

## Anomalies of elastic properties within the ordered $\beta$ -NbH<sub>x</sub> phase

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### Abstract

The monocrystalline and polycrystalline niobium hydrides  $\beta$ -NbH<sub>x</sub> were carefully investigated within the concentration range  $0.7 < x < 1$  at temperatures  $100 < T < 450$  K using the kHz frequency acoustic spectroscopy. It was found that within the temperature range of the  $\beta$ -phase (i.e. between the  $\alpha'$ - $\beta$  and  $\beta$ - $\varepsilon$  (or  $\beta$ - $\lambda$ ) transitions) temperature dependencies of the dynamic elastic modulus and the sound attenuation reveal some anomalies that suggest to the perturbation of the ordered hydrogen subsystem. These results are compared with the theoretical considerations predicting possible changes of equilibrium hydrogen concentrations in the two occupied sublattices of tetrahedral interstices.

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### 1. Introduction

#### 1.1. The system under consideration

In the b.c.c. N-site niobium lattice, the interstitial hydrogen atoms are preferentially distributed on the set of 6N tetrahedral interstices, forming six interpenetrating N-site b.c.c. lattices. In the hydrogen-rich NbH<sub>x</sub> alloys ( $0.7 < x < 1$ ) at high temperatures (in the region of  $\alpha'$ -phase) the H-atoms are distributed on the whole set of 6N tetrahedral interstitials, but below the  $\alpha'$ - $\beta$  transition temperature  $T_{\alpha'\beta}$  they are concentrated in two N-site sublattices [1,2]. It was established that in each occupied interstitial sublattice (denoted as sublattices 1 and 2) the ordered configurations of H-atoms are associated with two different superstructure wave vectors [1,2] and described [3] by a distribution function  $n(x,y,z; j)$  containing two long-range-order (LRO) parameters,  $\eta_1(j)$  and  $\eta_2(j)$ , ( $j = 1, 2$ ):

$$\begin{aligned} n(x,y,z; j) = & c(j) + \eta_1(j) \gamma_1 \exp[i\pi(x+y)] \\ & + \eta_2(j) \gamma_2 [\cos \pi x + \sin \pi x + \cos \pi y \\ & - \sin \pi y] \end{aligned} \quad (1)$$

Here  $n(x,y,z; j)$  is the probability that the site with coordinates  $(x,y,z)$  in the  $j$ -th b.c.c. sublattice will be occupied by a hydrogen atom;  $c(j) \equiv (N(j)/N)$  is hydro-

gen concentration in  $j$ -th sublattice ( $N(j)$  is the number of occupied sublattice sites);  $\eta_1(j)$  and  $\eta_2(j)$  are the static concentration wave amplitudes playing the role of LRO parameters;  $\gamma_1 = 0.25$  and  $\gamma_2 = 0.5$  are normalizing constants restricting the  $n(x,y,z; j)$  values within the range  $0 \leq n(x,y,z; j) \leq 1$  [3].

In the case of NbH<sub>x</sub> ( $0.7 \leq x < 1$ ) the hydrogen ordering is a two-step process: below the disorder–order transition temperature  $T_{\alpha'\beta}$  there is formed the  $\beta$ -phase—an equilibrium partially ordered state ( $\eta_1(j) \neq 0$ ,  $\eta_2(j) = 0$ ), characterized by equal occupancy of two sublattices:  $c(1) = c(2) = (x/2)$ , which is replaced at the order–order transition point  $T = T_{II}$  by a different ordered configuration: ( $\eta_1(i) \neq 0$ ,  $\eta_2(i) \neq 0$ ), characterized by unequal occupancy of two sublattices [1–3]. Particularly, in NbH<sub>0.75</sub> the low-temperature limit ordered state corresponds to sublattice concentrations:  $c(1) = 0.25$ ,  $c(2) = 0.5$  [3]. It is implied usually that hydrogen redistribution between sublattices [ $c(1) = c(2)$ ]  $\rightarrow$  [ $c(1) \neq c(2)$ ] coincides with the order–order transformation [3] and does not reveal itself as a separate phase transition.

#### 1.2. The problem under consideration

The phase diagram of NbH<sub>x</sub> system was considered to be known very well; particularly, in the concentration range  $0.75 < x < 1.0$  [4–6]. There were some doubts concerning the type of hydrogen ordering in the low-tempera-

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ture limit [5,6], but it was implied to be established [1–6]: (a) that the ordering is a two-step process containing the disorder–order and order–order phase transitions, and (b) that no additional perturbations exist within the temperature range of the  $\beta$ -phase. On the other hand, calculations have shown [7] (and more precisely in Ref. [8]) that in suitable conditions (for some special sets of the ordering system energy parameters) transformation  $[c(1)=c(2)]\rightarrow[c(1)\neq c(2)]$  can occur *above* the order–order transition point  $T_{II}$ , i.e. within the temperature range of  $\beta$ -phase. At the same time, the acoustic investigations of niobium hydrides [9,10] have revealed a number of perturbations within the  $\beta$ -phase of the system. In these circumstances it was interesting to obtain some additional experimental information concerning the hydrogen behavior within the temperature range of  $\beta$ -phase using the method of low-frequency acoustic spectroscopy.

## 2. Experimental

### 2.1. Samples

According to the manufacturer the polycrystalline and monocrystalline niobium samples had a purity of 99.98%.  $[11\times 3\times 0.8]$  mm niobium plates with two longitudinal slits dividing the plate into three blades (in the shape of a capital E) were spark-cut. Lateral blades served to fasten the specimen in a massive block holder, while the third blade represents the vibrator oscillating in transverse vibration mode.

### 2.2. Hydrogenation

The Nb specimens were loaded with hydrogen-gas at about 700–750 °C at the pressure 0.13–0.15 MPa. On reaching hydrogen concentrations  $x\geq 0.7$ , the samples were gradually cooled ( $\sim 10^\circ\text{C h}^{-1}$ ) and the  $(\alpha'-\beta)$  boundary line was crossed very slowly. Along this loading process trajectory the  $(\alpha+\alpha')$  biphasic region was avoided (see Nb–H phase diagram in Ref. [4]). We investigated monocrystalline samples  $\text{NbH}_x$  ( $x=0.74, 0.8, 0.83$ ) and a polycrystalline sample  $\text{NbH}_{0.91}$ .

The  $\alpha'$ -phase is cubic, while hydrogen ordering in the  $\beta$ -phase is accompanied by the distortions of the metal lattice, and on crossing the  $(\alpha'-\beta)$  boundary line the antiphase domains are formed (in the monocrystalline samples as well as within the grains of polycrystals). The motions of antiphase domain boundaries (the ‘domain walls’) are responsible for sound attenuation in the kHz range.

### 2.3. Apparatus

Standard scheme of acoustic experiments [11] was applied. The specimens mounted in the block holder were

placed into a thermostat. The natural-frequency of the acoustic resonator was  $\approx 1\text{--}1.5$  kHz. The equipment’s details are described elsewhere [9,10,12].

### 2.4. Measurements

The measurements were performed within the temperature range 150–450 K in the process of slow heating ( $0.1\text{--}0.5^\circ\text{C min}^{-1}$ ). The results of sound attenuation are presented in units of inverse quality factor of the acoustic resonator,  $Q^{-1}$ , while those of dynamic elastic modulus—in units of the resonance frequency square,  $\nu^2$ .

## 3. Results

### 3.1. Monocrystalline niobium hydride $\text{NbH}_{0.83}$

In Fig. 1 are given temperature dependencies of the dynamic elastic modulus (Fig. 1a) and sound attenuation (Fig. 1b and c) measured within the temperature range 280–390 K.

Temperature dependence of dynamic elastic modulus manifests a sharp anomaly in the temperature region 310–350 K (Fig. 1a). This anomaly is reflected as well in the temperature dependence of sound attenuation (Fig. 1b), though the effect is not so pronounced as in the case of elastic modulus (Fig. 1c).

It is known [4–6] that the hydride  $\text{NbH}_x$ , for  $x\sim 0.8$ , undergoes a disorder–order transition at  $T=T_{\alpha'\beta}\sim 390$  K and an order–order transition at  $T=T_{II}\sim 210$  K. Thus, the observed anomalies of elastic properties are within the temperature range of the  $\beta$ -phase.

Analogous anomalies in the temperature dependencies of the dynamic elastic modulus and sound attenuation were registered as well in the monocrystalline hydrides— $\text{NbH}_{0.74}$  (at temperatures  $\sim 290\text{--}360$  K) and  $\text{NbH}_{0.8}$  (at temperatures  $\sim 315\text{--}350$  K).

### 3.2. Polycrystalline niobium hydride $\text{NbH}_{0.91}$

In the polycrystalline sample, the mentioned above anomalies of the elastic modulus and sound attenuation appears after additional introduction of some strains by crossing the order–disorder transition point during the first slow heating. But these anomalies disappear after a number of temperature cycling which include subsequent crossing of the order–disorder transition point. In Fig. 2a are presented the temperature dependencies of the dynamic elastic modulus obtained during the first heating and crossing the order–disorder point (curve a), in the process of second heating (curve b) and after a number of subsequent heatings (curve c). In Fig. 2b are shown the corresponding sound attenuation curves (notations of the curves are the same as in Fig. 2a). It is significant that the

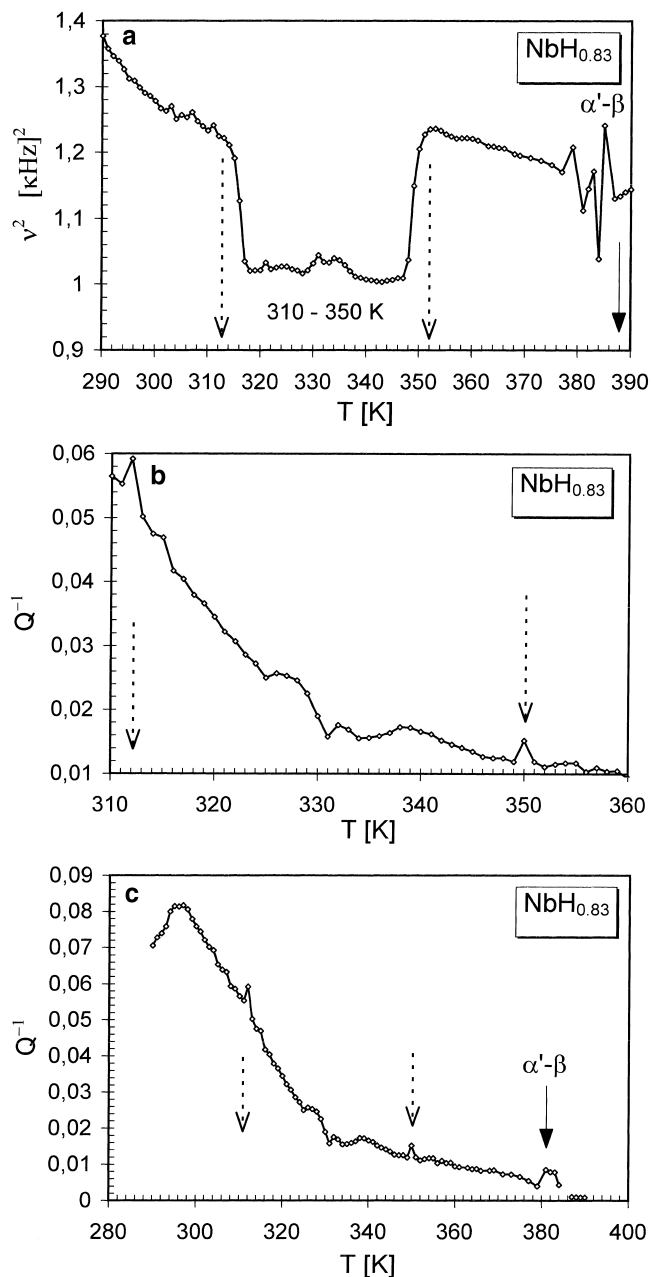


Fig. 1. Temperature dependencies of elastic modulus and sound attenuation in monocrystalline  $\text{NbH}_{0.83}$ . Dashed arrows indicate the temperature range of the elastic modulus anomaly (310–350 K). The solid arrow denotes the  $(\alpha' - \beta)$  disorder–order transition temperature ( $T_{\alpha'\beta} \approx 380$  K). (a) Temperature dependence of the elastic modulus; (b) temperature dependence of sound attenuation in the temperature range of the anomaly; (c) the whole curve of sound attenuation.

local maxima accompanying the elastic modulus anomaly exist only on the curve b.

In Fig. 3 are compared the sound attenuation curves collected from Fig. 1c (indicated as ' $x=0.83$ ') and Fig. 2b (indicated as curves a, b and c) associated with monocrystalline  $\text{NbH}_{0.83}$  and polycrystalline  $\text{NbH}_{0.91}$  samples, respectively.

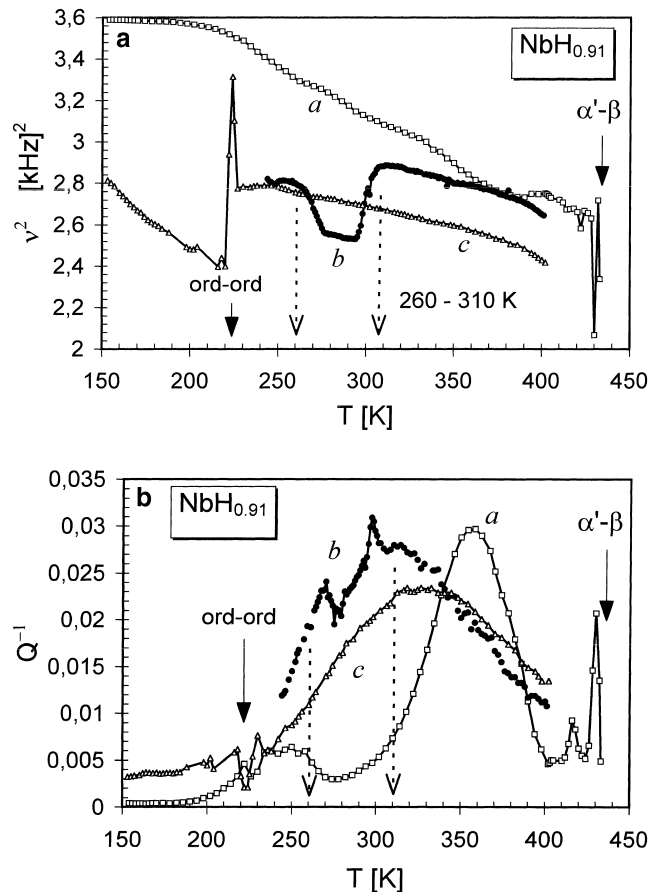


Fig. 2. Temperature dependencies of elastic modulus and sound attenuation in polycrystalline  $\text{NbH}_{0.91}$ . Dashed arrows indicate the temperature range of the elastic modulus anomaly (260–310 K). Solid arrows denote the  $(\alpha' - \beta)$  disorder–order  $T_{\alpha'\beta}$  and order–order  $T_{II}$  transition temperatures ( $T_{\alpha'\beta} \approx 430$  K;  $T_{II} \approx 220$  K). (a) First heating; (b) second heating; (c) after a number of temperature cycling. (a) Temperature dependencies of elastic modulus; (b) temperature dependencies of sound attenuation.

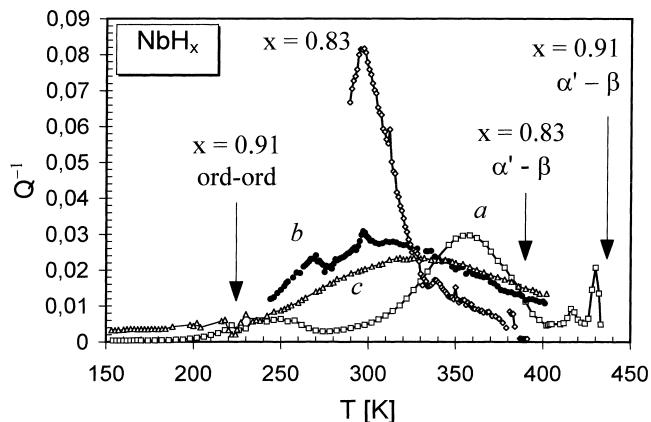


Fig. 3. Temperature dependencies of sound attenuation in the monocrystalline  $\text{NbH}_{0.83}$  (indicated as ' $x=0.83$ ') and polycrystalline  $\text{NbH}_{0.91}$  (in accordance with Fig. 2b indicated as a, b, c). Solid arrows denote transition temperatures (repeating notations in Figs. 1 and 2).

### 3.3. Additional information

From model calculations [7] it followed that in the system described by the distribution function (1), and particularly in the case of Nb–H hydrides, the disorder–order transformation should be *continuous* (of the second-order-type). The experimental results [9,10], in accordance with other measurements [4], had shown that this transformation is *discontinuous* (of the first-order-type)—it contains a bi-phase ( $\alpha' + \beta$ ) region. The latter conclusion was confirmed in the present measurements as well.

## 4. Discussion and conclusions

### 4.1. Discussion of the order of ( $\alpha' - \beta$ ) transition

The contradiction between the theory [7] and experimental data [9,10] concerning the order of ( $\alpha' - \beta$ ) transition in niobium hydrides illuminates the role of *lattice distortions* accompanying the redistribution of hydrogen atoms, which were not accounted in theoretical consideration. The energy  $\delta E$  spent on lattice distortions is registered as the latent heat of hydrogen transitions and it should be considered as the measure of interrelations between the ordering hydrogen subsystem and the host lattice.

### 4.2. Location of elastic property anomalies on the temperature scale

The disorder–order ( $\alpha' - \beta$ ) and the low-temperature order–order transition points are revealed in our curves by specific anomalies located at corresponding temperatures  $T_{\alpha'\beta}$  and  $T_{II}$  in accordance with the published Nb–H phase diagram [4]. In the monocrystalline and polycrystalline samples the elastic modulus anomalies are located between  $T_{\alpha'\beta}$  and  $T_{II}$ , i.e. inside the  $\beta$ -phase region. Transition points are indicated in the figures by solid arrows and the temperature limits of the anomaly—by dashed arrows (The order–order transition point we denoted as  $T_{II}$  because at different concentrations, below  $T_{II}$ , there can be formed  $\varepsilon$ -,  $\lambda$ -, or  $\gamma$ -phases, respectively [5,6]).

### 4.3. The reasons of the elastic anomalies (tentative explanation)

The  $\beta$ -phase is usually considered as characterized by the equal occupation of two interstitial sublattices by hydrogen atoms. But it was demonstrated [8] that in the case of the suitable values of the energy constants describing the H–H interactions, it can occur that below some temperature  $T_{rd}$  the equilibrium state of the hydrogen subsystem will be associated with a non-equal occupation of the sublattices. If in the hydrides under consideration the conditions ( $T_{\alpha'\beta} > T_{rd} > T_{II}$ ) are satisfied, then within the

$\beta$ -phase, at  $T \sim T_{rd}$ , we shall have a temperature region where the hydrogen equilibrium ordered distribution becomes unstable providing augmented mobility of hydrogen atoms. As a result, the bonds between the metal atoms and hydrogens are weakened, the lattice distortions and the strains are reduced, and this situation is revealed as the lattice softening within the temperature range where neither the ‘high-temperature’ ( $T > T_{rd}$ )  $c(1) = c(2)$  state, nor the ‘low-temperature’ ( $T < T_{rd}$ )  $c(1) \neq c(2)$  state, can not have a decisive superiority.

Thus, the sharp reduction of the elastic modulus within a restricted temperature range we try to associate with the augmented hydrogen mobility caused by the change of the equilibrium occupation of sublattices.

It have to be noted that as the redistribution of hydrogen atoms between the sublattices is not accompanied by a significant change of the equilibrium ordering within sublattices, it is sufficiently difficult to register this effect in neutronographical experiments.

### 4.4. Reproducibility of the observed effects

Investigation of the polycrystalline NbH<sub>0.91</sub> have shown, that at the first heating the temperature dependence of elastic modulus reflects the decreasing of the order parameter  $\eta_1(T)$  (curve a in Fig. 2a). The effect of lattice softening reveals itself only during the second heating (curve b in Fig. 2a), after crossing the ( $\alpha' - \beta$ ) transition point (in the previous heating), when some local (plastic) deformations are introduced in the host lattice. The subsequent temperature cyclings and introduction of new local deformations suppress the anomalous softening of the lattice and again we observe a continuous softening caused by the decreasing of the order parameter  $\eta_1(T)$  (Fig. 2a, curve c). In the case of monocrystalline samples after temperature cyclings the anomaly is reduced but still exists. Thus, we conclude that in the polycrystalline sample the anomalous softening exists only when the lattice contains a *restricted number* of local deformations. The origin of different behavior of monocrystalline and polycrystalline samples we can not explain.

### 4.5. The acoustic wave's energy dissipation

The energy dissipation processes in the hydrides NbH<sub>x</sub>, TaH<sub>x</sub> etc. are considered usually to be caused by the reorientation of the ‘solute atom–hydrogen’ pairs, or by hydrogen motions with respect to the host lattice (see, respectively, Refs. [13] and [14]). In our case of the low-frequency acoustic waves the main part of the energy dissipation seems to be associated with the *oscillations of antiphase domain walls* [9,10]. This conclusion follows from the comparison of the sound attenuation intensity in monocrystalline and polycrystalline samples (Fig. 3), and basing on the deformations of attenuation curves during the temperature cycling (see Fig. 2b). It is supported as

well by the disappearance of the attenuation in the  $\alpha'$ -phase.

## 5. Conclusions

The elastic property anomalies, observed in  $\text{NbH}_x$  samples as sharp softening of the host lattice within a restricted temperature region of the  $\beta$ -phase, are associated with the motion of antiphase domain walls and are induced by the hydrogen redistribution between the two occupied sublattices *without any changes of the ordering type in each of sublattices*.

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