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Refinement of a Th_2Ni_{17}-Type Structure: $CeMg_{1·03}$*

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The Th_2Ni_{17}-type structure found in the cerium–magnesium system has been studied by conventional single-crystal techniques. The space group is $P6_3/mmc$; unit cell constants are $a = 10·33$, $c = 10·25$ Å. The actual composition is $CeMg_{10·3}$; this is achieved mainly by substitution in the Th_2Ni_{17} structure of two magnesium atoms for one cerium atom a certain percentage of the time. The agreement of this work with earlier work on a barium–magnesium compound but disagreement with earlier work on uranium–zinc and plutonium–zinc compounds indicates that structures of the Th_2Ni_{17}-type may actually be two (or more) closely related structures.

Introduction

The Th_2Ni_{17} structure is a common A_2B_{17} structure which has so far been found for some of the combinations where A is one of the elements of the IIA, IIIB, IVB or VB groups and B is Be, Mg, Fe, Co, Ni or Zn. The prototype was studied by Florio, Baenziger & Rundle (1956), hereafter referred to as FBR, who reported a c/a ratio close to 1·0 and space group $P6_3/mmc$. They postulated a structure which they did not refine.

At about the same time, Goldish (1956) observed a presumably isomorphous phase in the barium–magnesium system. The structure proposed by Goldish differed from that proposed by FBR in being disordered; the composition also differed ($BaMg_{\sim 10·5}$). Later, Vold & Peterson (1961) reported a uranium–zinc compound which appeared isostructural but was found to have the space group $P6_322$. Their refinement was carried out by using only the reflections for which $h-k=3n$ since they found it necessary to assume a stacking disorder which would affect the other reflections.

There is a compound in the cerium–magnesium system which appears to be isostructural with Th_2Ni_{17} (Evdokimenko & Kripyakevich, 1963). When single crystals of this material were made available to us, we considered it worthwhile to carry out a structure refinement to try to clear up some of the questions concerning this structure. The details regarding the preparation of this material can be found in Wood & Cramer (1965).

Experimental

Single-crystal oscillation, Weissenberg and precession photos show that the space group, $P6_3/mmc$, observed for Th_2Ni_{17} is probably correct for the cerium–magnesium compound. Careful diffractometer scanning along hhl was done to exclude $P6_322$, which is the space group observed by Vold & Peterson (1961) for hexagonal U_2Zn_{17}. The extinction condition, hhl, $l \neq 2n$, is obeyed for the cerium–magnesium compound; this was not true for U_2Zn_{17}.

Lattice constants were obtained by a least-squares fit of powder data from a Cr $K\alpha$ ($\lambda = 2·2909$ Å) powder pattern. The pattern was not of a pure phase but exhibited a few weak lines of an as-yet-unidentified second phase. Cell constants are $a = 10·33 \pm 0·01$, $c = 10·25 \pm 0·01$ Å.

Intensities were recorded diffractometrically with zirconium-filtered Mo $K\alpha$ radiation ($\lambda = 0·7107$ Å). 193 independent reflections were recorded up to $2\theta \leq 40°$.

The structure proposed by FBR for Th_2Ni_{17} was used for a starting place. Atomic scattering factors were those for the neutral atoms as listed in *International Tables for X-ray Crystallography* (1962), and a weighting scheme appropriate for diffractometric data (Smith & Alexander, 1963) ($w = F_o^{1/4}, F_o < A; w = A^{5/4}F_o^{-1}, F_o > A$ with $A = 160$) was used. A refined version of the Th_2Ni_{17} structure gave a value of 12·7% for the conventional R index and temperature factors which varied from 0·3 to 3·4 Å^2. Since the temperature factor for Ce(1) (see Table 1) was 3·4 Å^2 and that of Ce(2) was only 0·7 Å^2, disorder was suspected. This was confirmed by a difference Fourier calculation. Peaks occur at $\pm 0,0,z$ with $z = 0·12$ and at $\pm \frac{2}{3},\frac{1}{3},\frac{1}{4}$. The evidence indicated that Ce(1) should be replaced by a pair of magnesium atoms a certain percentage of the time. To a considerably lesser degree, a pair of Mg(4) atoms was replaced by a cerium atom. Additional atoms Mg(5) and Ce(5) were therefore added. For the least-squares refinement, the occupancies of Ce(1) and Mg(4) were refined instead of their temperature factors; the latter were held constant to avoid parameter interaction and were set equal to 1·5 Å^2 on the basis of experience with Ce_5Mg_{42} (Johnson & Smith, 1967). The temperature factors of Mg(5) and Ce(3) were also held constant and the occupancies were determined from the occupancies of Ce(1) and Mg(4) respectively.

The agreement index of this disordered model is 5·3% for the 157 observed data (or 7·0% for all data). This is to be compared with 12·7% for the ordered model. The final parameters for the disordered model are given in Table 1. Observed and calculated structure factors are listed in Table 2.

It is easy to conceive other refinement schemes. For example it could be argued that the z parameters for

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Mg(4) and Mg(5) should be identical; or that Mg(2) and/or Mg(3) should be given additional freedom in the manner of the Goldish model (see discussion). It is not obvious that any useful purpose is served by their enumeration since they would only result in small changes in the parameters. Because of this, however, we feel it would be unwise to attach too much significance to the standard deviations given in Table 1.

Discussion

The composition of the crystal investigated is thought to be $CeMg_{10\cdot3}$ as determined by the results of the least-squares refinement. No chemical analysis was carried out because of the very small amount of material available. Although no attempt was made in the work of Wood & Cramer to investigate homogeneity range for this phase, it is conceivable that a range exists since it is structurally possible to accommodate an extended composition range with this model.

FBR suggested a way whereby it is possible to relate the $ThMn_{12}$, Th_2Ni_{17} and Th_2Zn_{17} structures to a $CaZn_5$-like subcell. Starting with an AB_5 ($CaZn_5$-like) lattice and replacing A atoms with pairs of B atoms aligned along the hexagonal axis it is possible to achieve ordered arrangements of various compositions. The $ThMn_{12}$ structure results from replacement of the A atom in two out of four subcells; Th_2Ni_{17} and Th_2Zn_{17} are two different arrangements which result by replacing A atoms in two out of six subcells. Other ordered as well as disordered arragements should be possible if the replacement scheme is more than just a coincidence. Thus the model which we propose for $CeMg_{10\cdot3}$ should not be viewed as complicated in any sense but rather follows as a logical consequence of the replacement scheme of FBR.

The coordination polyhedra of only two atoms, Ce(1) and Mg(3), are appreciably affected by the major disorder feature (substitution of two Mg(5) atoms for a Ce(1) atom). In both cases the change is to a higher coordination number with an arrangement already represented in the ordered structure. Ce(1) becomes like Ce(2); Mg(3) becomes like Mg(4).

Interatomic distances less than 4·5 Å are given in Table 3. Not included are short distances between atoms involved in the disorder which cannot both be present. The short Ce(3)–Mg(3) distance indicates that Mg(3) is probably displaced slightly when Ce(3) replaces Mg(4). Calculated standard deviations range from 0·003 to 0·021 Å.

The models of FBR and Goldish are compared with $CeMg_{10\cdot3}$ in Table 4. The FBR model with no disorder cannot be confirmed or disproved since there are no published data. The Goldish model differs primarily

Table 1. *Final parameters**

(e.s.d.'s in parentheses)

Atom	Wyckoff notation	$10^4 x$	$10^4 y$	$10^4 z$	B (Å^2)	Occupancy, %
Ce(1)	2(*b*)	0	0	$\frac{1}{4}$	1·5	69·5 (0·9)
Ce(2)	2(*c*)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	1·42 (0·02)	100
Ce(3)	2(*d*)	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{4}$	1·5	1·5 (0·6)
Mg(1)	6(*g*)	$\frac{1}{2}$	0	0	1·93 (0·23)	100
Mg(2)	12(*k*)	1667 (5)	3335	205 (5)	1·67 (0·13)	100
Mg(3)	12(*j*)	3593 (7)	321 (6)	$\frac{1}{4}$	1·76 (0·12)	100
Mg(4)	4(*f*)	$\frac{1}{3}$	$\frac{2}{3}$	8996 (10)	1·5	98·5 (0·6)
Mg(5)	4(*e*)	0	0	8882 (40)	1·5	30·5 (0·9)

* Temperature factors of Ce(1), Ce(3), Mg(4), and Mg(5) fixed at 1·5 Å^2. Occupancy of Ce(1) + Mg(5) = 100 %, and Ce(3) + Mg(4) = 100 %.

Table 2. *Observed and calculated structure factors*

h k ℓ	F_o	F_c	h k ℓ	F_o	F_c	h k ℓ	F_o	F_c	h k ℓ	F_o	F_c	h k ℓ	F_o	F_c	h k ℓ	F_o	F_c	h k ℓ	F_o	F_c
0 0 2	118	-110	3 0 4	145	142	6 0 4	199	195	2 1 9	64	-65	6 1 1	31	27	4 2 0	15	13	3 3 4	108	102
0 0 4	341	352	3 0 5	0	0	6 0 5	0	-2	3 1 0	11	2	6 1 2	12	-9	4 2 1	41	40	3 3 6	169	-172
0 0 6	134	-133	3 0 6	227	-225	6 0 6	75	-75	3 1 1	41	40	6 1 3	47	-44	4 2 2	15	-21	4 3 0	0	-9
0 0 8	228	228	3 0 7	0	0	6 0 7	0	2	3 1 2	10	-12	6 1 4	0	7	4 2 3	102	-100	4 3 1	14	-12
1 0 0	0	7	3 0 8	129	131	7 0 0	0	-14	3 1 3	65	-63	6 1 5	43	40	4 2 4	22	22	4 3 2	0	3
1 0 1	66	-63	3 0 9	0	0	7 0 1	9	-3	3 1 4	10	9	6 1 6	0	-3	4 2 5	22	20	4 3 3	29	31
1 0 2	18	-19	4 0 0	0	-9	7 0 2	0	8	3 1 5	58	56	7 1 0	87	80	4 2 6	9	-3	4 3 4	0	-2
1 0 3	93	89	4 0 1	9	-7	7 0 3	21	20	3 1 6	0	-3	7 1 1	0	2	4 2 7	60	-62	4 3 5	28	-29
1 0 4	13	14	4 0 2	0	0	7 0 4	0	-7	3 1 7	0	-7	7 1 2	101	-99	5 2 0	81	83	4 3 6	10	5
1 0 5	78	-75	4 0 3	84	81	7 0 5	22	-20	3 1 8	0	3	7 1 3	10	-2	5 2 1	0	1	5 3 0	9	10
1 0 6	0	-7	4 0 4	8	5	8 0 0	0	3	4 1 0	100	98	7 1 4	43	37	5 2 2	113	-108	5 3 1	63	64
1 0 7	12	15	4 0 5	8	9	8 0 1	43	46	4 1 1	4	11	8 1 0	25	16	5 2 3	9	-1	5 3 2	9	-14
1 0 8	9	5	4 0 6	13	14	8 0 2	0	-10	4 1 2	135	-130	8 1 1	48	-49	5 2 4	26	31	5 3 3	73	-76
1 0 9	57	-60	4 0 7	44	47	8 0 3	80	-83	4 1 3	0	-1	2 2 0	286	302	5 2 5	0	1	5 3 4	10	13
2 0 0	12	18	4 0 8	10	11	1 1 0	120	115	4 1 4	33	31	2 2 2	51	44	5 2 6	98	-102	5 3 5	63	67
2 0 1	77	76	5 0 0	0	14	1 1 2	161	-159	4 1 5	0	0	2 2 4	177	175	6 2 0	13	13	6 3 0	101	104
2 0 2	21	-26	5 0 1	77	81	1 1 4	27	24	4 1 6	121	-121	2 2 6	17	-21	6 2 1	50	-54	6 3 1	0	-2
2 0 3	160	-158	5 0 2	22	-20	1 1 6	135	-139	4 1 7	9	0	2 2 8	122	126	6 2 2	13	-19	6 3 2	124	-120
2 0 4	32	29	5 0 3	94	-98	1 1 8	56	62	4 1 8	54	60	3 2 0	18	17	6 2 3	97	96	6 3 3	0	2
2 0 5	42	38	5 0 4	8	17	2 1 0	17	17	5 1 0	29	20	3 2 1	82	-83	6 2 4	20	19	4 4 0	212	205
2 0 6	0	-1	5 0 5	85	85	2 1 1	77	-76	5 1 1	67	-67	3 2 2	20	-25	6 2 5	38	-35	4 4 2	13	2
2 0 7	90	-92	5 0 6	9	-10	2 1 2	25	-26	5 1 2	23	-25	3 2 3	97	101	7 2 0	20	12	4 4 4	128	130
2 0 8	21	27	5 0 7	36	-36	2 1 3	101	97	5 1 3	84	83	3 2 4	19	21	7 2 1	34	35	5 4 0	19	17
2 0 9	28	22	5 0 8	0	9	2 1 4	15	21	5 1 4	16	22	3 2 5	87	-88	7 2 2	17	-15	5 4 1	47	-47
3 0 0	243	250	6 0 0	286	291	2 1 5	84	-84	5 1 5	76	-73	3 2 6	9	-13	7 2 3	45	-46	5 4 2	17	-21
3 0 1	6	-1	6 0 1	0	-3	2 1 6	8	-12	5 1 6	13	-15	3 2 7	36	35	3 3 0	181	177	5 4 3	61	58
3 0 2	277	-280	6 0 2	43	-47	2 1 7	27	25	5 1 7	33	30	3 2 8	0	11	3 3 2	202	-203	5 4 4	14	19
3 0 3	7	1	6 0 3	0	3	2 1 8	0	10	6 1 0	9	3									

in the population parameters as well as in the fact that Mg(2) and Mg(3) have been given additional freedom.

The parameters of Table 1 were used to calculate an agreement value for the $h0l$ data obtained by Goldish for the barium–magnesium compound. Refining only the scale factor yields a value of 6·0% which is to be compared to his value of 10·1% for the same data. When all adjustable parameters are allowed to vary, the population parameters for Ba(1) and Ba(3) become 65% and 0·2% respectively resulting in a composition of $\mathrm{BaMg}_{10\cdot 7}$ although the actual ratio is a sensitive function of which and how many reflections are included in the refinement. In any event, the indication was clear that the $\mathrm{CeMg}_{10\cdot 3}$ model is a better description for the data of Goldish than the one he proposed although the structural difference is not large.

Table 3. *Interatomic distances in* $\mathrm{CeMg}_{10\cdot 3}$

	Ligancy	Distance	
Ce(1)	6 Mg(3)	3·557 Å	
	[2 Mg(5)	3·709]	
	6 Mg(2)	3·799	
	6 Mg(2)	4·073	
Ce(2)	2 Mg(4)	3·592	
	6 Mg(3)	3·649	
	6 Mg(2)	3·797	
	6 Mg(1)	3·932	
Ce(3)	6 Mg(3)	3·14	
	6 Mg(1)	3·932	
	6 Mg(2)	4·071	
Mg(1)	4 Mg(2)	2·989	
	4 Mg(3)	3·045	
	2 Mg(4)	3·155	or 2 Ce(3) 3·932
	2 Ce(2)	3·932	
Mg(2)	2 Mg(1)	2·989	
	2 Mg(2)	3·013	
	2 Mg(3)	3·102	
	2 Mg(3)	3·172	
	1 Mg(4)	3·228	or 1 Ce(3) 4·071
	1 Ce(2)	3·797	
	1 Ce(1)	3·799	or 1 Mg(5) 3·127
	1 Ce(1)	4·073	1 Mg(5) 3·277
Mg(3)	2 Mg(1)	3·045	
	1 Mg(3)	3·047	
	2 Mg(2)	3·102	
	2 Mg(2)	3·172	
	1 Mg(3)	3·239	
	2 Mg(4)	3·498	or 1 Ce(3) 3·14
	1 Ce(1)	3·557	or 2 Mg(5) 3·829
	1 Ce(2)	3·649	
	1 Mg(3)	4·043	
Mg(4)	1 Mg(4)	3·067	
	3 Mg(1)	3·155	
	3 Mg(2)	3·228	
	6 Mg(3)	3·498	
	1 Ce(2)	3·592	
Mg(5)	1 Mg(5)	2·832	
	3 Mg(2)	3·127	
	3 Mg(2)	3·277	
	1 Ce(1)	3·709	
	6 Mg(3)	3·829	

On the other hand, for the same set of reflections, but using the data of Vold & Peterson for $\mathrm{U_2Zn_{17}}$, the corresponding value is 19·8%. For all observed data, the R index is 18·5% and for all data, a value of 27·4% is obtained. Recent work in this laboratory with a plutonium-zinc compound of similar composition gives equally poor results with this model (Cramer & Wood, 1967). The results of these refinements, taken together with the fact that two different space groups are involved, indicate that the so-called $\mathrm{Th_2Ni_{17}}$ structure may actually be of two (or more) types upon close inspection. Although the composition of the material for which we have the most knowledge differs considerably from the 2:17 composition and the true structure of $\mathrm{Th_2Ni_{17}}$ itself must be regarded as unknown in fine detail, there does not at present seem to be any merit in changing the long established habit of saying that these have a $\mathrm{Th_2Ni_{17}}$-type structure so long as one understands that this is a simplification of the real picture. As more is discovered about these phases, a further differentiation may someday become useful.

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Table 4. *Comparison of structures*

Occupancies given in percentages

Florio *et al.*. (1956)	This work		Goldish (1956)		Comments on Goldish structure
Th	Ce(1) Mg(5)	70 % 30	Ba Mg	55 % 45	Same sites, occupancies differ.
Th	Ce(2)	100	Ba	100	
Ni	Mg(1)	100	Mg	100	
Ni	Mg(2)	100	Mg Mg	50 50	Two 12-fold positions with slightly different values of z.
Ni	Mg(3)	100	Mg Mg	25 70	Two 12-fold positions with slightly different values cf x and y. This site not fully occupied.
Ni	Mg(4) Ce(3)	98·5 1·5	Mg Ba	90 10	Same sites, occupancies differ.