1966).
29. Makarov & Vinogradov (1956).
30. Vold & Peterson (1961).
31. Cramer & Wood (1967).
32. Albrecht (1961).
33. Zarechnyuk & Kripyakevich (1963).

Bedford, & Krikorian (1961) have shown that $\text{Th}_2\text{Zn}_{17}$ and $\text{Th}_2\text{Ni}_{17}$ structure types exist in the Hf-Be system. We have calculated what the powder pattern of a mixture of these two phases would look like. Not unexpectedly, this pattern is identical to that reported by Kripyakevich *et al.* In summary, no data exist which require the ' U_2Zn_{17} ' structure type of Makarov & Vinogradov (1956) for their interpretation.

Apart from the by now well-established structure type, $\text{Th}_2\text{Zn}_{17}$, there remains one last survivor of the list presented in Table 1 - $\text{Th}_2\text{Ni}_{17}$. Johnson & Smith (1967) have shown the composition of the $\text{Th}_2\text{Ni}_{17}$ -like compound in the Ce-Mg system to be $\text{CeMg}_{10.3}$. We have recently attempted to investigate the prototype, *i.e.* $\text{Th}_2\text{Ni}_{17}$, but were unsuccessful in obtaining single crystals. The only other single-crystal refinement of a $\text{Th}_2\text{Ni}_{17}$ -like compound was carried out by Vold & Peterson (1961) on U_2Zn_{17} , using photographic intensities from a severely disordered crystal. Because of the disorder, they were prevented from carrying out the refinement in a manner which would give evidence on the fine features of the crystal structure. If the single refined structure is any guide to what we might expect for the rest of the compounds, then $\text{Th}_2\text{Ni}_{17}$ cannot be put into the list of Table 1 since it does not have the correct composition. Recent work with Pu-Zn (Cramer & Wood, 1967) indicates that the $\text{Th}_2\text{Ni}_{17}$ story is probably quite complicated. For the present, it is reasonable to maintain the A_2B_{17} designation for this phase so

long as one is aware that this composition is more grounded in history than in fact.

The sole surviving '2-17' compound of Table 1 is then $\text{Th}_2\text{Zn}_{17}$. Compounds of this structure type are rhombohedral with space group $R\bar{3}m$ and a hexagonal c/a ratio of 1.46 ± 0.01 (or rhombohedral angle $\alpha = 82.9 \pm 0.2^\circ$). In addition, these compounds frequently twin with domains of the obverse setting at times equal to those of the reverse setting; they are composed of elements which exhibit an r_A/r_B ratio of 1.12-1.46, and the B element has a hexagonal modification for its crystal structure when pure. The closely related ' $\text{Th}_2\text{Ni}_{17}$ ' structure has hexagonal symmetry with $c/a \sim 1.0$. Compounds with this structure are subject to stacking disorder along the c axis and quite possibly exhibit a composition AB_x with $x > 8.5$. These two structure types are often found in the same binary system, leading to considerable confusion.

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Refinement of the Crystal and Molecular Structure of Potassium Oxalate Monohydrate

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The structure of potassium oxalate monohydrate, $(\text{COOK})_2 \cdot \text{H}_2\text{O}$, has been refined by least-squares techniques based on three-dimensional X-ray data obtained at room temperature with Mo $K\alpha$ radiation. The material crystallizes with four formula units in space group $C2/c$ of the monoclinic system in a cell with dimensions $a=9.222$ (3), $b=6.197$ (2), $c=10.690$ (5) Å, $\beta=110.70$ (3)°. The conventional R value on F is 0.039 and the estimated standard deviations of atomic coordinates are of the order 0.001 Å. There is a hydrogen bond, 2.760 (2) Å in length, between one of the oxalate oxygen atoms and the water molecule; the other oxygen atom does not participate in hydrogen bonding. The carboxyl groups are not symmetric, the bond between carbon and the hydrogen bonded oxygen atom being 1.260 (2) Å and the other C–O bond being 1.247 (2) Å. The central carbon–carbon bond is long – 1.574 (2) Å – and residual electron density of 0.26 e.Å⁻³ is found in the center of this bond.

Introduction

The structure of potassium oxalate monohydrate, $(\text{COOK})_2 \cdot \text{H}_2\text{O}$, has been previously investigated by

three-dimensional X-ray (Hendricks, 1935; Pedersen, 1964) and two-dimensional neutron diffraction (Chidambaram, Sequeira & Sikka, 1964), and also by proton magnetic resonance techniques (McGrath & Paine,