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Specific heats of $NbH_{0.87}$ and $NbH_{0.90}$ in the temperature range 80–430 K

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Abstract

The specific heats of $NbH_{0.87}$ and $NbH_{0.90}$ were measured in the temperature range 80–430 K and the temperatures of the transitions between α', β, λ and γ phases were established. The reduced entropy changes Δs at the phase transitions for both materials and the Debye temperatures θ_D for $NbH_{0.90}$ were evaluated. The values of the activation energy E_{act} of hydrogen diffusion for $NbH_{0.87}$ and $NbH_{0.90}$ and their temperature dependence were estimated.

1. Introduction

The niobium hydride NbH_x, with hydrogen concentration $x = 0.7$–1.0, gives rise to several phases of different structure as a function of temperature [1]. The phase diagram of this system is presented in Fig. 1 [2]. The high-temperature α' phase (above approximately 420 K) is an unordered hydrogen solution in the b.c.c. niobium lattice. In this α' phase hydrogen atoms are randomly distributed among tetrahedral interstitial sites (TIS) of the basic metal lattice. On cooling the compound transforms to a face-centred orthorhombic β phase, where hydrogen atoms are located at specified TIS in the (110) planes of the metal lattice.

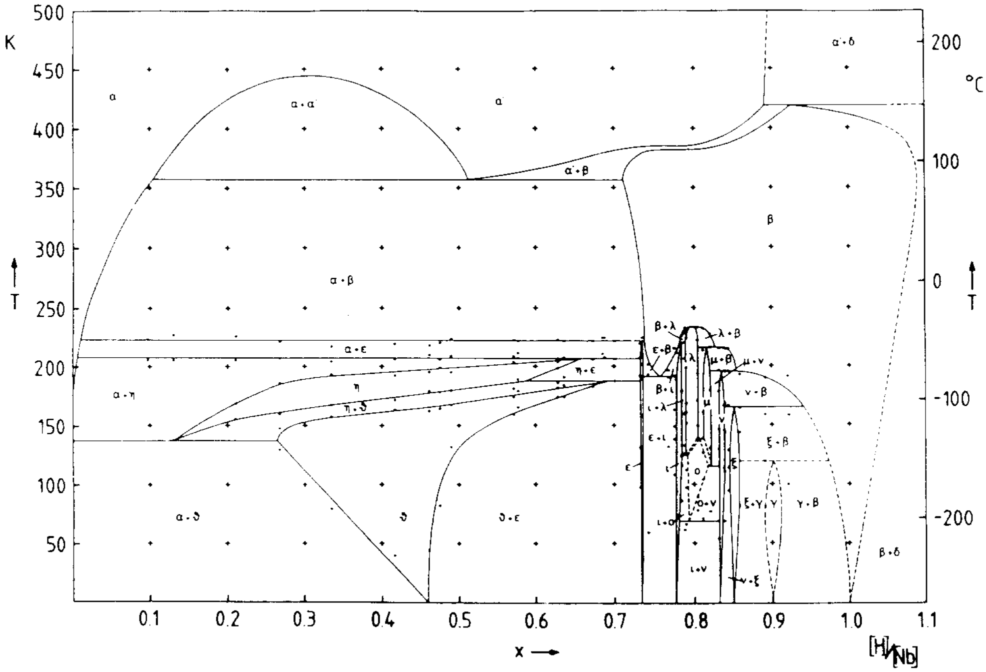

Fig. 1. Phase diagram of the NbH_x system [2].

It is assumed that the probability of the occupation of TIS by hydrogen atoms in the β phase is proportional to the concentration [3]. However, microcalorimetric investigations of NbH$_x$ have revealed a strong increase in the entropy changes $\Delta s(x)$ at the $\beta \rightarrow \alpha'$ phase transition above the critical hydrogen concentration $x_c \approx 0.82$ [4]. This is clearly interrelated with a higher degree of ordering in the hydrogen sublattice of the β phase for $x > x_c$ [5].

In a composition range with $x < 1$ in the β-phase of the NbH$_x$ system there are vacancies in the hydrogen sublattice. On cooling below the temperature of approximately 230 K, the compound undergoes a $\beta \rightarrow \lambda$ or $\beta \rightarrow \gamma$ phase transition, which can be interpreted as resulting from a reordering of hydrogen atoms (order I → order II). The temperatures of these transitions strongly depend on the hydrogen concentration.

The existence of a long-range superstructure in the $(001)_c$ direction of the basic niobium lattice in the λ phase was shown by electron diffraction experiments on NbH$_x$ foils [3]. Our knowledge so far is limited to the fact that the γ phase is pseudocubic [1].

The low-temperature phase transitions have been studied using resistivity measurements [6], differential thermoanalysis [1] and ultrasound absorption [7]. On the basis of these studies the limits of the existence regions of the β, λ and γ phases have been established.

Investigation of these phase boundaries using specific heat measurements has not been reported previously. Only two papers have reported the calorimetry of niobium–hydrogen compounds at low temperatures [8, 9]. The specific heat $C_p(T)$ of NbH$_{0.883}$ powder was measured in the temperature interval 21–386 K, but the low-temperature phase transition $\lambda \rightarrow \beta$ was not reported [8]. In another study [9] the electronic specific heat coefficient γ_e (approximately 2 mJ mol^{-1} K^{-2}) and the Debye temperature θ_D (approximately 352–360 K) were derived from specific heat data of the NbH$_x$ system for $x = 0.79$, 0.83 and 0.91 in the temperature range 1.5–16 K (no significant differences in γ_e and θ_D between λ and γ phases were observed at low temperatures). Thus it is of interest to investigate in detail the character of the specific heat of NbH$_x$ compounds over a wide range of temperature, in particular in the regions of existence of the α', β, λ and γ phases, to determine the low-temperature phase boundaries, the entropy changes Δs at the phase transitions and θ_D of these phases.

2. Experimental details

Samples of NbH$_x$ were prepared in the shape of cylinders with a diameter of approximately 4 mm and a height of about 4–5 mm. The methods of hydrogenation of niobium and the composition determination, with a precision of about 1%, are described in detail in ref. 10. Specific heat measurements were carried out in a fully automated adiabatic calorimeter [11] using both heat pulse (temperature step, 1 K) and continuous heating (heating rate, 5–10 mK s^{-1}) methods. The absolute accuracy of the measurements was ±1.5% and the resolution 1%. The masses of the NbH$_{0.87}$ and NbH$_{0.90}$ specimens were 224 mg and 853 mg respectively.

3. Results and discussion

The specific heat data of the investigated compounds are presented in Fig. 2. The peaks related to phase transitions are clearly visible. Because of their large magnitude some of the them are shown separately. The high-temperature peaks attributed to a $\beta \rightarrow \alpha'$ phase transition are presented in Fig. 3. Figure 4 shows two differently shaped peaks for the NbH$_{0.87}$ sample. According to the phase diagram (Fig. 1) they are related to the phase transitions $\lambda + \gamma \rightarrow \lambda$ and $\lambda \rightarrow \beta$. Figure 5 shows the $\gamma \rightarrow \beta$ phase transition for the NbH$_{0.90}$ sample.

Using the standard method, on the basis of $C_p(T)/T$ curve, the reduced entropy jumps $\Delta s = \Delta S/R$ at the phase transition temperatures were evaluated, where R (J mol^{-1} K^{-1}) is the gas constant. All the results are compiled in Table 1.

Let us discuss the results. Firstly, both the upper and lower limits of the $\beta \rightarrow \alpha'$ phase transitions agree well with the phase diagram of the NbH$_x$ system (Fig. 1). The limits of the $\lambda \rightarrow \beta$ and $\gamma + \lambda \rightarrow \lambda$ phase transitions for NbH$_{0.87}$ and of the $\gamma \rightarrow \beta$ transition for NbH$_{0.90}$ have been determined more accurately in the present study. Secondly, the entropy changes Δs are significantly lower at the low-temperature phase transitions than at

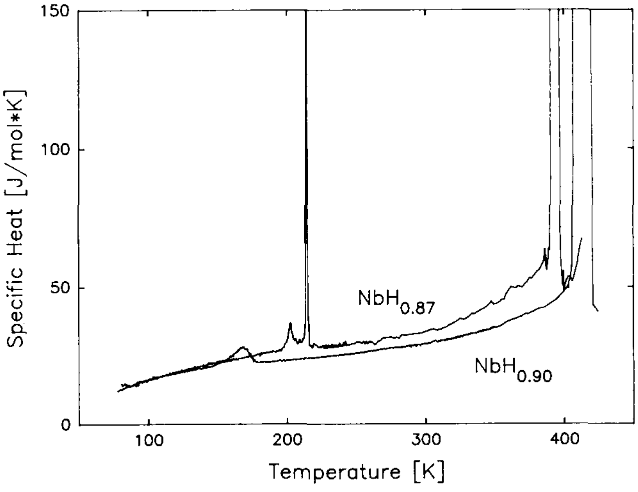

Fig. 2. Specific heat $C_p(T)$ of NbH$_{0.87}$ and NbH$_{0.90}$ samples. Some of the phase transition peaks are cut because of their magnitude.

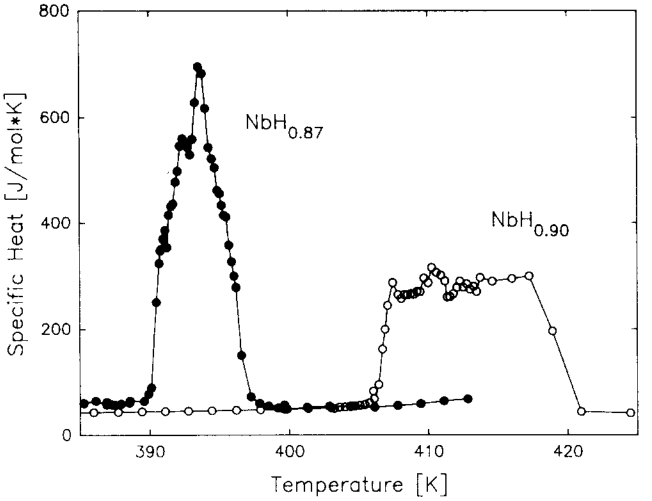

Fig. 3. $C_p(T)$ for $NbH_{0.87}$ (●) and $NbH_{0.90}$ (○) samples in the region of the $\beta \rightarrow \alpha'$ phase transition.

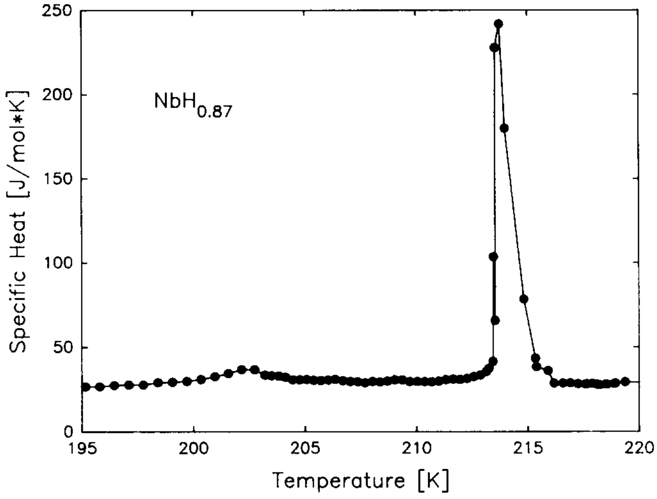

Fig. 4. $C_p(T)$ for $NbH_{0.87}$ in the region of $\lambda+\gamma \rightarrow \lambda$ (202.5 K) and $\lambda \rightarrow \beta$ (213.5 K) phase transitions.

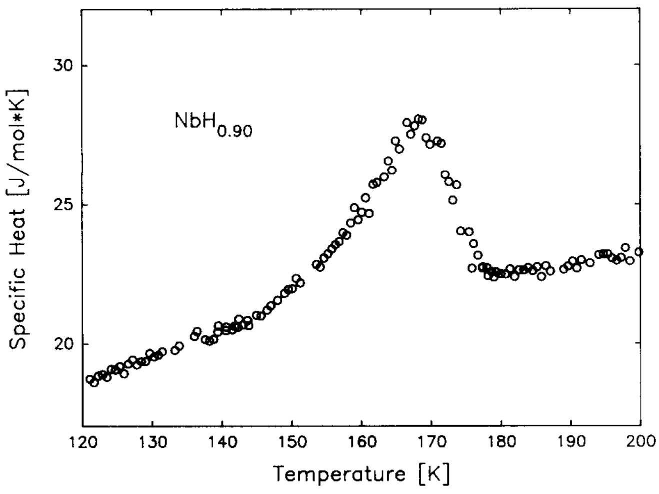

Fig. 5. $C_p(T)$ for $NbH_{0.90}$ in the region of the $\gamma \rightarrow \beta$ phase transition.

TABLE 1. Reduced entropy changes Δs at the phase transition temperatures

Compound	Transition	Temperature (K)	ΔT (K)	Δs
$NbH_{0.87}$	$\lambda \rightarrow \beta$	213–216	3	0.109
	$\gamma+\lambda \rightarrow \lambda$	195–208	13	0.0272
	$\beta \rightarrow \alpha'$	385.5–398	12.5	0.792
$NbH_{0.90}$	$\gamma \rightarrow \beta$	142–180	38	0.0638
	$\beta \rightarrow \alpha'$	403–421	18	0.885

the $\beta \rightarrow \alpha'$ transition. In the case of $NbH_{0.90}$ they are lower by one order of magnitude. Lastly, the Δs values at the $\beta \rightarrow \alpha'$ transition are in accordance with the data form ref. 4.

The experimental data of $C_p(T)$ were fitted by a calculated curve in order to evaluate the Debye temperature θ_D of the γ and β phases. The specific heat of the NbH_x system can be described by the equation

$$C_p = C_{el} + C_{opt} + (C_p - C_v) + C_{latt} \qquad (1)$$

where the linear electronic term $C_{el} = \gamma_{el} T$ and $\gamma_{el} \approx 2 \times 10^{-3}$ J mol^{-1} K^{-2} for both investigated materials [9]. The quantity C_{opt} represents the contribution of the optical vibrations of hydrogen. This contribution can be described by the sum of Einstein functions. In the NbH_x system the Einstein frequencies of the hydrogen subset are $\theta_{E1} \approx 1400$ K and, twice degenerated, $\theta_{E2} \approx 1900$ K [1]. The term $(C_p - C_v)$ is usually small enough to be neglected. For instance, for $NbH_{0.90}$ at 200 K $(C_p - C_v)/C_p = 0.3\%$, where $(C_p - C_v) = (3\alpha)^2 BVT$, the coefficient of linear expansion $\alpha = 4 \times 10^{-6}$ K^{-1} [12], the compression modulus $B = 198 \times 10^9$ J m^{-3} [13] and the molar volume $V = 12.53 \times 10^{-6}$ m^3 mol^{-1} [1]. The lattice contribution C_{latt} was extracted for the calculation of θ_D on the basis of the Debye model.

For $NbH_{0.90}$ the best agreement of the calculated curve with the experimental data was achieved for $\theta_D = 312 \pm 2$ K in the temperature interval 89–137 K, *i.e.* for the γ phase, and for $\theta_D = 290 \pm 2$ K in the range 185–231 K, *i.e.* for the β phase. The experimental results for $T > 231$ K deviate markedly from the calculated curve for the β phase.

For the $NbH_{0.87}$ sample in the temperature interval 90–111 K, *i.e.* in the region of coexistence of the λ and γ phases, the calculated curve with $\theta_D = 312 \pm 3$ K shows the best agreement with the measured $C_p(T)$ data. At higher temperature the specific heat is increasing so rapidly that it is impossible to fit it by any Debye function with the θ_D parameter taken as 200–400 K.

We emphasize that the difference between the specific heat values of the $NbH_{0.87}$ and $NbH_{0.90}$ materials is very reasonable for $T > 111$ K. In the β phase field, at

$T=250$ K, the specific heat of $NbH_{0.87}$ is 13% higher than that of $NbH_{0.90}$, whereas the difference in hydrogen content is only 3%. Our results are presented in Table 2 and agree well with the data from ref. 8. Around the composition range of the three samples presented it is possible to notice a tendency of a reduction in C_p in the β phase with increasing hydrogen content. It would be interesting to find the composition limit of this anomalous behaviour by measuring the specific heat of NbH_x samples with smaller x.

The temperature dependence of the specific heat of NbH_x with $x=0.87$–0.9 is not clear. We suggest the following explanation. We assume that, on heating above a certain temperature, which depends on the sample composition, an additional contribution to the specific heat appears. This effect has been described as a supplementary term to eqn. (1), ΔC_p, which may be attributed to the formation of vacancies in the hydrogen sublattice and to hydrogen diffusion by a vacancy mechanism. In ref. 14 the excess part of the specific heat of Ta_2D above a calculated curve was used to evaluate the activation energy E_{act} of hydrogen diffusion at $T>200$ K. Following that method we also prepared a plot of $\ln(\Delta C_p T^2)$ against T^{-1} (Fig. 6). A series of straight lines were obtained, the slopes of which can be ascribed to E_{act}/k_B, where k_B (J K^{-1}) is the Boltzmann constant. For a calculated curve of $C_p(T)$ for $NbH_{0.87}$ in the β phase region, a Debye temperature $\theta_D=290$ K was assumed, the same as that measured for the $NbH_{0.90}$ sample. The calculated value of E_{act} for the investigated materials in different temperature intervals are shown in Table 3. However, these data should be treated as a rough approximation only. They may be significantly influenced by the diffusion of hydrogen atoms located on antistructural sites, *i.e.* out of the regular hydrogen sublattice [15].

TABLE 2. Specific heats of NbH_x

β phase ($T=250$ K)	C_p (J K^{-1} mol^{-1})
$NbH_{0.87}$	29.4
$NbH_{0.883}$	27.9 [8]
$NbH_{0.90}$	25.6

TABLE 3. Activation energies of hydrogen diffusion for $NbH_{0.87}$ and $NbH_{0.90}$

$NbH_{0.87}$	Temperature range	$NbH_{0.90}$	Temperature range
E_{act} (eV)	(K)	E_{act} (eV)	(K)
0.076	125–188		
0.086	238–271		
0.12	271–311	0.18	250–329
0.23	311–390	0.27	329–400

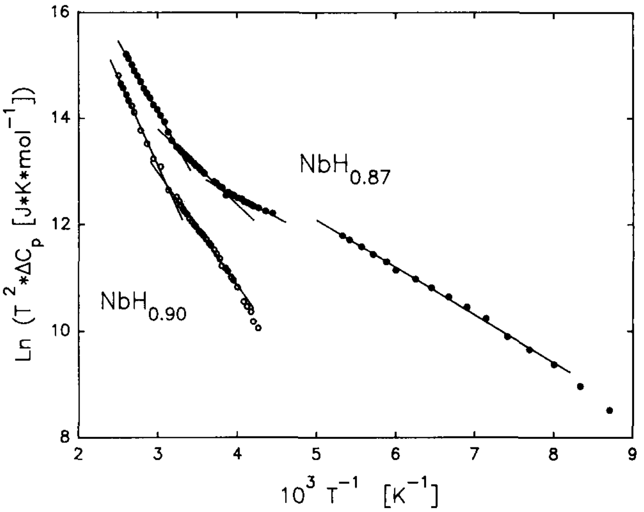

Fig. 6. Plot of $\ln(T^2\Delta C_p)$ *vs.* T^{-1} for $NbH_{0.87}$ (●) and $NbH_{0.90}$ (○) compounds. The slopes of the straight lines represent different activation energies E_{act} of hydrogen diffusion.

The C_p value of $NbH_{0.90}$ is not sensitive to hydrogen diffusion by a vacancy mechanism at $T<250$ K. Although our method of E_{act} evaluation is not direct, the calculated values are in good agreement with nuclear magnetic resonance (NMR) data: $E_{act}=0.24$ eV for the β phase of $NbH_{0.90}$ ($T=250$–330 K); $E_{act}=0.24$ eV for the β phase of $NbH_{0.78}$ [1].

If E_{act} of the investigated materials derived from calorimetric measurements is reliable, then the differences between the E_{act} values in the NbH_x system in the field of the β phase ($T>250$ K) are clearly related to the higher degree of ordering in the hydrogen sublattice in $NbH_{0.90}$ and to the stronger interaction of hydrogen atoms [5]. Steps in the temperature dependence of E_{act} could be interpreted as a manifestation of new mechanisms of hydrogen diffusion at elevated temperatures [16]. However, this conclusion should be corroborated by additional experiments.

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