PHYSICAL REVIEW B VOLUME 46, NUMBER 13 1 OCTOBER 1992-I

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Experimental observation of hydrogen ordering in TbD_{2+x}

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(Received 22 July 1992)

A neutron-scattering investigation gives evidence of deuterium ordering at lower temperatures in a superstoichiometric heavy-rare-earth dihydride, TbD_{2+x}. The ordering occurs within the ensemble of deuterium atoms located on octahedral interstitial sites of the fcc lattice. The ordered state is described by an interstitial DO_{22} ($I4/mmm$) structure revealing the presence of a repulsive deuterium-deuterium interaction.

The rare earths (R) readily absorb hydrogen and, in general, form hydrides with concentrations up to three hydrogen atoms per rare-earth atom. The hydrogen electrons contribute, together with the rare-earth conduction electrons, to the formation of low-lying bonding bands, yielding drastic changes in the electronic properties of the system. Thus, the dihydrides behave like good monovalent metals, with room-temperature resistivities of the order of 10 $\mu\Omega$ cm, while the trihydrides are insulating saltlike compounds. This change of the type of crystal binding is connected with a decrease of the unit-cell volume observed with increasing hydrogen concentration.[1]

Rare-earth-hydrogen systems show a great variety of phenomena in their electric and magnetic properties, which are the subject of intense investigations. Despite this interest, structural features of hydrogen ordering are generally unknown, especially for RH_2 systems and have only been disclosed in very few cases. A structural characterization of hydrogen ordering is, however, essential for the understanding of the complex hydrogen-induced phenomena occurring in rare-earth-hydrogen systems.

The RH_2 system has a fluorite structure (fcc) in which the hydrogen atoms occupy all tetrahedral (T) interstices; further absorption of hydrogen brings about a subsequent filling of octahedral (O) interstitials sites. At higher temperatures a nonstoichiometric RH_{2+x} system may be considered as a lattice gas, where the surplus hydrogen atoms (x atoms) randomly occupy octahedral interstices of a fcc lattice.

In a few light rare-earth-hydrogen systems where the x atoms are continuously soluble up to the trihydride, e.g., in CeH_{2+x}, superlattice reflection induced by hydrogen ordering have been found by neutron-scattering techniques.[2,3] Different ordered structures ($I4_1/md$ and $I4/mmm$) have been observed in function of concentration. All ordered states of hydrogen observed within the octahedral interstitial lattice are characterized by $[1,\frac{1}{2},0]$ wave vectors of the fcc matrix, indicating an ordering on (420) fcc lattice planes. Likewise, an interstitial ordered structure of the Ni_4Mo type was proposed in LaH_{2+x} for values of x near 0.8.[4] The Ni_4Mo structure is also a member of the (420) family of ordered superstructures and corresponds to an ordered state, where four consecutive (420) planes are occupied with hydrogen and every fifth (420) plane remains empty. Generally, ordering on (420) planes of fcc lattices was observed in a few systems [Ni_nMo and PdD_x (Ref. 14)] and was analyzed in theoretical treatments,[5] especially considering the Ni_nMo series, in terms of an instability of the solid solution against a $[1,\frac{1}{2},0]$ ordering wave.

Moreover, the proposed order-disorder phenomenon in these light RH_{2+x} systems seems to be connected with a metal-semiconductor transition occurring for high values of x ($0.7<x<0.9$).[6] In fact, it is the collapse of the ordered octahedral vacancy sublattice with increasing temperature, leading to a breakdown of a delocalized carrier band, which is supposed to drive the metal-semiconductor transition.

For heavier rare-earth hydrogen compounds at present no diffraction data on hydrogen ordering phenomena exist in the literature. An anomaly in resistivity near 250 K found several years ago in TbH_{2+x} was the first indication for a possible structural change occurring at lower temperatures.[7] Later, the phenomenon was also confirmed in the systems GdH_{2+x} (Ref. 8) and DyH_{2+x} (Ref. 9). Finally, a metal-semiconductor transition was observed in YH_{2+x}, a system that can be considered an analog to the heavy-rare-earth hydrides, which was also related to a hydrogen ordering phenomenon.[10]

The important point to stress here is the fact that, in contrast to the light RH_{2+x} compounds, the heavy RH_{2+x} systems possess a rather limited solubility in the fluorite phase, with the hexagonal trihydride phase precipitating already above $x = 0.25$ in the case of TbH_{2+x} and $x = 0.1$ in YH_{2+x}. Thus the anomaly in resistivity was confirmed for $0.15 \leq x \leq 0.25$ in the former[7] and for $0.08 \leq x \leq 0.10$ in the latter.[10] This implies also that the ordering phenomenon expected in these systems would concern the ordering of hydrogen atoms within a vacancy-rich sublattice.

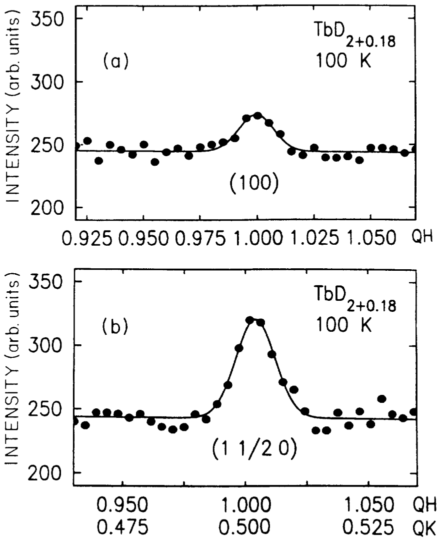

FIG. 1. Neutron intensity near fcc superlattice points observed in $TbD_{2.18}$ at 100 K. (a) near the [1,0,0] reciprocal lattice point (b) near the $[1,\frac{1}{2},0]$ reciprocal lattice point. The peak intensity approximately corresponds to 10^{-2} the intensity of the [200] fundamental reflection.

In this paper we present experimental evidence of hydrogen ordering in TbD_{2+x} obtained by neutron-scattering techniques. Measurements were done covering a series of hydrogen concentrations and allowing the establishment of a low-temperature phase diagram for one of the heavier rare-earth-hydrogen systems. We find that the ordered low-temperature structure is an analog of the Al_3Ti-type configuration, i.e., a tetragonal body-centered structure [Strukturbericht symbol DO_{22} or ($I4/mmm$) in the space-group notation], corresponding to Ni_3Mo ordering within the Ni_nMo series, i.e., three empty (420) planes in the x lattice followed by a filled one.

Most of the investigations were performed on the triple-axis spectrometer Valse located at a cold neutron-guide position of the Orphee reactor in Saclay. Additional data were obtained on the diffractometer G4.1 located at the same neutron guide. An incident neutron energy of 14.7 meV was used, and a pyrolytic graphite filter was put into the incident beam in order to eliminate second-order contaminations. Samples of TbD_{2+x} with different deuterium concentrations were prepared by direct absorption into a 4*N*-grade Tb ingot in two steps: (1) heat-

TABLE I. Observed and calculated intensities of fundamental (marked by a +) and superstructure powder lines in $TbD_{2.18}$ at 67 K. $I_{calc(1)}$ are the calculated values for a "perfectly" ordered $TbD_{2.18}$ structure. $I_{calc(2)}$ shows the results for a $TbD_{2.18}$ system, where 20% of the x deuterium atoms are randomly distributed on the vacant sites of the present DO_{22} ($I4/mmm$) structure. The relative intensities of the superstructure lines are thereby not affected. In the table tetragonal indices for the ($I4/mmm$) structure are also represented. The calculations were made with the program PULVERIX taking into account of Lorentz factor and multiplicity (Ref. 15).

h	*k*	*l*	*h*	*k*	*l*			I_{calc}		I_{calc}
	Tetragonal			Cubic		$2\theta_{calc}$	$2\theta_{obs}$	(1)	I_{obs}	(2)
0	0	2	0	0	1	27.04	27.03	27.5	13.3	14.5
1	0	1	1	0	$\frac{1}{2}$	30.31	30.33	88.7	36.8	46.8
1	1	0	1	1	0	38.62	38.65	28.3	26.6	14.9
1	1	2	1	1	1^+	47.78	47.78	1000	1000	1000
1	0	3	1	0	$\frac{3}{2}$	49.86	49.86	36.3	29.7	19.1
2 0	0 0	0 4	2 0	0 0	0^+ 2^+	55.76	55.75	345	280	345
2	0	2	2	0	1	63.04		contaminated		
2	1	1	2	1	$\frac{1}{2}$	64.78	64.87	48.3	32.9	25.4
1	1	4	1	1	2	69.88	69.88	21.8	9.4	11.5
2 1	1 0	3 5	2 1	1 0	$\frac{3}{2}$ $\frac{5}{2}$	78.03	78.02	57.0	34.4	30.0

ing at 550–600 °C to give the "pure" dihydride, in our case $TbD_{2.00}$ and (2) adding the excess hydrogen atoms (x) at 250–300 °C. After completion of the hydride formation the samples were crushed to powder. Trials to prepare high-quality single crystals of TbD_{2+x} were unsuccessful. The neutron measurements were done between room temperature and 70 K in order to remain above the range of magnetic ordering.

At 100 K sharp superlattice reflections were observed in TbD_{2+x} for all samples with x varying between 0.095 and 0.18. An example is given for $x=0.18$ in (Fig. 1). On the other hand, no superlattice reflections could be found in samples with $x=0.08$.

The positions of the reflections observed are compatible with the following superlattice points of the fcc lattice, namely, $(1,\frac{1}{2},0)$, $(1,\frac{3}{2},0)$, (1,0,0), and (1,1,0). Additional measurements on the diffractometer G4.1 confirmed the presence of $(1,\frac{1}{2},2)$, (1,1,2), and $(1,\frac{3}{2},2)$ fcc reflections at higher Q values. These superlattice points and also the observed intensities are in agreement with calculated structure factors of an interstitial DO_{22} ($I4/mmm$) structure (Ni_3Mo type). This structure is stoichiometric at 25-at. % hydrogen. The DO_{22} structure can be generated by two ordering wave vectors, i.e., $[1,\frac{1}{2},0]$ and [1,0,0] (Ref. 5) both of which are observed in TbD_{2+x} (Fig. 1). [In CeD_{2+x} a controversial situation exists in the literature. Two different ordered structures—($I4/mmm$) (Ref. 3) and ($I4_1/md$) (Ref. 2) were proposed for the same $CeD_{2.29}$ system. This discrepancy is related to the presence of the [1,0,0] ordering wave. The [1,0,0] reflection is present in the ($I4/mmm$) structure but is absent in ($I4_1/md$).] In this case the simultaneous observation of both superlattice reflections (Fig. 1) and their disappearance at higher temperatures confirm the DO_{22} structure ($I4/mmm$) and excludes the possibility of any higher-order contamination, especially at the [1,0,0] superlattice point.

Table I shows that the relative superlattice intensities are quite well reproduced by the calculation of a perfectly ordered stoichiometric DO_{22} ($I4/mmm$) structure. The intensity ratio, however, between the observed superlattice intensities and the fundamental reflections is reduced by a factor near 1.7, in the present nonstoichiometric $TbD_{2.18}$ system. A good agreement with the experimental values is obtained if in the calculations about 20% of the x deuterium atoms are randomly distributed on the vacant octahedral sites of the perfectly ordered DO_{22} structure. This means that the amplitude of the ordering wave is reduced by a random occupation of all octahedral sites by a small fraction of hydrogen atoms. For the samples with lower hydrogen concentrations a similar agreement could be obtained. It was not necessary to introduce an additional distortion neither of the tetrahedral nor of the terbium sublattice.

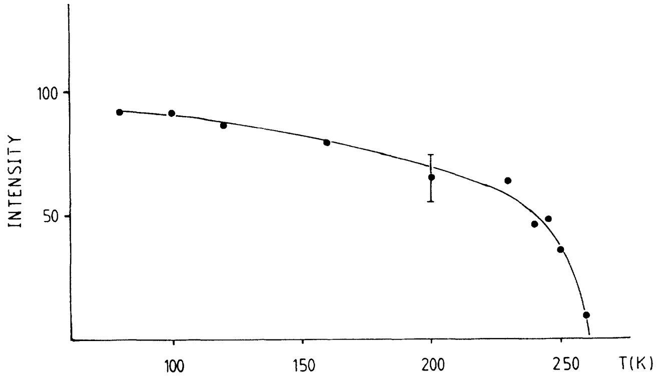

FIG. 2. Temperature dependence of the $[1,\frac{1}{2},0]$ reflection in $TbD_{2.18}$.

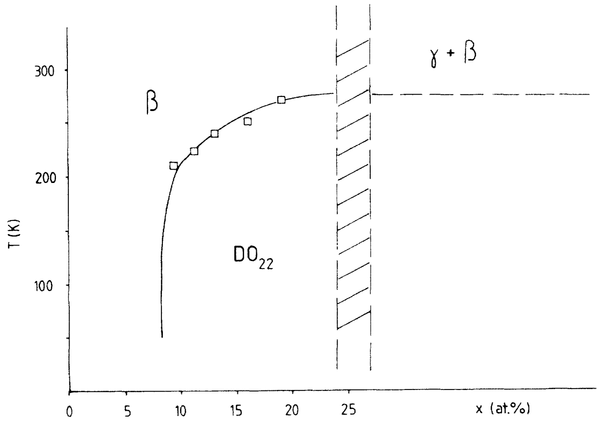

FIG. 3. Phase diagram of the interstitial DO_{22} structure in TbD_{2+x}. For $x=0.08$ no superlattice reflections were found.

In an A_3B alloy the DO_{22} structure corresponds to an ordered state, where three consecutive (420) planes are occupied by A atoms and every fourth (420) plane by B atoms. Consequently, in the present TbD_{2+x} system the experiment indicates that three interstitial (420) planes

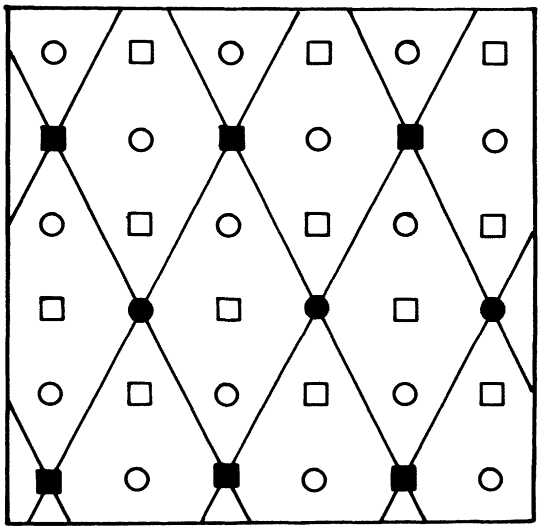

FIG. 4. The DO_{22} structure in TbD_{2+x} shown in a projection on a (002) fcc lattice plane. Only octahedral interstitial sites are shown. The symbols are circles for level zero, squares for level $\frac{1}{2}$, and filled symbols for occupied sites.

are vacant but every fourth is occupied with hydrogen atoms.

The temperature dependence of the $(1,\frac{1}{2},0)$ reflection is shown for a $TbD_{2.18}$ system in Fig. 2. The figure indicates a drastic intensity decrease within a narrow temperature region below the critical temperature. During the intensity decrease the width of the reflection remains narrow and within the experimental resolution. Above T_c the sharp intensity has disappeared, and within the counting statistics no indication for a short-range order intensity could be obtained. On cooling—with a cooling rate near 2 K/min—no hysteresis and time effects could be detected in the superlattice intensities. This indicates that the hydrogen atoms are still mobile in a temperature range near 220 K, in agreement with the recovery behavior after the quenching experiments observed in Ref. 7.

Similar measurements were performed for all other hydrogen concentrations, and a phase diagram was established (Fig. 3). It should be noted that at concentrations below $x = 0.08$, where the DO_{22} structure (Ni_3Mo) has disappeared, no other superlattice reflection could be found. Especially, no intensity was observed near $[\frac{4}{5},\frac{2}{5},0]$ positions corresponding to superlattice points of the Ni_4Mo structure. Therefore, in TbD_{2+x} no transition to a Ni_4Mo structure, stoichiometric near 20-at. % deuterium, occurs for lower concentrations.

It should be noted that during this experiment no distortion of the metal lattice connected with hydrogen ordering could be detected, contrary to some light RH_{2+x} systems, e.g., in LaH_{2+x} (Ref. 4) or SmH_{2+x} (Ref. 11). The Debye-Scherrer lines of the fundamental reflections remained sharp during the different temperature cycles. The observed shifts of the lines were in accordance with the normal thermal lattice expansion. From the widths of the lines a safe upper limit for a possible tetragonal distortion—i.e., a c/a value below 1.001—could be deduced.

In the literature energy calculations of ordered structures show that the DO_{22} $(I4/mmm)$ lattice is an ordered ground state in fcc systems.[12] These calculations take first (V_1) and second (V_2) neighbor interactions into account. The DO_{22} structure is stable near 25 at. % if $V_1 > 0$ and $0 < V_2/V_1 < 0.5$. On the other hand, the Ni_4Mo structure, stoichiometric at 20 at. %, is unstable within this approximation but may be favored if interactions up to the fourth neighbor are included [13]. Ni_4Mo ordering was observed in PdD_x, where likewise an ordering phenomenon of deuterium atoms and vacancies occurs on octahedral interstices of a fcc lattice.[14]

The present observation of DO_{22} $(I4/mmm)$ ordering within a wide concentration range therefore indicates that in TbD_{2+x} the ordering is governed by interactions between first and second neighbors. The ordered state in TbD_{2+x} corresponds to a configuration where a deuterium atom is exclusively surrounded by vacant interstices (Fig. 4). The ordered state in TbD_{2+x}, therefore, reflects the presence of a repulsive interaction between the x deuterium atoms located on octahedral sites of the fcc lattice.

These results further show that the ordering tendency in TbD_{2+x} is quite similar to that found in the light rare-earth hydrides: In CeD_{2+x} the ordering is characterized by $[1,\frac{1}{2},0]$ wave vectors over the entire concentration range of the solid solution phase. Likewise, in $LaH_{2.8}$ the proposed Ni_4Mo structure is related to hydrogen ordering on (420) planes. In all these systems the ordering temperatures are even within the same temperature range. Therefore, we can conclude that although the phase diagram of light and heavier rare-earth-hydrogen compounds differ considerably, the ordering tendencies seem to be essentially similar.

In summary, we have experimentally established a phase diagram for the TbD_{2+x} system. The ordered state is characterized by a DO_{22} $(I4/mmm)$ structure revealing a repulsive deuterium-deuterium interaction between the deuterium atoms located on octahedral interstices.

Our work was partly supported by the Fonds zur Förderung der Wissenschaftlichen Forschung in Austria.

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[*] Also at Laboratoire des Solides Irradiés, Ecole Polytechnique, F-91128, Palaiseau, France, April 1992.

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