Phase Transitions in the CeH_2-CeH_3 System*

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Pure polycrystalline samples of CeH_x have been synthesized and the hydrogen content determined volumetrically. Over 600 lattice constants have been measured in the temperature range 100–370 K and the composition range $2.00 \leqslant H/Ce \leqslant 3.00$, so that a first $T-x$ phase diagram can be constructed. Two fields of the tetragonal distortion have been found. The first one exists starting at approx. 360 K and could be traced down to the lowest temperature of the X-ray measurements (100 K). At room temperature its phase boundaries are $2.30 \lesssim H/Ce \lesssim 2.55$. The second tetragonal field exists only below *ca.* 250 K for the composition $2.80 \lesssim H/Ce \lesssim 2.95$. Miscibility gaps between the tetragonal and cubic phase exist at both sides of the tetragonal distortion fields. Their boundaries may be responsible for many phase transitions reported previously.

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Recently, the investigation of phase transitions in the REH_2-REH_3 systems (where RE stands for rare earth) has attracted appreciable interest. After the discovery of the metal (REH_2)–semiconductor (REH_3) transition three decades ago [1], neutron diffraction investigations on CeH_x phases have shown the existence of superstructures with tetragonal symmetry (see for example ref. 2), indicating already at that time that the idea of a homogeneous solid solution range might be over optimistic. Nevertheless, interpretation of physical properties has not up to now considered the influence of structural transformations occurring in the same composition field.

In previous publications [3, 4] we have presented a revised $T-x$ phase diagram of the $Ce-H_2$ system, and the dependence of lattice constants on concentration in the CeH_2-CeH_3 range at room temperature, as well as some first low-temperature measurements. Here we present a first proposal for the $T-x$ phase diagram in the CeH_2-CeH_3 composition range and $100 \leqslant T \leqslant 370$ K.

Experimental

Experimental details about the preparation of the high purity samples have been given in the past [3–7].

For the low-temperature work (100–370 K) the Guinier–Simon (Enraf-Nonius) camera with Cu $K\alpha_1$ monochromatic radiation has been used. The back

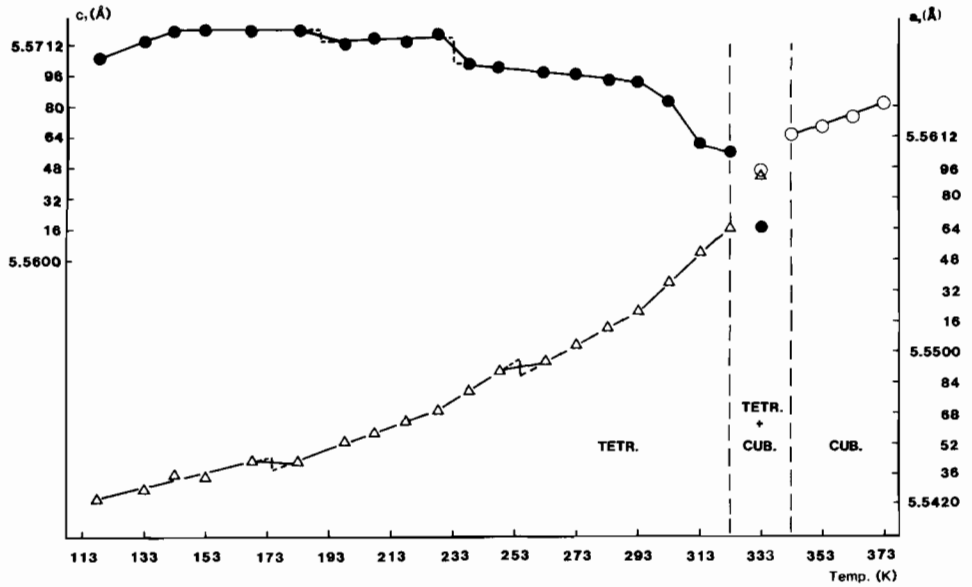

Fig. 1. Temperature dependence of the cell parameters for $CeH_{2.34}$: △, a-axis period of the tetragonal phase (right-hand scale); ●, c-axis period of the tetragonal phase (left-hand scale); ○, a-axis period of the cubic phase.

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reflection geometry allowing the measurement of the reflection range (224)–(444) has been applied. NBS silicon has been used as internal standard. Accuracies of ±0.0001 Å for the cubic phase and ±0.0003 for the tetragonal phase have been achieved.

The thermal expansion coefficients $\Delta L/L$ of the samples have been measured between 4.2 and 300 K by means of a capacitance method. This method is useful owing to its high sensitivity but its disadvantage is the lack of specificity. Accompanied however by lattice parameter measurements it is a powerful instrument for the investigation of phase transformations. Furthermore, a combination of $\Delta L/L$ and $\Delta a/a$ measurements can give information about the concentration of defects [8].

Results and Discussion

As an example we show the dependence of lattice parameters *versus* temperature for $CeH_{2.34}$ in Fig. 1. Starting from 320 K down to the lowest temperature of the X-ray measurements (100 K) only the tetragonally distorted phase ($I4_1/md$) exists for this

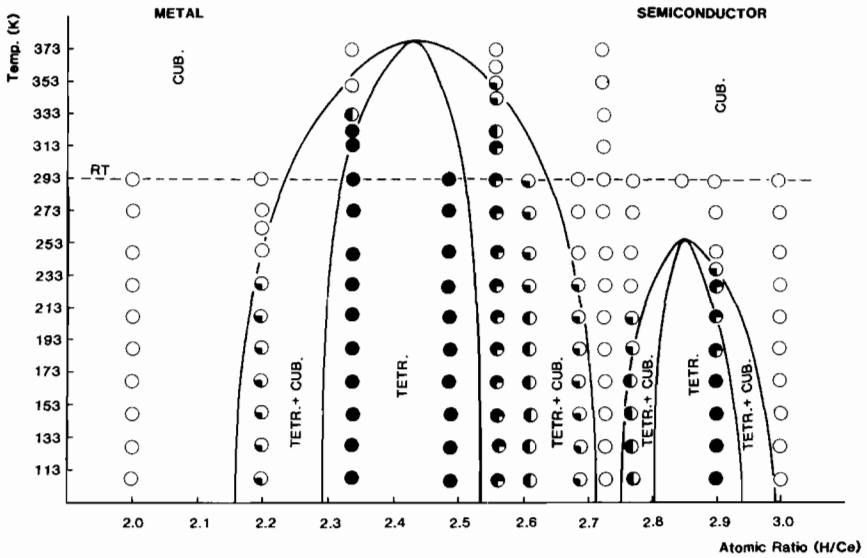

Fig. 2. A first proposal of the T–x phase diagram of the solid solutions CeH_2–CeH_3 in the temperature range 100–370 K: ○ only cubic phase exists; ● only tetragonal phase; ◔ mostly cubic phase in the two-phase region; ◐ comparable cubic and tetragonal; ◕ mostly tetragonal phase in the two-phase region; RT = room temperature.

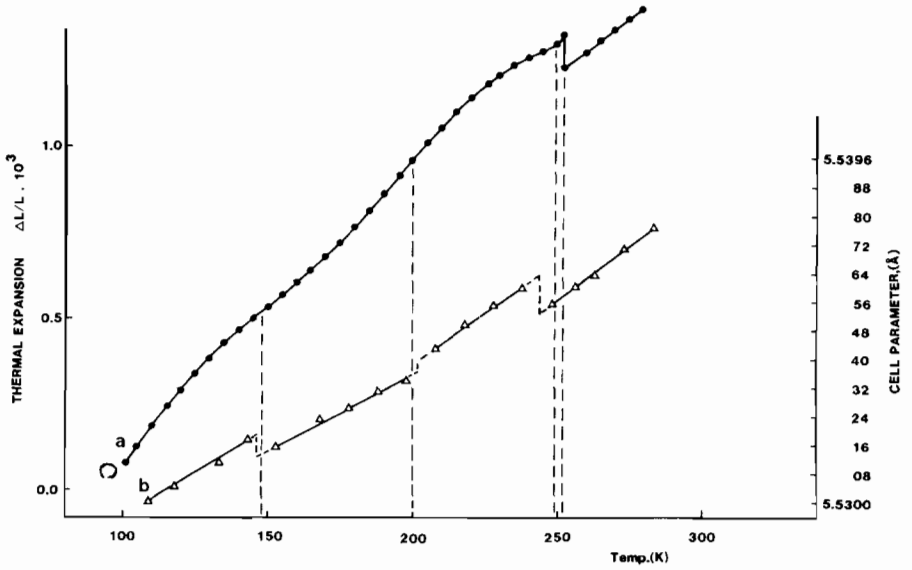

Fig. 3. Thermal expansion $\Delta L/L$ (a) and cell parameter (b) *vs.* temperature for the cubic $CeH_{2.73}$ sample. Three isostructural phase transitions are shown.

composition [3]. Above 340 K only the cubic phase exists. As expected from the phase rule, a miscibility gap appears between these two temperature regions. It can be seen from Fig. 1 that the *c*-axis period of the tetragonal phase does not vary strongly in the temperature range 140–290 K and the difference between the *c*- and *a*-axis periods decreases with the increase in the temperature. At 333 K (two-phase region) the *a*-axis period of the tetragonal phase and the *a*-axis period of the cubic phase have nearly the same values.

On the basis of our 600 lattice constant measurements *versus* temperature of samples with compositions in the range CeH_2–CeH_3, we have constructed the T–x phase diagram which is shown in Fig. 2.

Two fields of tetragonal distortion exist in the temperature range 100–370 K. The first one appears at approx. 360 K and at room temperature its phase boundaries are $2.30 \lesssim H/Ce \lesssim 2.55$. The second tetragonal field exists only below *ca.* 250 K for the composition range $2.80 \lesssim H/Ce \lesssim 2.95$. Miscibility gaps between the tetragonal and cubic phase exist at both sides of the tetragonal distortion fields. Their boundaries may be responsible for many of the phase transitions reported previously (see for example ref. 9). However, in addition to the structural phase transformations appearing when crossing the phase boundaries of Fig. 2, we have also observed several 'isostructural' transitions. Such transitions are shown for the cubic composition $CeH_{2.73}$ down to 100 K, accompanied by small lattice expansions or contractions. Good agreement is achieved with the results of the thermal expansion, which are also shown in Fig. 3, indicating that both measurements reflect the same property. We have briefly discussed the opposite case in ref. 4. Isostructural phase transitions are found both in the cubic and tetragonal fields of the CeH_2–CeH_3 system and will be reported in more detail in a coming publication.

The phase diagram proposed in Fig. 2 is the first attempt to coordinate the items of information existing in this system. Thus the metal-to-semiconductor transition at $H/Ce \approx 2.7$ might probably be triggered from the structural transformation. Also the two superstructures found in the past by neutron diffraction [2] are probably located in the tetragonal fields shown in Fig. 2. High-temperature measurements which are in progress now will show the exact phase boundaries and transformations of the upper part of the diagram. The final investigations have to be made by neutron diffraction so that the exact structural features of this fascinating system can be definitely established.

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Note Added in Proof

Recent work in our laboratory led to an increased accuracy of the determination of the hydrogen concentration (K. Conder and E. Kaldis, *J. Less-Common Met.*, to be published). As a result the ratios H/Ce in Fig. 2 must be reduced by 0.1.