THE EFFECTS OF HYDROGEN ON THE SINGLE CRYSTALLINE
ELASTIC CONSTANTS OF NIOBIUM

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M.S. Thesis Submitted to Iowa State University

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Date Transmitted: June 1977

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TABLE OF CONTENTS

Abstract	Page iv
INTRODUCTION	1
Crystal Elasticity	4
EXPERIMENTAL PROCEDURE	6
Sample Materials	6
Sample Preparation	6
Instrumentation	12
Ultrasonic	12
Hydriding system	14
RESULTS	20
DISCUSSION	25
BIBLIOGRAPHY	35
ACKNOWLEDGMENTS	37

The effects of hydrogen on the single crystalline
elastic constants of niobium

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SUMMARY

A special hydriding system was designed and constructed to satisfy conditions for hydriding niobium. This system controlled the temperature and hydrogen atmosphere surrounding the niobium while ultrasonic measurements were recorded. Ultrasonic wave velocities were determined by measurement of the times for ultrasonic pulses to transit and then echo through known dimensions of test specimens. The method which was employed is commonly known as the pulse-echo-overlap method.

This study confirmed the general trends of earlier investigations (8,9). In this study C' continued to decrease and C_{44} continued to increase up to 4.69 atomic percent hydrogen which is the maximum concentration which has yet been examined. In the case of the niobium-hydrogen system the Snoek effect may well be a contributory factor to the decrease of C' with increasing hydrogen concentration. However, crystallographic considerations preclude this effect from contributing a concentration dependence to C_{44} or B . The observation of the present work implies that other factors must also be contributing to the overall behavior.

The effects of hydrogen on the single crystalline
elastic constants of niobium

by

Daniel Michael Schlader

A Thesis Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
MASTER OF SCIENCE

Department: Materials Science and Engineering

Major: Metallurgy

Approved:

J.F. Smith
In Charge of Major Work

For the Major Department

For the Graduate College

Iowa State University
Ames, Iowa

1977

INTRODUCTION

The phase relationships in the niobium-hydrogen system have been the subject of a number of investigations (1-4). Interest in this system has increased since the idea of a controlled thermonuclear reactor (CTR) was first formulated. A major problem in the development of a CTR is finding a satisfactory 'first-wall' material, and niobium has become a good prospect for the first wall of a CTR.

Niobium has a body-centered cubic (BCC) crystal structure of the Strukturbericht A2 type with space group symmetry $Im\bar{3}m$. In this structure the niobium atoms are located at the equivalent positions $(000, 1/2 \ 1/2 \ 1/2)$. Hydrogen diffuses into this BCC structure interstitially. Various studies (5-7) have concluded that the hydrogen atoms settle in the tetrahedral sites $(1/2 \ 1/4 \ 0)$ of the BCC niobium (Figure 1).

A phase diagram after Schober et al. [2] is shown in Figure 2 for the region of interest to the present investigation. A solid immiscibility gap may be noted in this diagram. This gap limits the study of the BCC structure to a concentration of $3.68 \pm .24$ atomic percent hydrogen at 298 K (4). Above this concentration a second phase appears and this phase has a distorted BCC structure. To avoid this second phase, when studying niobium-hydrogen at concentrations greater than 3.68 atomic percent, the study must be done above room temperature.

TETRAHEDRAL POSITIONS IN A BCC LATTICE

○ Nb
• H

Figure 1. Diagram of tetrahedral sites

Figure 2. Partial phase diagram for the NbH system

Past studies on the effects of hydrogen on the elastic constants of niobium single crystals were limited by this immiscibility gap. A study by Fisher, Westlake and Ockers (8) at 298 K showed that C' decreased with increasing hydrogen solute and that C_{44} increased with increasing hydrogen solute. Here C' and C_{44} are the two independent elastic shear constants. The hydrogen concentration in the Fisher investigation did not exceed 3.06 atomic percent.

A later study up to 2.46 atomic percent hydrogen by Magerl, Berre and Alefeld (9) confirmed the observations of Fisher et al. with respect to the hydrogen effects on C' and C_{44} . However, Magerl et al. extended the temperature range of measurement and found these effects to persist, qualitatively the same, up to at least 573 K. They also observed an isotope effect wherein a smaller change in C' was associated with niobium containing deuterium than with niobium containing an equivalent amount of hydrogen. The present investigation was undertaken to extend measurements to higher hydrogen concentrations.

Crystal Elasticity

Combination of Hooke's law and Newton's second law can be used to relate the elastic constants of a material to the velocities of ultrasonic wave propagation (10). A treatment of the elasticity theory and of the relationship of the elastic constants to ultrasonic velocities can be found in

Kittel (10). For cubic crystals with the $m\bar{3}m$ point group symmetry the number of independent elastic constants is three: C_{11} , C_{12} and C_{44} . Propagation of waves in the $[110]$ direction maximizes the resolution of the constants. The ultrasonic wave velocities are related to the three independent elastic constants in the following way,

$$\rho V_L^2 = \frac{1}{2}(C_{11} + C_{12} + 2C_{44}),$$

$$\rho V_{T[001]}^2 = C_{44},$$

and

$$\rho V_{T[1\bar{1}0]}^2 = \frac{1}{2}(C_{11} - C_{12}) = C',$$

where ρ is the crystal density, V_L is the longitudinal wave velocity, $V_{T[001]}$ is the velocity of the transverse wave polarized in the $[001]$ direction and $V_{T[1\bar{1}0]}$ is the velocity of the transverse wave polarized in the $[1\bar{1}0]$ direction.

EXPERIMENTAL PROCEDURE

Sample Materials

Niobium was obtained from the Naval Research Laboratories. This niobium was electron-beam melted into a disk and was additionally outgassed for one hour and twenty-five minutes at 6×10^{-6} torr. Table 1 shows an impurity analysis from Ames Laboratory, U.S. Energy Resources Development Administration: values in column one were obtained from spark source mass spectrometric analysis; values in column two from vacuum fusion analysis; and values in column three from carbon combustion analysis.

Palladium was used in this study to coat the niobium to obtain a 'permeable membrane' for hydrogen entry into the sample. The palladium was procured from Engelhard Industries Division of Carteret, New Jersey in the form of 50 mil wire. After the palladium was received it was electron-beam melted into a disk and outgassed for one hour at 10^{-7} torr to insure purity. The disk shape facilitated handling when the electron-beam process was used to coat the niobium. Hydrogen was introduced into the niobium single crystal by heating the palladium-coated crystal in a hydrogen atmosphere. The hydrogen was 99.998% pure (11).

Sample Preparation

The initial niobium disk was 1.25 inches in diameter and approximately 0.375 inches thick. This disk was cemented to

Table 1. Impurity content in ppm atomic of the niobium used in this investigation

Impurity	Spark source mass spectro- metric analysis	Vacuum fusion analysis	Carbon combustion analysis
H		645	
Li	<0.1		
Be	<0.002		
B	0.4		
C			62
N		112	
O		354	
F	<0.3		
Ne	0.1		
Na	0.7		
Mg	0.3		
Al	0.2		
Si	20		
P	<100		
S	<1		
Cl	3		
Ar	<0.4		
K	0.5		
Ca	2		
Sc	0.5		
Ti	5		
V	<0.04		
Cr	<0.09		
Mn	<0.2		
Fe	3		
Co	<0.05		
Ni	<0.07		
Cu	<0.2		
Zn	<0.04		
Ga	<0.05		
Ge	<0.08		
As	<0.02		
Se	<0.02		
Br	<0.1		
Kr	<0.3		
Rb	<0.02		
Sr	<0.06		
Y	<0.3		
Zr	9		
Mo	13		
Ru	<1		
Rh	<0.1		

Table 1. (Continued)

Impurity	Spark source mass spectro- metric analysis
Pd	<0.2
Ag	<0.2
Cd	<0.01
In	<0.03
Sn	<0.08
Sb	<0.01
Te	<0.4
I	<0.08
Xc	<1
Cs	<0.004
Ba	<0.04
Hf	19
Ta	770
W	300
Re	<0.5
Os	<0.7
Ir	<0.3
Pt	<0.4
Au	<0.08
Hg	<0.01
Tl	<0.06
Pb	<0.2
Bi	<0.05
Ra	<0.3
Th	16
U	<0.3
La	0.8
Ce	<1
Pr	<0.9
Nd	<0.5
Sm	<0.3
Eu	<0.2
Gd	<2
Tb	<0.7
Dy	<1
Ho	<0.7
Er	<0.6
Tm	<0.1
Yb	<0.4
Lu	<0.9

the head of a triple-axis goniometer with a mixture of Duco cement and graphite powder. The back reflection x-ray technique of Meyerhoff, Bailey and Smith (12) was used to determine the orientation of a [110] crystallographic direction. The goniometer was then adjusted so that two parallel faces normal to a [110] direction could be cut with a Sparcatron electromachining apparatus. After cutting, these two faces were hand-lapped on progressively finer metallographic polishing paper, finishing with 600 grit paper. After this lapping operation, the (110) faces were parallel to within ± 0.0003 cm. With a 'reference salt crystal' technique developed by Bailey and Greiner (13) the orientation of the [110] direction was again checked. The polished crystal faces were found to be within $\pm 1^\circ$ of being normal to the [110] direction.

A layer of palladium was electron-beam evaporated onto two opposing uncut faces of the crystal to form 'permeable membranes' on the niobium surface. Such use of palladium was suggested by H. Birnbaum (14) on the basis of his experience with niobium foils. After initial difficulties, a satisfactory palladium coat was obtained by first electropolishing the surface to be coated. Then the niobium crystal was mounted only a few inches from the palladium disk in an electron-beam apparatus which operated under a pressure of 10^{-7} torr. The electron-beam then heated the palladium disk which radiated heat to the niobium. Heating was done slowly

and incrementally in steps. This gave the niobium time to heat to sufficiently high temperatures to form a good bonding surface for the adhesion of palladium. After the palladium became molten the power of the beam was rapidly raised to cause the palladium to boil and spray onto the niobium surface. This process coated only the surface facing the palladium, thus no palladium came in contact with either of the two (110) faces.

After the palladium was applied to two of the crystal surfaces, the niobium single crystal was bonded to a fused silica buffer rod. The function of this buffer rod was to connect quartz transducers which were maintained at room temperature and atmosphere with the niobium sample which was maintained at elevated temperatures under a hydrogen atmosphere. Thus the bond between the crystal and the buffer rod had to withstand high temperatures and high hydrogen concentrations and still transmit both longitudinal and transverse sonic waves with little attenuation. Some success was achieved with water-glass bonds at temperatures below 483 K and with bonds made with a vacuum adhesive called Torr Seal (15) at temperatures below 373 K. However, it was desired to make measurements as high as 573 K and with a phenolic epoxy resin (16) suggested by E. S. Fisher (17) satisfactory bonds were obtained.

To prepare a phenolic epoxy resin bond, the crystal sur-

face and the rod surface were first cleaned with fresh acetone. Then a small drop of resin was placed on the top of the rod. A (110) face of the niobium crystal was positioned on the resin and the crystal was pressed against the buffer rod. At the same time a longitudinal wave was sent through the rod and into the crystal. When a satisfactory ultrasonic signal was obtained the bond was allowed to cure. A weight of at least 20 grams was kept in place on the upper (110) face of the crystal during curing. The curing consisted of heating to 363 K at a rate of two to three degrees per minute in an argon atmosphere. The argon was used to lessen the possibility of poisoning the palladium surface. The curing time was usually fifteen to eighteen hours. After the bond cured, the weight was removed. The buffer rod with the niobium single crystal was then inserted into the hydriding system. There the crystal was heated in a vacuum of 10^{-3} torr to the temperature of measurement at a rate of two degrees per minute.

When the temperature of measurement was reached, hydrogen was introduced into the system. While the hydrogen was diffusing into the niobium single crystal, three transit times were monitored sequentially, the transit times of two shear waves and one longitudinal wave. Changing hydrogen concentrations were reflected in changing transit times. After two days time the longitudinal wave became distorted and the transit time was no longer recorded. As the hydrogen

concentration neared equilibrium, the two shear transit times tended toward constancy, and at equilibrium, the transit times remained unchanged within the precision of measurement. These times were recorded and the crystal was removed from the system and analyzed.

Instrumentation

Ultrasonic

Ultrasonic wave velocities were determined by measurement of the times for ultrasonic pulses to transit and then echo through known dimensions of test specimens. The method which was employed is commonly known as the pulse-echo-overlap method. This method of measurement was first described by May (18) and Papadakis (19) and modifications were added by Chung, Silversmith and Chick (20). A description of the present system has been presented by Eshelman (21).

This system consists of the following components: a counter, a pulse-generator, an oscilloscope, a repetition-rate oscillator, a pulsed oscillator, a frequency divider and a limiter. With this system an ultrasonic pulse is sent through a specimen and returning echoes reverberate in the specimen. The transit time t between successive echoes is measured by matching the period $1/f$ of the repetition-rate oscillator to the transit time. This is accomplished by adjusting the frequency of the repetition-rate oscillator and then measuring the frequency. The repetition-rate oscillator

then drives the oscilloscope at frequency f to paint echoes on the screen. Successive echoes appear on consecutive sweeps of the oscilloscope and fine adjustment produces precise overlap of the echo traces.

To determine the individual elastic constants the appropriate velocities of the crystal were measured. By using the transit times of the pulse-echo-overlap system, the velocities were calculated thusly

$$v = \frac{2d}{t}$$

where v is the velocity, d the thickness of the sample, and t the transit time.

Shear waves were obtained by bonding a 10 MHz Y-cut quartz transducer to the silvered bottom of the fused silica buffer rod with salol (phenyl salicylate). For longitudinal measurements a 10 MHz X-cut quartz transducer was bonded to the rod with Nonaq stopcock grease.

The elevated temperatures of this investigation made necessary the employment of a buffer rod technique. The theory and description of such technique can be found in McSkimin (22) and Papadakis (23). The buffer rod was formed of fused silica and was 28 cm in length and 1.9 cm in diameter; the ends were hand-lapped to be parallel within ± 0.0013 cm.

The buffer rod was first tested without a specimen for signal response. Shear waves formed an excellent ultrasonic

pattern, however, longitudinal waves produced a distorted pattern of poor quality. The pattern was distorted by smaller parasite echoes appearing behind each buffer rod echo. Several modifications were tested to eliminate these parasites which were thought to be caused by mode conversion within the rod itself. At the suggestion of Charles Hagan (24), the chief engineer for Microsonics in Weymouth, Massachusetts, the rod was painted with a butyl base silver paint. The paint acted as an absorber and eliminated the parasites. Since the parasites returned after heating the buffer rod for several days in hydrogen, it may be better to use a silicone or Teflon paint instead.

Hydriding system

A special hydriding system was designed and constructed to satisfy conditions for hydriding niobium. This system (Figure 3) controlled the temperature and hydrogen atmosphere surrounding the niobium while ultrasonic measurements were recorded. The central component of the system was a stainless steel cylinder (Figure 4) which had been flanged at the top and bottom. The top was covered with a 0.25 inch thick plate and the bottom with a 0.5 inch thick plate. Both plates were sealed with o-rings lubricated with Dow Corning high vacuum silicone grease. The cylinder was 24 inches in height, 6 inches in diameter and had a 0.125 inch thick wall.

Figure 3. Diagram of hydriding system

Figure 4. Cross section of hydriding cylinder

The bottom plate was constructed with two Stupakoff power terminals for the furnace, a Conax leadthrough for the chromel vs alumel thermocouples and a hole in the center which served as an entrance for the buffer rod and sample. The thermocouples were sealed to the leadthrough with Torr Seal vacuum adhesive. One thermocouple was spot-welded directly to the sample and was connected to a Doric digital thermocouple indicator model DS350-T3. The temperature of the sample was measured to within $\pm 0.1^\circ$. The other thermocouple was suspended above the furnace and was connected to a West temperature controller model JYSCR which also provided the power for the furnace. With this arrangement the sample temperature was controlled to within $\pm 1.0^\circ$ of the temperature of measurement. The buffer rod was sealed to the bottom plate with a simple screw clamp and o-ring combination that encircled the buffer rod.

Three rods were screwed into the bottom plate and were used to space baffles and to support a furnace plate. The baffles and furnace plate had holes which accommodated the buffer rod and sample. A small heating element rested on this smaller plate and encircled the upper 2 inches of the buffer rod with the sample bonded to it. A heat shield covered the heating element and served to support the furnace thermocouple. Above the heat shield a baffle tower extended to the top of the cylinder. All the internal metal components were made of stainless steel.

The cylinder had four tubular extensions, one near the top and three near the bottom. The upper tube served as a vacuum outlet. A vacuum system capable of 10^{-7} torr was connected to this tube at a gate valve which is illustrated in Figure 4. This system was used primarily to outgas the cylinder. During an experimental run the gate valve was closed and a smaller pump was used to maintain the dynamic system. The outlet for this pump extended downward from the vacuum tube. This pump provided a vacuum of 10^{-3} torr. The hydrogen which flowed through this pump was vented directly through a hood duct which led to the outside atmosphere.

At the lower end of the cylinder there were three tubes: two served as pressure sensing outlets and one served as the hydrogen inlet for the cylinder. One pressure sensing device was a Granville-Phillips thermo-gauge which was connected to a Granville-Phillips thermo-gauge controller model 260-016. The other tube led to a Heise bourdon tube gauge model CMM. The thermo-gauge was used to measure pressures below 10 torr while the Heise gauge measured pressures above 1 torr to within ± 0.1 torr. The hydrogen inlet tube was connected to a Granville-Phillips servo driven valve model 213-036. The valve was wired to a Granville-Phillips automatic pressure controller (APC) model 216-006. The APC regulated the flow of hydrogen into the cylinder. The thermo-gauge controller was wired to the APC and served as a pressure transducer. In combination the two instruments controlled the hydrogen

pressure of the dynamic system to within ± 0.2 torr in a range of 0-6 torr. Above this range the pressure was controlled manually with approximately the same precision.

A Texas Instruments "Servo/Riter" strip chart recorder monitored the temperature and pressure. The thermocouple indicator and thermo-gauge controller were both equipped with an analog output. For safety the cylinder and Heise gauge were placed in a hood. If any hydrogen leak had developed the hydrogen would have been immediately vented.

RESULTS

One single crystal was used for all measurements in this study. In principle, three wave polarizations are possible for each crystallographic direction of wave propagation so that it should be possible to measure three different transit times for each direction of wave propagation. In practice it was found that the signal from the longitudinal wave became distorted and unreadable after prolonged time at elevated temperatures. Thus three transit times were recorded during the early part of each hydrogen run but were subsequently lost due to wave pattern distortion. It may be noted however, that during the initial part of the run from 0 to 1.9 atomic percent hydrogen with the temperature at 573 K and hydrogen pressure at 0.2 torr, the transit time of the longitudinal pulse increased monotonically until the signal became unreadable. During the run from 1.9 to 4.69 atomic percent hydrogen with the same temperature, but with hydrogen pressure at 4.2 torr, the longitudinal transit time decreased until the signal became unreadable. This transit time behavior is indicative of a minimum in $C_L = 1/2(C_{11} + C_{12} + 2C_{44})$ at some hydrogen concentration in the range of measurement at 573 K.

Loss of readability in the echo pattern for C_L was not from bond deterioration because in both runs the shear waves continued to produce very good signals. The pattern distortion is believed to have resulted from the deterioration of

the silver paint on the sides of the buffer rod. Evidence for the deterioration of the coating was the appearance of parasite echoes. These echoes and their significance have already been mentioned.

For transverse waves, transit times were measured and then converted into the wave velocities. For room temperature velocities the thickness of the crystal before hydrogen addition had been measured with a micrometer. The room temperature thickness of the crystal was again measured with a micrometer after measurements with 1.9 atomic percent hydrogen addition.

For dimensional correction due to thermal expansion the values of Tottle (25) were utilized and for expansion due to hydrogen solute the data of Wriedt and Oriani (26) were utilized. Tottle's relation for the thermal coefficient of expansion for niobium is

$$L = L_0 [1 + 6.892(10^{-6})T + 8.17(10^{-10})T^2]$$

where L_0 is a room temperature linear dimension and T degrees centigrade. Wriedt and Oriani's value for the expansion of niobium-hydrogen alloys at room temperature was reported as

$$\Delta a = 0.0017 + .0003 \text{ \AA per atomic percent hydrogen}$$

where a is the lattice parameter. No additional data were available so the above two terms were linearly combined to approximate the composite dimensional correction for niobium-

hydrogen alloys.

Experimental values for transit times were combined with specimen dimensions and converted to elastic constants through use of the equations on page five of the text. In this conversion dimensionally corrected x-ray densities were employed and the results are shown in Table 2. The elastic constants were reproducible to $\pm 0.3\%$.

Table 2. Elastic moduli of Nb and NbH

T (K)	X _H (at % H)	ρ (gm/cm ³)	C ₄₄	C'	B=1/3(C ₁₁ +2C ₁₂)
				(10 ¹¹ dyne/cm ²)	
298	0	8.576	2.806	5.661	17.052
548	0	8.524	2.877	5.450	
573	0	8.519	2.891	5.431	16.737
298	1.9	8.550	2.917	5.604	16.954
548	1.9	8.524	2.970	5.386	
573	1.9	8.498	2.981	5.363	
573	4.69	8.468	3.113	5.264	

The hydrogen concentration of the niobium-hydrogen crystal was determined from vacuum fusion analysis after each of the two runs. The precision of each hydrogen analysis was ± 0.08 atomic percent. For the 1.90 atomic percent hydrogen concentration a single piece from the niobium-hydrogen single crystal was analyzed. Since the single crystal was destroyed at the higher concentration, the crystal was sectioned and pieces of the sample were analyzed. Figure 5 shows a top view of this crystal with the pieces outlined. Each piece was a column of the crystal extending from the top (110) face

Figure 5. Niobium-hydrogen crystal

to the bottom (110) face. The results of the analyses appear in Table 3. The concentration of the second section was aberrant. In accordance with Chauvenet's criterion (27) and because concentration gradients should be absent because of the rapidity of hydrogen diffusion in the vicinity of 573 K (28), (see next paragraph) the aberrant value was discarded. The remaining three values indicate a concentration of 4.69 ± 0.03 atomic percent hydrogen.

Table 3. Crystal sections of NbH

NbH crystal section	Crystal sections of NbH H (atomic percent)
1	4.74
2	4.07
3	4.66
4	4.66

The crystal was considered to be homogeneous on the basis of the vacuum fusion analyses and the rapid diffusion rate of hydrogen in niobium. Schaumann, Völkl and Alefeld (28)

found that for temperatures greater than 300 K the hydrogen diffusion in niobium can be expressed as

$$D = 5.0 \pm 1(10^{-4}) \text{ cm}^2/\text{sec} \exp[-12.301/T]$$

which indicates that at 573 K D is $5.843(10^{-5}) \text{ cm}^2/\text{sec}$. The rate limiting step seems to be hydrogen diffusion through the palladium layer since the time for homogenization can be estimated at 1.9 hours from the following equation which is due to Geiger and Poirier (29):

$$\tau = 4L^2/\pi^2 D$$

where L is 1 cm, the average diffusion distance of the sample and D the diffusion rate. The hydrogen concentration reached equilibrium when the two shear transit times remained unchanged as mentioned earlier and this usually took two to three days. Therefore there was ample time for homogenization to take place.

DISCUSSION

This study confirms the general trends of earlier investigations (8,9). In this study C' continued to decrease and C_{44} continued to increase up to 4.69 atomic percent which is the maximum concentration which has yet been examined. Table 4 compares values of the elastic constants of niobium and niobium-hydrogen from this study with the results from the two earlier investigations (8,9). The data of Fisher et al. were taken directly from published tables (8). C' and C_{44} from the work of Magerl et al. were read from published graphs (9) with a Kirem "Koinzidenz Massstab" (30) which is a device capable of reading distances to ± 0.0001 cm. In Table 4 precisions are quoted for dC_{44}/dX_H and dC'/dX_H when three or more datum points were available for the application of a linear least squares fit (27). All the data have been plotted in Figures 6 through 11.

Fisher et al. have postulated that the composition dependence of C' is due to an orientation-relaxation process of the hydrogen atoms which is referred to as the Snoek relaxation effect (31). Magerl et al. have pointed out that the Snoek relaxation should affect only C' and not C_{44} or C_L . Evidence supporting the Snoek effect can be seen in a comparison of the jump frequency of hydrogen with the induced vibrational frequency of the host lattice. The jump rate of hydrogen between tetrahedral sites has been determined by

Table 4. Comparison of the elastic constants and slopes of Nb and NbH. All elastic constants in units of 10^{11} dyne/cm²

T (K)	X _H (at% H)	C ₄₄	C'	C ₁₁	C ₁₂	dC ₄₄ /dX _H (10^{11} dyne/cm ² at% H)	dC'/dX _H (10^{11} dyne/cm ² at% H)	Reference
298	0	2.806	5.661	24.600	13.278			This study
298	1.9	2.917	5.604			.058	-.030	
298	0	2.792	5.672	24.601	13.257			(9)
298	1.33	2.871	5.644					"
298	2.46	2.922	5.617			.053 $\pm$.004	-.022 $\pm$.001	
298	0	2.800	5.690	24.474	13.094 ^a			(8)
298	0.1	2.820	5.680					"
298	1.06	2.860	5.680					"
298	3.06	2.960	5.600			.050 $\pm$.003	-.28 $\pm$.006	"
548	0	2.877	5.450					This study
548	1.9	2.970	5.386			.049	-.034	"
548	0	2.859	5.467					(9)
548	2.46	2.961	5.403			.041	-.026	"
573	0	2.891	5.431					This study
573	1.9	2.981	5.363					"
573	4.69	3.113	5.264			.047 $\pm$.000	-.036 $\pm$.000	"
573	0	2.868	5.450					(9)
573	2.46	2.970	5.381			.041	-.028	"

^aResolved from published values of C₁₁ and C'.

Figure 6. Hydrogen dependence of C_{44} at 298 K

Figure 7. Hydrogen dependence of C' at 298 K

Figure 8. Hydrogen dependence of C_{44} at 548 K

Figure 9. Hydrogen dependence of C' at 548 K.

Figure 10. Hydrogen dependence of C_{44} at 573 K

Figure 11. Hydrogen dependence of C' at 573 K

Schaumann et al. (28) by using the relation

$$\Gamma = \frac{48}{a^2} D$$

where Γ is the jump rate, a the lattice parameter and D the diffusivity. At 573 K the jump rate may be calculated as $2.57(10^{12})$ jumps per second. In this study the ultrasonic frequency of the propagated pulses was 10^7 Hz. The differences between these frequencies is quite large so that the hydrogen atoms have ample time to redistribute to minimize strain in the applied stress field.

Another indication that the Snoek effect is a contributory factor in the elastic behavior of vanadium-hydrogen, niobium-hydrogen and tantalum-hydrogen alloys is the observation by Magerl et al. (9) that C' decreases at a faster rate with the isotope H^1 than with the deuteride isotope H^2 . In contrast the elastic constants C_{44} and $B = 1/3(C_{11} + 2C_{12})$ were insensitive to isotopic differences except in the single case of the tantalum-hydrogen system where a small difference was observed in C_{44} for concentrations X_H or $X_D > 8$ atomic percent.

In the case of the niobium-hydrogen system the Snoek effect may well be a contributory factor to the decrease of C' with increasing hydrogen concentration. However, crystallographic considerations preclude this effect from contributing a concentration dependence to C_{44} or to B . Thus the observation in the present work that C_{44} is also concentra-

tion dependent implies that other factors must also be contributing to the overall behavior. Magerl et al. (9) have noted that there may be many causes for the observed concentration dependence and suggest as an example that volume expansion may be a contributory factor. However, the following evidence indicates that volume expansion is only a minor factor. For example both the temperature dependence of the elastic constants and the thermal coefficients of expansion are known for pure niobium. Thus if we match the volume of a particular niobium-hydrogen alloy at room temperature with an equivalent volume of pure niobium at elevated temperature any differences in the elastic constants should be intrinsic effects associated with the presence of hydrogen. For example the volume of the unit cell of niobium-hydrogen (1.9 atomic percent) is $36.075 \text{ \AA}^3$ which matches the volume of the unit cell of pure niobium at 413 K. The elastic constants for 1.9 atomic percent hydrogen in niobium are $2.918(10^{11})$ dyne/cm² for C_{44} and $5.604(10^{11})$ dyne/cm² for C' which compare with $2.820(10^{11})$ dyne/cm² for C_{44} and $5.566(10^{11})$ dyne/cm² for C' for pure niobium at 413 K. A marked difference may be noted. Therefore it may be concluded that volume expansion and Snoek relaxation account for only part of the difference. The remaining amount is due to other intrinsic reactions within the lattice.

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ACKNOWLEDGMENTS

I would first like to acknowledge my wife, Katie, who has shown both support and patience throughout my work.

I want to especially thank Dr. J. F. Smith, my major professor, for the time and guidance he provided in this investigation; and to Dr. D. M. Bailey and J. D. Greiner for the helpful discussions during this investigation.

I am indebted to E. J. Ritland for the preparation of the palladium coating on the specimen. I also wish to thank many other staff, students and friends who have made this project easier.