

Phase Relationships in the Systems SmH_2 - SmH_3 and SmD_2 - SmD_3

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The phase relationships in the system SmH_2 - SmH_3 have been reinvestigated. Contrary to the literature, the phase widths of SmH_2 and SmH_3 are significantly less extended: $\text{SmH}_{1.95-2.30}$ (cubic, fluorite-related) and $\text{SmH}_{2.82-2.90}$ (hexagonal, tysonite-related). In addition, a new intermediate phase of the composition Sm_3H_7 has been found. This tetragonally distorted fluorite-related phase is similar to the superstructure phase Sm_3F_7 with regard to the crystal data of the basis structure and the anion/cation ratio. Systematic phase investigations were carried out also in the system SmD_2 - SmD_3 , leading to analogous results. The present work shows that the phase relationships in rare-earth hydrides and deuterides are closely related to those of the systems SmF_2 - SmF_3 and EuF_2 - EuF_3 .

1. Introduction

It is well known that many structural analogies exist between hydrides and fluorides (1). This is of course not unexpected if one considers the similarity of the ionic radii of the hydride and fluoride anion (2). The closest structural resemblance is observed in the case of the alkalis, the alkaline earths, and aluminum. Surprisingly, the hydrides and fluorides of the lanthanides are less closely related, though the electronegativities and ionic radii of the 4f-elements are similar to those of the corresponding main-group elements. The most significant differences exist between the fluorides and hydrides of Eu and Yb. The difluorides crystallize in a cubic structure ($Fm\bar{3}m$) and the di-

hydrides are orthorhombic ($Pnma$). There exist trifluorides, but no trihydrides. The other rare-earth elements form trifluorides and trihydrides, but no difluorides to be compared with the dihydrides, samarium being the only exception. All the constituent phases exist and the systems SmH_2 - SmH_3 and SmF_2 - SmF_3 can be compared over the full range of composition. These systems are of course not entirely analogous, since samarium has different valence states in $\text{Sm}^{\text{II}}\text{F}_2$ and $\text{Sm}^{\text{III}}\text{H}_2(e)$ (3) and SmF_3 crystallizes in an orthorhombic structure at room temperature and SmH_3 is hexagonal (trigonal) (3, 4). Nevertheless, both systems show some similarities if one compares corresponding investigations within the SmH_2 - SmH_3 (5, 7) and SmF_2 - SmF_3 (8-12) systems. The cubic fluorite-related solid solutions $\text{SmH}_{2+\delta}$ and $\text{SmF}_{2+\delta}$ have very extended phase widths as well as the hexagonal tysonite-related phases $\text{SmH}_{3-\delta}$ and $\text{SmF}_{3-\delta}$. Such ex-

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tended phases usually become narrower at lower temperatures and additional ordered phases are frequently observed within the region of the original high-temperature solid solutions (13). This is especially the case if the samples are annealed for a long time and/or slowly cooled down to room-temperature. In this way several intermediate fluorite-related superstructure phases have been found in a recent phase study on the system SmF_2 – SmF_3 (12). For comparison, we have reinvestigated the system SmH_2 – SmH_3 using small cooling gradients. The system SmD_2 – SmD_3 has been studied in the same way.

2. Experimental

Samarium hydrides and deuterides within the composition range $\text{Sm}X_{1.80-2.00}$ were prepared by direct synthesis from samarium metal (Auer-Remy, 99.9%), hydrogen (Messer-Griesheim, purity 5.0), and deuterium (Messer-Griesheim, purity 2.7). The gases were purified by Oxysorb systems (Messer-Griesheim). The reactions were carried out in molybdenum crucibles under adjusted H_2 or D_2 pressures, respectively, at 200–500°C for several hours. Different cooling rates were applied to study different states of equilibrium. Further experimental details are already described elsewhere (14–16). The experimental error of the anion/cation ratio is $\Delta x = \pm 0.02$ for the $\text{Sm}X_x$ phases.

Samples of the composition range $\text{Sm}X_{1.8-2.5}$ were characterized by the Guinier X-ray diffraction technique (Jagodzinski camera, copper radiation with $\lambda_{\text{CuK}\alpha_1} = 1.54056 \text{ \AA}$, silicon NBS-SRM 640 with $a = 5.43088 \text{ \AA}$ as internal standard). The numerical data evaluation was carried out by means of the programs EGUIN (17) and LSUCRE (18). Samples with an anion/cation ratio > 2.5 proved to be air and moisture sensitive. Therefore,

these samples were sealed in capillaries and characterized by the Debye–Scherrer X-ray diffraction method (double radius camera, copper radiation with $\lambda_{\text{CuK}\alpha_1} = 1.54184 \text{ \AA}$, internal standard as above). Experimental intensities $I/I_{0,\text{exp}}$ were measured on a photometer (GIII, Carl Zeiss, Jena). Theoretical intensities $I/I_{0,\text{calc}}$ were calculated by means of the program LAZY-PULVERIX (19). The crystal data of SmH_2 , SmD_2 , Sm_3D_7 , SmH_3 , and SmD_3 will be submitted to the Joint Committee on Powder Diffraction Standards (JCPDS, formerly ASTM), Swarthmore, Pennsylvania. The crystal data of Sm_3H_7 are given in this paper.

3. Results and Discussion

Different reaction temperatures and H_2 or D_2 pressures were necessary to obtain samples with different H/Sm or D/Sm ratio, respectively, (see Table I). Following the gas absorption at the appropriate reaction temperatures, two different cooling rates, I or II, were applied. X-Ray investigations at room temperature revealed two different phase relations (see Fig. 1) and it is obvious that two different states of equilibrium were frozen in (HT = higher temperature and LT = lower temperature). Though the actual temperatures are unknown, it appears from a comparison of the different phase relations in Fig. 1 that our investigations correspond most likely to those one would expect at lower temperatures, while the

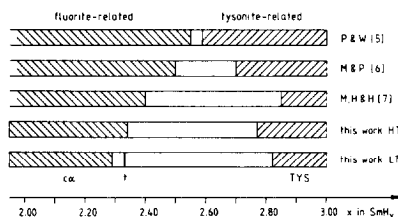


FIG. 1. Phase relationships in the system SmH_2 – SmH_3 .

TABLE I
EXPERIMENTAL DETAILS ON THE PREPARATION OF SAMARIUM HYDRIDES AND DEUTERIDES

Conditions of reactions	H: Sm and D: Sm ratio x		
	$1.8 < x < 2.0$	$2.0 \leq x \leq 2.5$	$2.5 < x < 3.0$
Temperature ($^{\circ}\text{C}$)			
SmH_x	400-500	300-450	250-300
SmD_x	350-500	300-450	200-250
Cooling rate ($^{\circ}\text{C/hr}$)			
I (\rightarrow HT)	25	25	25
II (\rightarrow LT)	4	4	4
Pressure (Torr)			
H_2	$\sim 200 \rightarrow 0$	100-600	650-750
D_2	$\sim 100 \rightarrow 0$	200-600	~ 700

data by Pebler and Wallace (5) or Messer and Park (6) represent phase relations characteristic for higher temperatures. Three conclusions can be drawn from these observations: (1) The slower the cooling process is carried out the more room-temperature phase relationships are approached. (2) The HT phase relations are closely related to those in the system SrF_2 - EuF_3 at 800°C (20) as far as the phase widths of the fluorite-related solid solution ($c\alpha$) and the tysonite-related solid solution (TYS) are concerned. (3) The LT phase relationships correspond in their trend well with those found in LnF_2 - LnF_3 and MF_2 - REF_3 systems (21), especially with respect to the decreasing phase width of $c\alpha$ and the appearance of intermediate phases (see below).

The lattice parameters a of the cubic hydrides and deuterides ($c\alpha$ phases) are listed in Table II together with the equations of the correlation between lattice parameter and chemical composition of the solid solution. These data refer to high-temperature phase relationships. The low-temperature lattice parameters are identical to the high-temperature values for X/M compositions ≤ 2.29 . The phase widths were graphically determined (see Fig. 2 and Fig. 3):

$\text{SmH}_{1.95-2.34}$ and $\text{SmD}_{1.95-2.34}$ (HT)

and

$\text{SmH}_{1.95-2.29}$ and $\text{SmD}_{1.95-2.28}$ (LT).

In all $c\alpha$ phases, one observes a linear decrease of the lattice parameter with increasing content of hydrogen or deuterium.

The X-ray characterization of the tysonite-related phases $\text{SmH}_{3-\delta}$ and $\text{SmD}_{3-\delta}$ turned out to be much more difficult because of their sensitivity to air and moisture. Therefore, we were not able to clarify if the lattice parameters change with the composition or not. Thus, the lower phase boundaries were established only

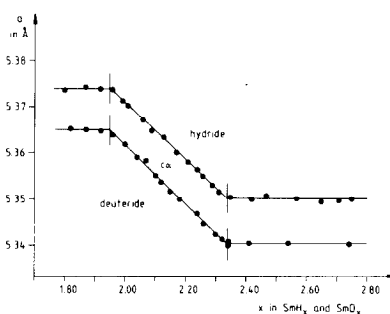


FIG. 2. Nonstoichiometry of SmH_2 and SmD_2 (high-temperature phase relationships HT, cooling rate 25°C/hr).

TABLE II
LATTICE PARAMETERS OF FLUORITE-RELATED ($Fm\bar{3}m$) SAMARIUM HYDRIDES AND DEUTERIDES (HT)

Hydrides ^a			Deuterides ^b		
x in SmH_x	a (Å)	$V' = V/Z$ (Å ³)	x in SmD_x	a (Å)	$V' = V/Z$ (Å ³)
1.80	5.3736(4)	38.791(8)	1.82	5.3653(3)	38.612(6)
1.87	5.3744(4)	38.809(9)	1.87	5.3650(4)	38.606(9)
1.92	5.3740(5)	38.800(10)	1.91	5.3648(4)	38.601(8)
1.96	5.3737(3)	38.794(6)	1.96	5.3640(3)	38.584(7)
1.99	5.3714(6)	38.744(13)	2.00	5.3620(4)	38.541(8)
2.01	5.3704(5)	38.722(11)	2.04	5.3592(4)	38.480(9)
2.06	5.3674(4)	38.657(8)	2.07	5.3564(5)	38.420(11)
2.09	5.3648(6)	38.601(12)	2.10	5.3552(4)	38.394(8)
2.13	5.3635(5)	38.573(10)	2.15	5.3518(5)	38.321(10)
2.17	5.3601(7)	38.500(15)	2.18	5.3502(5)	38.287(11)
2.21	5.3580(4)	38.455(9)	2.24	5.3470(5)	38.218(11)
2.24	5.3567(6)	38.427(13)	2.26	5.3447(6)	38.169(12)
2.26	5.3552(7)	38.394(16)	2.30	5.3425(5)	38.122(10)
2.29	5.3531(7)	38.349(15)	2.31	5.3415(5)	38.100(11)
2.31	5.3520(6)	38.326(12)	2.32	5.3413(6)	38.096(13)
2.35	5.3507(7)	38.298(15)	2.34	5.3409(4)	38.088(9)
2.42	5.3502(7)	38.287(16)	2.34	5.3400(5)	38.068(10)
2.47	5.3510(6)	38.304(13)	2.41	5.3405(6)	38.079(12)
2.57	5.3504(8)	38.291(18)	2.54	5.3407(7)	38.083(16)
2.65	5.3495(7)	38.272(15)	2.74	5.3403(6)	38.075(13)
2.71	5.3498(9)	38.278(19)			
2.74	5.3505(8)	38.293(18)			

^a $\text{SmH}_{1.95-2.34}$: $a = -0.06114x + 5.4932$.

^b $\text{SmD}_{1.95-2.34}$: $a = -0.06291x + 5.4873$.

on the basis of the appearance of the $c\alpha$ (or t) reflections beside the TYS reflections: $\text{SmH}_{2.77-2.90}$ and $\text{SmD}_{2.78-2.90}$ (HT), $\text{SmH}_{2.82-2.90}$ and $\text{SmD}_{2.84-2.90}$ (LT).

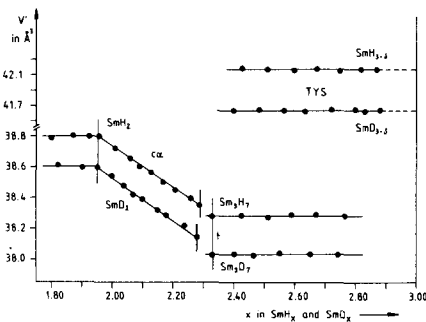


FIG. 3. Low-temperature phase relationships in the systems Sm-H and Sm-D (LT, cooling rate 4°C/hr).

The lattice parameters of $\text{SmH}_{2.82}$ and $\text{SmD}_{2.84}$ are listed in Table III. For both tysonite-related phases we chose the small unit cell with $Z = 2$ and space group $P6_3/mmc$ because no superstructure reflections were observed on the X-ray diffraction patterns. Neutron diffraction, however, has revealed a superstructure for HoD_3 with $a_S = 3^{1/2}a_B$, $c_S = c_B$, and $Z = 6$ (22). The same superstructure can easily be observed for $\text{LaF}_3 - \text{NdF}_3$ by X-ray diffraction (23, 24), but electron diffraction from single crystals of LaF_3 (25) showed clearly that both forms, $Z = 2$ and $Z = 6$, exist. Furthermore, anion-deficient, tysonite-related phases $(M, RE)\text{F}_{3-\delta}$ show in the main no superstructure reflections, e.g. (24). It is,

TABLE III
LATTICE PARAMETERS OF Sm_3H_7 , Sm_3D_7 , SmH_{3-6} , AND SmD_{3-6}

Phase, space group experimental composition	a (Å)	c (Å)	c/a	$V' = V/Z, \text{Å}^3$ ($Z = 2$)
Sm_3H_7 $I4/m$ ec $\text{SmH}_{2.33}$	3.7780(3)	5.3647(6)	1.4200	38.285(7)
Sm_3D_7 $I4/m$ ec $\text{SmD}_{2.33}$	3.7716(6)	5.3503(9)	1.4186	38.054(12)
SmH_{3-6} $P6_3/mmc$ ec $\text{SmH}_{2.82}$	3.7870(3)	6.7926(8)	1.7934	42.183(8)
SmD_{3-6} $P6_3/mmc$ ec $\text{SmD}_{2.84}$	3.7726(4)	6.7632(9)	1.7927	41.681(9)

therefore, questionable whether the anion-deficient, tysonite-related SmH_{3-6} and SmD_{3-6} phases have this superstructure or not. This problem can only be solved by neutron diffraction, because X-ray diffraction naturally does not reveal a superstructure solely caused by ordering of hydrogen or deuterium anions.

The most interesting feature of our LT phase relationships is the appearance of two new intermediate phases of the composition Sm_3H_7 and Sm_3D_7 , which coexist with the corresponding tysonite phases in the region $2.35 \leq x \leq 2.78$ (cf. Fig. 3). They have a tetragonally distorted, fluorite-related basis structure with $a_t \approx 0.5(2)^{1/2}a_F$, $c_t \approx a_F$, and $Z = 2$ corresponding to the formula $\text{Sm}X_{2+6}$ (compare (26)). The lattice parameters are listed in Table III. These phases are analogous to Sm_3F_7 (12), Eu_3F_7 (20), Yb_3F_7 (26), and $M_2\text{REF}_7$ with $M = \text{Ca}, \text{Sr}, \text{Ba}$ and $RE = \text{Ln}, \text{Y}, \text{and La}$ (20, 21, 26-30) as far as the anion/cation ratio and the lattice geometry of the basis structure are concerned. But in contrast to all these phases no superstructure reflections could be observed on the Guinier patterns of Sm_3H_7 and Sm_3D_7 . The powder data of Sm_3H_7 are given in Table IV. In the case of the fluorides the appearance of such intermediate phases at lower temperatures

is caused by ordering of cations ($\text{Ln}^{\text{II}}/\text{Ln}^{\text{III}}$ and $M^{\text{II}}/\text{RE}^{\text{III}}$) and an ordered reorganization of the anion lattice after incorporation of interstitial anions (21, 26, 31). The situation in the case of Sm_3H_7 and Sm_3D_7 is of course somewhat different, because samarium has the valence state III in hydrides and deuterides. Therefore, the above phases have to be formulated as $\text{Sm}_3^{\text{III}}\text{H}_7(e)_2$ and $\text{Sm}_3^{\text{III}}\text{D}_7(e)_2$,

TABLE IV
CRYSTAL DATA OF Sm_3H_7^a

hkl	d_{calc}	d_{obs}	$I/I_{0,\text{exp}}$	$I/I_{0,\text{calc}}$
1 0 1	3.0889	3.0876	100	100
0 0 2	2.6823	2.6821	15	16
1 1 0	2.6714	2.6702	25	32
1 1 2	1.8928	1.8934	21	25
2 0 0	1.8890	1.8890	15	13
1 0 3	1.6163	1.6164	12	15
2 1 1	1.6115	1.6111	22	30
2 0 2	1.5444	1.5443	10	13
0 0 4	1.3412	1.3408	4	2
2 2 0	1.3357	1.3360	6	4
2 1 3	1.2281	1.2283	10	14
3 0 1	1.2260	1.2258	6	7
1 1 4	1.1986	1.1987	5	7
2 2 2	1.1957	1.1960	7	7
3 1 0	1.1947	1.1945	6	7
2 0 4	1.0936	1.0936	5	6
3 1 2	1.0913	1.0913	10	13

^a For lattice parameters see Table III.

and the tetragonal distortion of the above fluorite parent structure arises then only from ordering of the anion lattice. In the above fluorite-related phases, X-ray diffraction cannot reveal such ordering, but neutron diffraction could. Indeed, Titcomb *et al.* (32) determined a superstructure in $\text{CeD}_{2.29}$, $\text{LaD}_{2.30}$, and $\text{PrD}_{2.37}$ by profile analysis of powder neutron diffraction. The interpretation of their data led to an unit cell with $a_S \approx a_F$, $c_S \approx 2a_F$, and $Z = 8$ with an ideal formula of $\text{RE}_8\text{F}_{20} = \text{REF}_{2.5}$. The discrepancies between experimental and theoretical formulas are explained by nonstoichiometry and a high level of intrinsic disorder. No order could be observed in $\text{CeD}_{2.5}$ but below $\text{CeD}_{2.40}$. All these tetragonal phases have the same basis structure, though the ratio c/a is less than $2^{1/2}$ in $\text{CeD}_{2.29}$, but greater than $2^{1/2}$ in $\text{LaD}_{2.30}$, $\text{PrD}_{2.37}$, $\text{SmH}_{2.33}$, and $\text{SmD}_{2.33}$. The superstructure problems, however, are not solved at least for the latter two phases, but the analogy to the Ln_3F_7 phases (21, 26) is remarkable in any case, though their superstructure is different in comparison to $\text{CeD}_{2.29}$. Furthermore, $\text{CeD}_{2.75}$ is also reported to have a tetragonally distorted, fluorite-related structure at temperatures below -18°C (33). If the F-centered indexing is changed to the usual body-centered ($Z = 4 \rightarrow Z = 2$) then the c/a ratio is $>2^{1/2}$ as in the case of Sm_3H_7 (1.4200) and Sm_3D_7 (1.4186). If the actual deuterium/cerium ratio were significantly less than 2.75, it could be possible that the analogous Ce_3D_7 phase has been observed.

In summary, the present investigation of the systems $\text{SmH}_2\text{--SmH}_3$ and $\text{SmD}_2\text{--SmD}_3$ shows that the low-temperature phase relationships are very similar to those in the system $\text{SmF}_2\text{--SmF}_3$, especially with regard to the fluorite-related region. In contrast to the latter system, in hydrides and deuterides ordering takes

place only in the anion sublattice. Though until now only one type of intermediate phases (Sm_3X_7) has been found, additional fluorite-related compounds may exist at lower temperatures. Efforts to prepare such ordered phases are in progress. In this context, it should be mentioned that kinetic measurements in the system $\text{PuH}_2\text{--PuH}_3$ (34) may be interpreted by the formation of similar intermediate phases as in the systems $\text{SmH}_2\text{--SmH}_3$, $\text{SmD}_2\text{--SmD}_3$, and $\text{LnF}_2\text{--LnF}_3$ (21).

The general conclusion can be drawn that the lanthanide (and possibly actinide) hydrides and deuterides resemble the corresponding fluorides much more than one has expected.

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