Acta Cryst. (1967). **22**, 551

$D8_8$ Phases of the Rare Earth Elements with Tin and Lead

BY W. JEITSCHKO AND E. PARTHÉ

School of Metallurgical Engineering and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, U.S.A.

(*Received* 6 *April* 1966)

The crystal structures of twelve stannides: La_5Sn_3, Ce_5Sn_3, Pr_5Sn_3, Nd_5Sn_3, Sm_5Sn_3, Gd_5Sn_3, Tb_5Sn_3, Dy_5Sn_3, Ho_5Sn_3, Er_5Sn_3, Tm_5Sn_3, Lu_5Sn_3 and ten plumbides: Pr_5Pb_3, Nd_5Pb_3, Sm_5Pb_3, Gd_5Pb_3, Tb_5Pb_3, Dy_5Pb_3, Ho_5Pb_3, Er_5Pb_3, Tm_5Pb_3 and Lu_5Pb_3 were determined to be of the $D8_8$ type. A plot of cube root of the molar volume *versus* ionic radius of the rare earth elements indicates that their valence electron contribution is the same in these compounds but differs from the electron contribution of Yb in Yb_5Pb_3.

Introduction

The extensive study of different transition metal alloys during the last decade has shown that the $D8_8$ structure type* occurs in many binary and ternary systems. The total number of known $D8_8$ phases where the transition metal component varies from the third to the eighth group and the other component consists of elements of the Al, Si and P groups is now more than fifty. Most of the known compounds contain elements of the Si group.

The present study was undertaken to find out firstly, whether this structure type occurs also with the stannides and plumbides of the rare earth elements and secondly, whether the electronic contribution of the different rare earth elements within the isotypic series is the same or not.

In an earlier publication (Parthé, 1967) it has been shown that the alloying behaviour of the various rare earth elements with one particular alloying partner may vary from one element to the next to a considerable extent. These variations might seem surprising as the outer electron configuration of the rare earth elements is nearly the same. However, sufficient experimental data are available now to indicate that ideal alloying behaviour without deviations for certain rare earth elements is rather an exception. It is well known that the rare earth elements themselves show marked deviations in melting point, boiling point, electrical resistivity and other physical properties.

Sample preparation

The rare earth metals were obtained with a stated purity of 99·9 wt.% from Bernard Ring, Inc., New York, N.Y. and Nuclear Corporation of America, Phoenix, Ariz. The Baker Chemical Co., Phillipsburg, N.J. provided the tin with a purity of 99·9 wt.%, and the lead (L-28 ACS certified) came from Fisher Scientific Company, Fair Lawn, N.J. An independent oxygen determination showed that the lead contained 15 ppm and the tin 105 ppm oxygen.

Compositions involving only elements with high boiling points (La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Lu, Sn and Pb) have been prepared by arc melting the components under a purified argon atmosphere. Each button was remelted three times to assure homogeneity. The weight losses during arc melting were checked by weighing the samples before and after the melting process and amounted to about 1 wt.% for tin compounds and about 2 wt.% for lead compounds, which can be explained by the lower boiling point for lead. Efforts were made to take care of these losses by adjusting the starting compositions.

Compounds involving elements with low boiling points (Sm, Tm) have been prepared by sintering powder mixtures in evacuated quartz tubes at 700°C for one month. Great care was taken to avoid any contamination of the material by performing all operations such as filing the rare earth metals, weighing and mixing in a dry box filled with argon gas free of oxygen, nitrogen and water vapor. It was found necessary to raise the temperature of the furnace slowly (700°C is reached after two weeks). If not, the mixture reacts violently, dispersing the sample over the whole interior of the quartz tube and resulting in an improper homogenization of the sample. However, the evaluation of powder patterns of samples which had not been dispersed showed that even after extended annealing periods the samples were still not yet in perfect equilibrium. Notwithstanding, the annealing temperature was purposely not raised as this could lead to a side reaction of the sample with the quartz tube. Well-crystallized samples of Sm and Tm compounds were prepared in the arc melting furnace using very low arc voltages.

The oxygen content of selected samples was determined by fusion extraction technique and amounted to 0·25 at.% for Ho_5Pb_3, 0·18 at.% for Nd_5Sn_3, 0·16 at.% for Er_5Sn_3 and 0·08 at.% for Nd_5Pb_3. Selected alloys were analyzed for nitrogen; the N content in all cases was below 250 ppm. Since all the samples react

---

* Notation after *Strukturbericht*.

with the moisture of the air, it was absolutely necessary to protect the samples during the grinding and the diffraction experiment. The ground samples were placed in glass capillaries (0·2–0·3 mm diameter) filled with ligroin which was dried with solid sodium, and were X-rayed in Debye–Scherrer cameras (114·6 mm diameter, Cr $K\alpha$ radiation) using the asymmetric film placement.

The structure of Ho_5Sn_3 and Ho_5Pb_3

The powder pattern of Ho_5Sn_3 was indexed on the basis of a hexagonal unit cell with $a=8{\cdot}847$, $c=6{\cdot}458$, and $c/a=0{\cdot}7300$. Assuming two formula units Ho_5Sn_3 per unit cell the X-ray density was calculated to be 8·9 g.cm^{-3}. The extinctions for $h0hl$ with $l=2n+1$ lead to possible space groups $P6_3/mcm$ (D_{6h}^3), $P\bar{6}c2$ (D_{3h}^2), $P6_3cm$ (C_{6v}^3), $P\bar{3}c1$ (D_{3d}^4) and $P3c1$ (C_{3v}^5). From the close resemblance of the Ho_5Sn_3 pattern to the pattern for Y_5Ge_3 (Parthé, 1960) it was concluded that the compound crystallizes with the $D8_8$ structure type. For the first trial, space group $P6_3/mcm$ (D_{6h}^3) was chosen and 4 Ho atoms were placed in position $4(d)$, 6 Ho in $6(g)_{\rm I}=0{\cdot}24$ and 6 Sn in $6(g)_{\rm II}$ with $x_{\rm II}=0{\cdot}606$. The rather good agreement between observed and calculated intensities gave proof that Ho_5Sn_3 crystallizes with the $D8_8$ structure type. For this and subsequent intensity calculations we used a computer program by Jeitschko & Parthé (1966).

The refinement of the parameters was carried out with the trial and error method. For this purpose the line intensities of the powder films were estimated by comparison with an intensity strip and corrected for absorption (Bradley, 1935). Intensity calculations for systematically varied combinations of the two parameters were performed and the quotients of calculated intensities of neighbouring lines were compared with those of observed intensities. By this method one obtains for each pair of diffraction lines a series of possible parameter combinations. However, there is only one combination of the two parameters which gives correct intensity ratios for all diffraction line pairs. A least-squares refinement was not thought very useful as there are few lines on the powder films which are not overlapped.

The final refined parameters for Ho_5Sn_3 are:

$$x_{\rm I}\,({\rm Ho}) = 0{\cdot}234 \pm 0{\cdot}003$$
$$x_{\rm II}\,({\rm Sn}) = 0{\cdot}605 \pm 0{\cdot}005\,.$$

The agreement between observed and calculated intensities can be studied in the left hand part of Table 1.

A similar result was obtained for the compound Ho_5Pb_3 which crystallizes with a hexagonal unit cell with $a=8{\cdot}915$ Å, $c=6{\cdot}541$ Å and $c/a=0{\cdot}7336$. The re-

Table 1. *Calculated and observed d values and intensities for* Ho_5Sn_3 *and* Ho_5Pb_3 *with* $D8_8$ *structure* (Cr $K\alpha$ *radiation*)

Ho_5Sn_3 $a=8{\cdot}847$, $c=6{\cdot}458$ Å					Ho_5Pb_3 $a=8{\cdot}915$, $c=6{\cdot}541$ Å				
hkl	d_c	d_o	I_c	I_o	hkl	d_c	d_o	I_c	I_o
100	7·662	—	0·20	—	100	7·721	—	0·79	—
110	4·424	—	0·06	<0·3	110	4·458	—	0·17	<0·3
200	3·831	3·80	0·54	0·5	200	3·860	—	0·01	<0·3
111	3·650	—	0·04	<0·3	111	3·684	3·65	0·70	0·6
002	3·229	2·21	1·60	1·5	002	3·271	3·25	2·44	2·5
102	2·975	2·96	2·35	2·5	102	3·012	3·00	1·09	0·9
210	2·896	2·88	3·59	4	210	2·918	2·90	2·54	2·5
211	2·642	2·63	10·00	10	211	2·665	2·65	10·00	10
112	2·608	2·59	7·14	7	112	2·637	2·62	7·19	7
300	2·554	2·54	3·29	3	300	2·574	2·56	3·85	4
202	2·469	2·459	0·55	0·5	202	2·496	2·482	1·04	1·1
220	2·212	—	0·07	<0·2	220	2·229	—	0·02	<0·2
212	2·156	—	0·05	<0·2	212	2·177	—	0·04	<0·2
310	2·125	2·117	0·39	0·4	310	2·141	2·131	0·59	0·6
221	2·092	2·085	0·88	1·0	221	2·110	2·103	1·08	1·0
311	2·019	2·011	0·49	0·6	311	2·035	2·027	1·51	1·7
302	2·003	—	0·02	<0·2	302	2·023	—	0·11	<0·2
113	1·936	—	0·01	<0·2	113	1·960	—	0·12	<0·2
400	1·915	1·907	0·17	0·2	400	1·930	—	0·06	<0·2
222	1·825	1·819	1·91	2·0	222	1·842	1·835	1·52	1·7
312	1·775	1·770	0·21	0·2	312	1·792	—	0·01	<0·2
320	1·758	—	0·06	<0·2	320	1·772	—	0·00	<0·2
213	1·728	1·724	2·86	3	213	1·747	1·742	2·90	3
321	1·696	1·692	0·85	0·8	321	1·710	1·706	0·73	0·7
410	1·672	1·669	1·28	1·2	410	1·685	1·682	0·62	0·6
402	1·647	1·644	1·49	1·4	402	1·662	1·658	0·82	0·8
411	1·619	—	0·06	<0·2	004	1·635	1·632	1·17	1·3
004	1·615	1·612	1·13	1·2	411	1·632	—	0·08	<0·2
104	1·580	—	0·01	<0·2	104	1·600	—	0·03	<0·2
322	1·544	1·541	0·47	0·9	223	1·559	1·556	0·51	1·2
223	1·543		0·42		322	1·558		0·82	
500	1·532	1·530	0·59	0·5	500	1·544	1·541	0·83	0·8

Table 1 (*cont.*)

Ho_5Sn_3
$a=8{\cdot}847$, $c=6{\cdot}458$ Å

hkl	d_c	d_o	I_c	I_o
114	1·517	1·510	0·01	0·3
313	1·512		0·25	
204	1·488	1·483	0·09	0·4
412	1·485		0·23	
330	1·475	—	0·03	< 0·2
420	1·448	1·446	0·95	1·0
331	1·438	1·436	1·27	1·3
421	1·413	1·408	0·15	1·6
214	1·410		1·24	
502	1·3844	1·383	3·15	3
510	1·3761	1·375	0·31	0·3
304	1·3647	1·363	1·68	2·5
323	1·3615		0·72	
511	1·3459	1·340	0·57	2·2
332	1·3413		1·42	
422	1·3212	1·3200	0·18	0·2
413	1·3204		0·06	
224	1·3040	—	0·07	< 0·2
314	1·2855	1·2845	0·40	0·5
600	1·2770	—	0·09	< 0·2
512	1·2659	—	0·05	< 0·2
430	1·2596	1·2590	0·26	0·2
115	1·2398	—	0·01	< 0·2
431	1·2363	1·2355	0·89	1·3
404	1·2345		0·30	
520	1·2269	1·2265	0·59	0·6
333	1·2165	1·2162	2·07	2·2
521	1·2053	1·2050	1·58	1·9
423	1·2014		0·27	
324	1·1890	1·1872	0·20	2·5
602	1·1875		2·13	
215	1·1796	1·1793	5·21	5
432	1·1735	1·1732	0·30	0·2
610	1·1684	1·1682	3·82	4
414	1·1614	1·160	7·45	9
513	1·1594		1·96	

$R=0{\cdot}08$

Ho_5Pb_3
$a=8{\cdot}915$, $c=6.541$ Å

hkl	d_c	d_o	I_c	I_o
114	1·535	—	0·02	< 0·2
313	1·528	1·526	0·78	0·9
204	1·506	—	0·00	< 0·2
412	1·498	1·495	0·35	0·3
330	1·486	—	0·03	< 0·2
420	1·459	1·457	1·03	0·9
331	1·449	1·447	1·12	1·1
214	1·427	1·423	0·86	1·6
421	1·424		0·76	
502	1·3963	1·394	3·42	4
510	1·3867	1·385	0·34	0·3
304	1·3802	1·378	1·95	2·3
323	1·3748		0·61	
511	1·3565	1·353	0·61	1·5
332	1·3528		0·84	
413	1·3331	1·3316	0·08	0·6
422	1·3325		0·44	
224	1·3184	—	0·02	< 0·2
314	1·2996	1·2986	0·60	0·7
600	1·2868	—	0·03	< 0·2
512	1·2767	—	0·00	< 0·2
430	1·2693	—	0·18	< 0 2
115	1·2553	—	0·10	< 0·2
404	1·2477	1·2456	0·10	1·3
431	1·2460		1·12	
520	1·2363	1·2359	0·72	0·8
333	1·2278	1·2275	1·71	1·6
521	1·2148	1·2135	1·23	2·5
423	1·2126		1·28	
324	1·2015	—	0·01	< 0·2
602	1·1974	1·1970	1·57	6
215	1·1937	1·1934	4·41	
432	1·1833	—	0·17	< 0·2
610	1·1774	1·1772	3·27	9
414	1·1734		2·67	
513	1·1701	1·6996	1·61	

$R=0{\cdot}10$

Definition of R: $R=\dfrac{\Sigma\,/I_o-I_c/}{\Sigma\,I_o}$

fined adjustable parameters for Ho_5Pb_3 were found to be:

$$x_{\text{I}}\ (\text{Ho}) = 0{\cdot}238 \pm 0{\cdot}004$$

$$x_{\text{II}}\ (\text{Pb}) = 0{\cdot}606 \pm 0{\cdot}002\ .$$

The *hkl*, *d* and intensity values for Ho_5Pb_3 are shown in the right hand part of Table 1.

Structures of other rare earth stannides and plumbides

The powder patterns of eleven other rare earth stannides: La_5Sn_3, Ce_5Sn_3, Pr_5Sn_3, Nd_5Sn_3, Sm_5Sn_3, Gd_5Sn_3, Tb_5Sn_3, Dy_5Sn_3, Er_5Sn_3, Tm_5Sn_3, Lu_5Sn_3 and nine other rare earth plumbides: Pr_5Pb_3, Nd_5Pb_3, Sm_5Pb_3, Gd_5Pb_3, Tb_5Pb_3, Dy_5Pb_3, Er_5Pb_3, Tm_5Pb_3, Lu_5Pb_3 were similar in appearance to the patterns of Ho_5Sn_3 and Ho_5Pb_3. All the compounds are isostructural and crystallize with the $D8_8$ structure type. Their lattice constants and axial ratios are given in Table 2 (λCr $K\alpha_1 = 2{\cdot}28962$ Å).

The lattice constants were obtained by an extrapolating technique first described by Wilson & Lipson (1941) and in more detail in *International Tables for X-ray Crystallography* (1959). The extrapolation was essential here as all specimens were X-rayed in glass capillaries, resulting in a relatively large absorption shift of the diffraction lines.

Efforts were made to prepare the corresponding tin and lead compounds with Eu and Yb, but without success. After termination of our experiments we received notice of an extensive phase diagram study of the binary systems Yb–Pb and Eu–Pb by McMasters & Gschneidner (1966). In both systems a compound with composition R_5Pb_3 is formed peritectically. In the case of Yb_5Pb_3 the compound was found to crystallize with the $D8_8$ structure type with $a=9{\cdot}32_5$ and $c=6{\cdot}92_9$ Å. Our failure to prepare Eu_5Pb_3 and Yb_5Pb_3 can obviously be traced to our preparation technique as it is nearly impossible to synthesize a peritectic phase by arc melting.

It is probable that all these phases have a certain range of homogeneity within which the lattice constants may change. This has been definitely proven in the case of La_5Pb_3, in which the lattice constants vary from $a=9{\cdot}528$, $c=6{\cdot}993$ Å for $La_{0\cdot625}Pb_{0\cdot375}$ to $a=9{\cdot}528$, $c=6{\cdot}955$ Å for $La_{0\cdot68}Pb_{0\cdot32}$. Similar results have been obtained for Er_5Sn_3 and Gd_5Pb_3. In all cases the axial ratio is smaller on the rare-earth-rich side of the homogeneity range. The chemical compositions of these samples were controlled by measuring the weight losses during arc melting just as described above for the stoichiometrically composed phases. No attempts have been made to find out whether this homogeneity range is caused by substitution, the formation of vacancies, or the filling of interstitial sites.

Table 2. *Lattice constants of rare earth stannides and plumbides with $D8_8$ structure*

	Stannides					Plumbides			
	a (Å)	*c* (Å)	*c/a*			*a* (Å)	*c* (Å)	*c/a*	
La_5Sn_3	9·435 (5)	6·961 (5)	0·7378 (5)	(*a*)	La_5Pb_3	9·528 (5)	6·993 (3)	0·7339 (6)	(*c*)
	9·416	6·926		(*b*)					
Ce_5Sn_3	9·328 (5)	6·788 (5)	0·7277 (5)	(*a*)	Ce_5Pb_3	9·473 (4)	6·825 (2)	0·7204 (4)	(*c*)
Pr_5Sn_3	9·281 (5)	6·779 (5)	0·7304 (5)	(*a*)	Pr_5Pb_3	9·354 (5)	6·827 (5)	0·7298 (6)	(*a*)
	9·285	6·752		(*b*)		9·337	6·814		(*d*)
Nd_5Sn_3	9·204 (5)	6·725 (4)	0·7306 (5)	(*a*)	Nd_5Pb_3	9·291 (5)	6·785 (5)	0·7303 (6)	(*a*)
	9·200	6·717		(*b*)		9·264	6·770		(*d*)
Sm_5Sn_3	9·106 (4)	6·651 (4)	0·7304 (4)	(*a*)	Sm_5Pb_3	9·170 (3)	6·699 (3)	0·7305 (4)	(*a*)
	9·089	6·610		(*b*)		9·163	6·687		(*d*)
Gd_5Sn_3	9·032 (3)	6·595 (4)	0·7302 (4)	(*a*)	Gd_5Pb_3	9·093 (4)	6·651 (5)	0·7314 (5)	(*a*)
	9·020	6·568		(*b*)		9·077	6·637		(*d*)
Tb_5Sn_3	8·951 (3)	6·535 (4)	0·7301 (4)	(*a*)	Tb_5Pb_3	9·026 (3)	6·607 (4)	0·7320 (4)	(*a*)
	8·947	6·535		(*b*)		9·019	6·596		(*d*)
Dy_5Sn_3	8·884 (4)	6·484 (4)	0·7299 (4)	(*a*)	Dy_5Pb_3	8·964 (3)	6·568 (4)	0·7327 (4)	(*a*)
	8·889	6·491		(*b*)		8·957	6·546		(*d*)
Ho_5Sn_3	8·847 (3)	6·458 (4)	0·7300 (3)	(*a*)	Ho_5Pb_3	8·915 (3)	6·541 (4)	0·7336 (4)	(*a*)
	8·848	6·461		(*b*)		8·922	6·532		(*d*)
Er_5Sn_3	8·810 (4)	6·442 (4)	0·7312 (4)	(*a*)	Er_5Pb_3	8·870 (3)	6·508 (4)	0·7337 (4)	(*a*)
	8·799	6·442		(*b*)		8·867	6·504		(*d*)
Tm_5Sn_3	8·773 (3)	6·406 (3)	0·7302 (3)	(*a*)	Tm_5Pb_3	8·842 (3)	6·491 (3)	0·7341 (4)	(*a*)
	8·776	6·411		(*b*)		8·832	6·487		(*d*)
					Yb_5Pb_3	$9{\cdot}32_5$	$6{\cdot}92_9$	0·734	(*e*)
Lu_5Sn_3	8·700 (3)	6·355 (4)	0·7305 (4)	(*a*)	Lu_5Pb_3	8·764 (2)	6·419 (2)	0·7325 (2)	(*a*)
	8·679	6·349		(*b*)		8·765	6·413		(*d*)

(*a*) This work.
(*b*) Palenzona & Merlo (1966).
(*c*) Jeitschko & Parthé (1965).
(*d*) Palenzona & Fornasini (1966).
(*e*) McMasters & Gschneidner (1966).

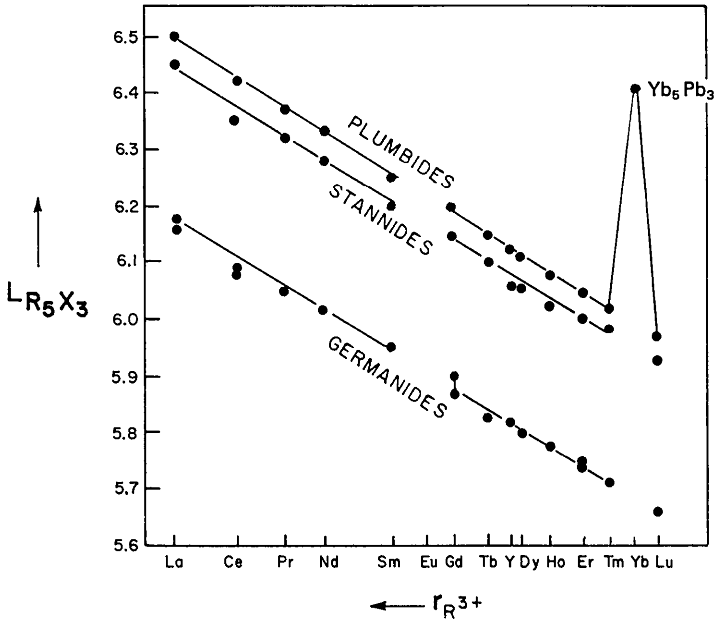

Fig. 1. $L_{R_5X_3}$ *versus* $r_{R^{3+}}$ graphs for rare earth germanides, stannides and plumbides with $D8_8$ structure (trivalent rare earth radii by Templeton & Dauben, 1954).

After completion of our manuscript we were informed through a private communication that a research group in Italy recently investigated the same rare earth compounds. For the sake of completeness we have extended Table 2 to include the results of Palenzona & Merlo (1966) and Palenzona & Fornasini (1966). Their results are essentially identical with ours.

Discussion of results

With our present knowledge it seems impossible to predict *a priori* when the $D8_8$ structure will be formed. However, one can investigate whether or not the valence electron contribution of the rare earth elements in these compounds varies from element to element. It has been shown in an earlier paper (Parthé, 1967) that such information can be obtained from a graph such as that shown in Fig. 1.

The ordinate $L_{R_5X_3}$ is the cube root of the volume of one formula unit R_5X_3. As each unit cell of the $D8_8$ structure contains two formula units R_5X_3 the value of $L_{R_5X_3}$ can be calculated by the formula:

$$L_{R_5X_3} = \left[\frac{(a^2/2)\sqrt{3}c}{2}\right]^{1/3}$$

where a and c are the hexagonal lattice constants. $L_{R_5X_3}$ is thus the length of the 'formula unit cube'. It was found convenient to define L this way to allow the comparison of different structure types having different numbers of formula units per unit cell. On the abscissa of Fig. 1 are plotted the trivalent ionic radii of the rare earth elements. The use of the ionic radii does not necessarily indicate that there exists a considerable amount of ionic bonding in these compounds; rather the ionic radii serve as a convenient measure for the size of the rare earth elements in one particular well-defined state. A plot of the $L_{R_5X_3}$ values *versus* r_{R3+} should give a straight line without deviation provided all rare earth elements make the same valence electron contribution.

In Fig. 1 are plotted the data for all known rare earth germanides, stannides and plumbides of composition R_5X_3. The results for the germanides have been calculated from lattice constant values published by Gladishevskij (1964). With the exception of Yb_5Pb_3 all data fall approximately on three straight lines, one for germanides, one for stannides and one for plumbides, indicating the same electronic state of the different rare earth elements in the $D8_8$ structure. Irregularities occur with Eu and Yb. It seems to be difficult or even impossible to form Eu and Yb compounds of composition R_5X_3. If they exist they form peritectically or are stable only in a limited temperature range as for example Yb_5Sb_3 (Bodner & Steinfink, 1965). The extra large L value of Yb_5Pb_3 indicates that Yb contributes fewer electrons than the other rare earth atoms in the corresponding plumbides with $D8_8$ structure. The scatter of the data points makes it difficult to recognize small deviations, but it seems that the plot for Ce_5Ge_3 is slightly below the line, Ce_5Sn_3 to a lesser degree, while Ce_5Pb_3 is on the line. The very small deviation for the Ce compounds disappears if the X partner is heavy. Similar observations have been made for the deviations of the equiatomic Ce compounds with N, P, As, Sb and Bi, where again the deviation is well pronounced in the nitride, but disappears with the bismuthide (Parthé, 1967).

This study is a contribution from the Laboratory for Research on the Structure of Matter, University of Pennsylvania, supported by the Advanced Research Projects Agency, Office of the Secretary of Defense. The research was sponsored by the U.S. Public Health Service under USPH grant DE-02135. The financial assistance of the sponsoring agency is gratefully acknowledged.

References

BODNER, R. E. & STEINFINK, H. (1965). Paper presented at Fifth Rare Earth Research Conference, Ames, Iowa.

BRADLEY, A. J. (1935). *Proc. Phys. Soc.* **47**, 879.

GLADISHEVSKIJ, E. I. (1964). *Zh. Strukturnoi Khim.* **5**, 919.

GVILDYS, J. (1965). Argonne National Laboratory Program Library B106.

International Tables for X-ray Crystallography (1959). Vol. II, p. 225. Birmingham: Kynoch Press.

JEITSCHKO, W. & PARTHÉ, E. (1965). *Acta Cryst.* **19**, 275.

JEITSCHKO, W. & PARTHÉ, E. (1966). *A Fortran IV Program for the Intensity Calculation of Powder Patterns.* Report of the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pa., U.S.A.

MCMASTERS, O. D. & GSCHNEIDNER, K. A. (1966). Private communication and internal report of Ames Laboratory, Ames, Iowa.

PALENZONA, A. & FORNASINI, M. L. (1966). *Atti. Acc. Lincei*, **40**, 1040.

PALENZONA, A. & MERLO, F. (1966). *Atti Acc. Lincei.* **40**, 617.

PARTHÉ, E. (1960). *Acta Cyst.* **13**, 868.

PARTHÉ, E. (1967). In *Bull. Soc. chim. Fr.* In the press.

TEMPLETON, D. H. & DAUBEN, C. H. (1954). *J. Amer. Chem. Soc.* **76**, 5237.

WILSON, A. J. C. & LIPSON, H. (1941). *Proc. Phys. Soc.* **53**, 245.