

Progress in the T-X Phase Diagram of the Solid Solution $\text{CeH}_2 - \text{CeH}_3$

Part II: Neutron Diffraction Investigations. Trihydrides*

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In this paper we present first neutron diffraction investigations on solid solutions $\text{CeD}_2 - \text{CeD}_3$ prepared in our laboratory. Several new superstructures have been found and the highlight of this investigations is the existence of a non-cubic trihydrides (CeD_3 , CeH_3) which was proved both by X-ray and neutron diffractions.

Introduction

Aim of this investigation was to support the phase diagrams studies of the system $\text{CeD}_2 - \text{CeD}_3$ presented in the Part I of this work using neutron diffraction so that information both from the deuterium and the metal sublattice structures could be gathered. The results have shown the existence of several new superstructures for some of which structure models are proposed.

For La, Ce and Pr both dihydrides and trihydrides are thought to crystallize in the same fcc CaF_2 structure. However, this structural characterization of the trihydrides was made long time ago in samples with an appreciable deviation ($\geq 5\%$) of the stoichiometry and not always the highest purity. In this paper we present for the first time some evidence that the CeH_3 (the same is true for LaH_3) deviates from the cubic symmetry, if it is pure and stoichiometric, similar to the heavier RE-Hydrides which are hexagonal.

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Experimental

Some details about the synthesis of the deuterides and hydrides have been reported before [1,2] and in the Part I of this work. The deuterium for the synthesis (AGA Zürich – purity 99.8%: $N_2 < 60$ ppm, $H_2O < 40$ ppm, $O_2 < 20$ ppm and $H_2 \approx 0.2\%$) was additionally purified by passing through a palladium diffusion unit at 340°C . Both trihydrides and trideuterides were synthesized at 500°C . At this temperature and under H_2 pressure of 6 bar the composition $CeD_{2.5}$ (or $CeH_{2.5}$) is reached. Cooling ($5^\circ\text{C}/\text{h}$) under constant pressure of 6 bar to room temperature leads to higher hydrogen contents.

Two methods were used to investigate the phase relationships:

- X-ray powder diffraction investigations at room temperature using a Debye–Scherrer camera (for trihydrides and trideuterides).
- and for the seven deuterated samples available up to now, neutron diffraction in the range $10 \leq T \leq 350$ K. A double axis multicounter diffractometer (DMC) was used at the 10 MW SAPHIR reactor of PSI/Würenlingen, with a focusing Ge_{311} single crystal monochromator ($\lambda = 0.1708$ nm).

Results and Discussion

First Neutron Diffraction Investigations

These were performed for the compositions $CeD_{2.23}$ (293 K), $CeD_{2.59}$ (293 and 10 K), $CeD_{2.64}$ (153 and 7 K) and $CeD_{2.75}$ (293 and 213 K). Further investigations in the trideuteride region are reported in the next section. Figure 1 shows an overview of the spectra of some of these compositions.

$CeD_{2.23}$

This composition shows at room temperature a tetragonal structure in agreement with Fig.6 of Part I [7]. This structure is similar to that found by Schefer et al [3] for a sample $CeD_{2.29}$ at $T = 4.2$ K. Rietveld refinement using the tetragonal space group I4 gives rather satisfactory error factors $R_1 = 0.059$ and $R_{wp} = 0.114$ and lattice constants $a = b = 0.5547$ nm and $c = 1.1121$ nm. Figure 2 shows the observed intensity as well as the negligible difference between observed and calculated

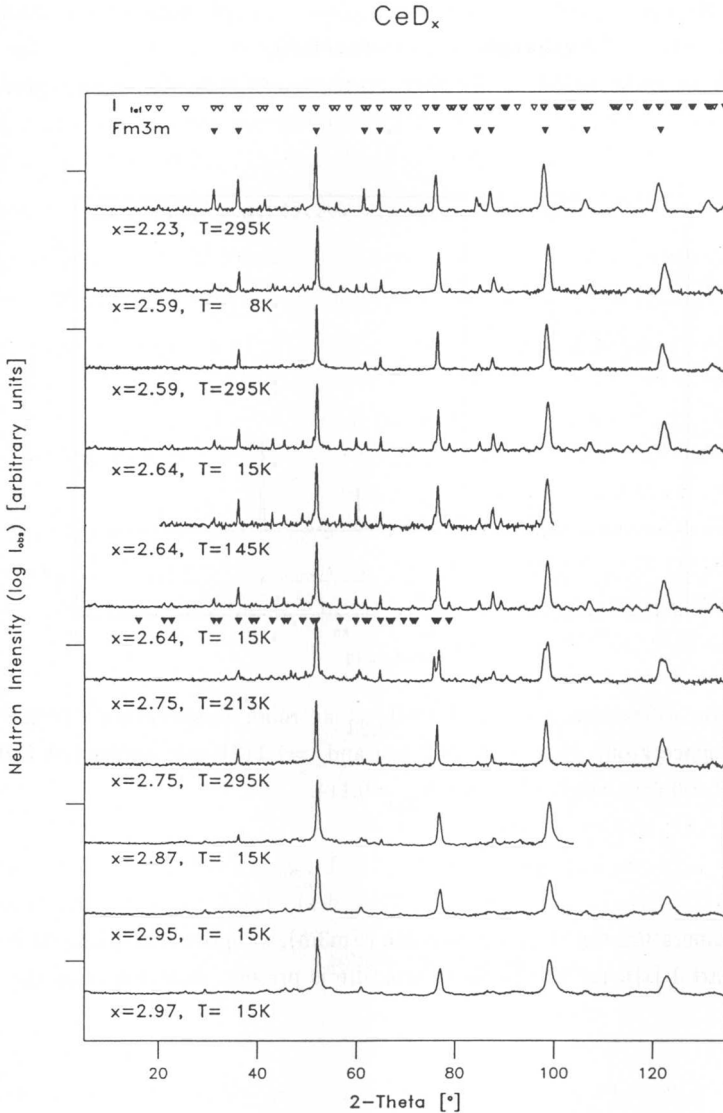


Fig.1 Change of the neutron intensity (logarithmic) as a function of the 2θ angle for various stoichiometries and temperatures. The calculated reflections for the tetragonal body centered structure and the cubic Fm3m space group are shown in the upper part.

intensities. An open question, however, remains the application of the structure model (I4) whose fully occupied lattice corresponds to $\text{CeD}_{2.75}$, for the composition of only $\text{CeD}_{2.23}$. Further structure refinements should give the answer.

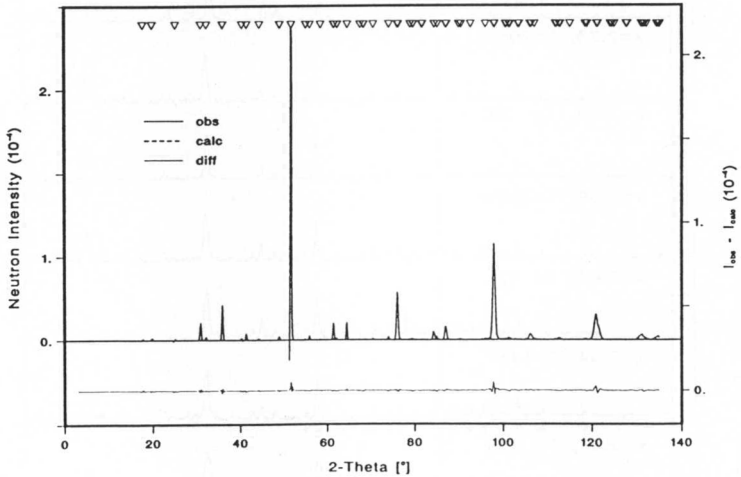


Fig.2 Neutron diffraction spectra of $\text{CeD}_{2.23}$ at room temperature ($T=293$ K). Tetragonal space group I4 $a=b=0.5547$ nm and $c=1.1121$ nm; agreement factors: integrated $R_I=0.059$, weighted profile $R_{wp}=0.114$.

$\text{CeD}_{2.59}$

At room temperature the structure is cubic (Fm3m), in agreement with our X-ray data (see Part I [7]). At 10 K a superstructure is present. Indexing is on the way now.

$\text{CeD}_{2.64}$

At 150 K a superstructure appears, i.e. at the temperature where the X-ray data [7] clearly show only the cubic structure. The conclusion is that the cerium sublattice of the superstructure must have cubic face centred symmetry and that the superstructure appears due to shifts at the deuterium atoms. At 15 K the same superstructure is observed. Possible indexing gives a tetragonal I-centered lattice

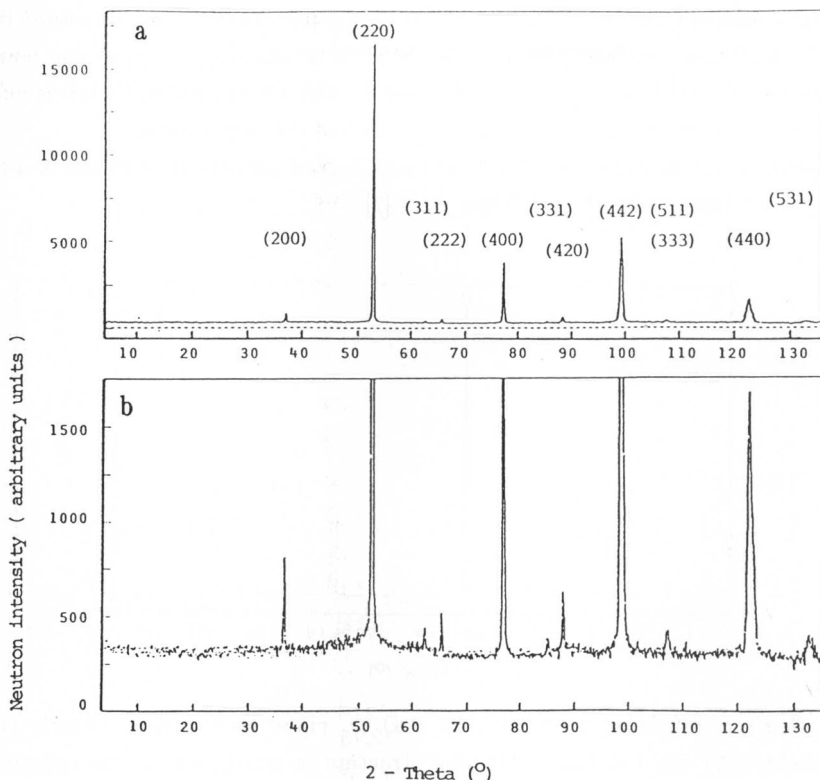


Fig.3 a) Neutron diffraction spectra of the $\text{CeD}_{2.75}$ at room temperature. The cubic symmetry $\text{Fm}\bar{3}\text{m}$ is clearly shown by the indexing.

b) At higher resolution, no impurity lines appear in the background.

with $a=b=0.8719$ nm and $c=0.5514$ nm. However, a larger unit cell might be necessary in order to have a deuterium occupancy in agreement with the measured stoichiometry.

$\text{CeD}_{2.75}$

Figure 3a shows the pure $\text{Fm}\bar{3}\text{m}$ cubic structure at room temperature, resulting from the statistical distribution of deuterium on tetrahedral and octahedral sites displaced along the $\langle 111 \rangle$ directions from the ideal positions. The spectra show clearly that no contamination is present in the samples (Fig. 3). At $T=213$ K a

structure with a clear tetragonal splitting is existing (Fig.4). This structure is, however, different from the tetragonal one at $x=2.23$. Indexing is on the way now. It seems, therefore, that the cerium sublattice is cubic up to 2.05 (in x), tetragonal up to 2.6, cubic up to 2.65, tetragonal up to 2.85 and then again cubic.

In general, the neutron diffraction data are in good agreement with the X-ray data of Fig.6 presented in Part I of this work [7].

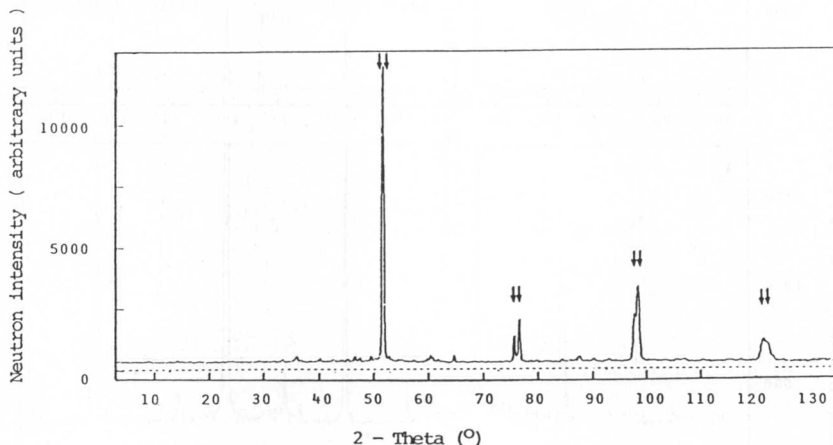


Fig.4 Neutron diffraction spectra of the $\text{CeD}_{2.75}$ phase at $T=216$ K. Clearly (in agreement with Fig.6 of Part I [7]) the structure is tetragonal, as the splitting shows (arrow pairs).

Noncubic Structure of $\text{CeH}_{3-\delta}$

Most unexpected was the discovery by X-rays [4] that the trihydrides and trideuterides of cerium ($\text{CeH}_{2.95}$ – $\text{CeH}_{2.98}$) are not cubic. We mean, of course samples whose hydrogen content has been exactly (± 0.005) determined by the volumetric method [5] and which have been synthesized and handled under conditions of very high purity. Figure 5 shows the neutron diffraction spectra of $\text{CeD}_{2.970 \pm 0.005}$ at 15 and 350 K. The nearly cubic reflections are shown in brackets, easily recognizable due to their much higher intensities (approx. 100x). In addition 11 feeble reflections are shown (broken arrows) in the angle range up to 120° . Even more clear however, is the change of structure shown in the X-ray powder diagram (Table 1).

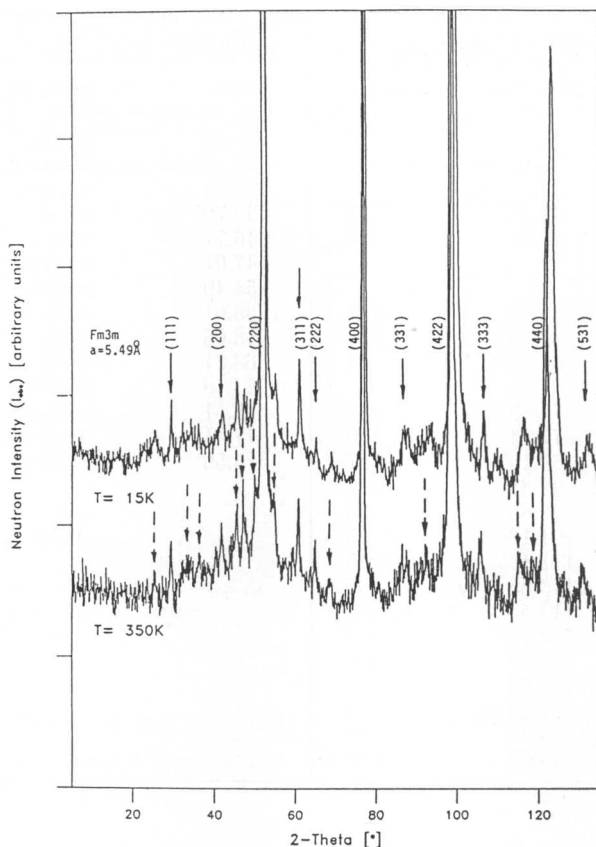


Fig.5 Neutron diffraction spectra of a trideuteride sample with composition $\text{CeD}_{2.970 \pm 0.005}$, both at $T=350\text{K}$ and $T=15\text{K}$. The indexing of the quasi-cubic reflections (solid arrows) has been done for Fm3m ($a=0.549\text{ nm}$) but the agreement between observed and calculated ones is very bad (Fig.6). In addition 11 less strong reflections are existing (see broken arrows). No appreciable changes appear between the two temperatures.

For the calculation of the cubic reflections the Fm3m symmetry was assumed, using a lattice constant $a=0.55250 \pm 0.00004\text{ nm}$ extrapolated, for $x=2.97$ from slightly H-poorer deuterides. Clearly both, 2Θ values and calculated intensities show appreciable differences from the observed ones, indicating the existence of another structure in the cerium-sublattice.

Calculated cubic Fm3m			Observed (D-Scherrer)		$\Delta 2\theta$
h k l	2θ	intensity	2θ	intensity	
1 1 1	27.95	1000	26.65	strong	0.22
			28.17	medium	
			28.91	medium	
2 0 0	32.38	513	32.70	weak	0.32
2 2 0	46.45	405	46.71	strong	0.26
			47.07	medium	
			54.49	strong	
3 1 1	55.08	451	55.61	medium	0.53
2 2 2	57.76	130	58.08	weak	0.31
4 0 0	67.79	64	68.31	weak	0.52
			73.79	medium	
			75.51	medium	
3 3 1	74.85	184	77.41	medium	0.66
4 2 0	77.14	170	86.50	medium	0.27
4 2 2	86.16	137		medium	0.34
5 1 1	92.85	117			
3 3 3	92.85	39		not sharp	
4 4 0	104.12	55			
5 3 1	111.14	215			
4 4 2	113.55	109			
6 0 0	113.55	27			
6 2 0	123.71	123			
5 3 3	132.19	139			
6 2 2	135.28	147			
4 4 4	150.00	74			
5 5 1	169.32	616			
7 1 1	169.32	616			

Table 1

Calculated Fm3m for $a=0.5525$ nm and observed X-ray (Debye-Scherrer) reflections of the non cubic trideuteride phase $CeD_{2.970\pm 0.005}$. $\Delta 2\theta$ shows clearly the appreciable deviations of the observed reflections from the calculated cubic ones. In addition to these nearly cubic reflexions, however, several other strong and medium reflections exist.

In principle, four possible cases may be considered for the understanding of the new diffraction pattern of $CeH_{3-\delta}$:

a) Contamination

All possible conditions were double checked, fresh batches of metal were used, and

the Pd–Purifier adjusted at higher temperatures for deuterium diffusion. Several samples synthesized under these conditions gave reproducible spectra. A further direct proof of the absence of contaminations is given in Fig.3. The $\text{CeD}_{2.75}$ sample which shows exclusively only the cubic reflections has been synthesized under exactly the same purity conditions as the $\text{CeD}_{2.97}$ sample.

b) Coexistence of Two Phases.

Under this assumption and according to the diffraction patterns, one of the two phases should be cubic and one noncubic. It is easily shown that this is not the case. Figure 6 shows the attempt to fit the strong, nearly cubic reflections to the space group $\text{Fm}\bar{3}\text{m}$. For $T=350\text{ K}$ the error factors are $R_1=0.11$ and $R_{\text{wp}}=0.32$, and for $T=13\text{ K}$: $R_1=0.097$ and $R_{\text{wp}}=0.26$, in both cases unacceptably high. Also an inspection of Table 1 shows that no cubic phase can be fitted to the data.

c) One Slightly Noncubic Phase.

Our original idea was that, similar to the heavier RE–hydrides, a hexagonal cerium trihydride might exist. Indexing of both neutron and X–ray spectra for a hexagonal lattice gave high R–factors. Calculations with ABCAB and several other sequences of closed packed structures gave too many reflections. The indexing work is continued.

d) Two Noncubic Phases.

The only indication for this case comes from NMR–measurements [6]. Measurement of the Proton Relaxation Time T_1 at 40MHz for one of our samples in the temperature range $416 < T < 900$ gave two signals. Judging from the high background of the X–ray films (in contrast to H–poorer samples) we thought originally, that a second amorphous phase is existing in these samples. However, the neutron diffraction did not show an amorphous component.

Concluding, it can be said that the up to now existing evidence indicates a superstructure for the trihydrides of cerium and lanthanum [4]. How far this superstructure could produce the unexpected signals of the proton resonance is not clear at present.

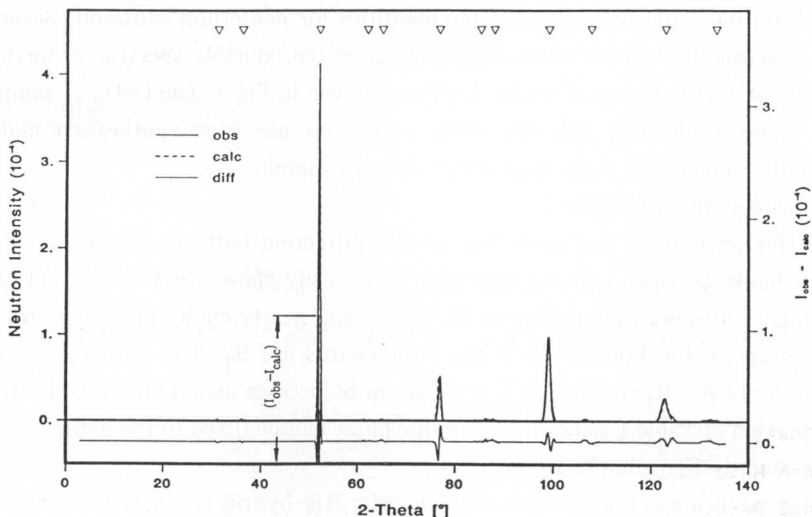


Fig.6 Difference neutron spectra ($I_{\text{obs}} - I_{\text{calc}}$) at $T=15\text{K}$ for the trideuteride $\text{CeD}_{2.970 \pm 0.005}$. The difference particularly in the first reflection is very strong.

References

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