

Hydrogen absorption and its effect on low-temperature electric properties of niobium

S. Isagawa

National Laboratory for High Energy Physics, Oho-machi, Tsukuba-gun, Ibaraki 300-32, Japan

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The excess resistivity of niobium foil samples due to doped hydrogen increases with concentration up to 8–12 at. % H, which is almost independent of temperature. The Nb-H structure at room temperature or above is quenched to 77 K or 9.5 K by relatively rapid cooling. The abrupt decrease of resistivity is observed, which corresponds to the precipitation of the ordered orthorhombic hydride phase. The superconducting transition temperature T_c is rather insensitive to hydrogen concentration in α solid solution. Hydride phase, however, shows no sign of superconductivity down to 1.3 K. Hydrogen is found to be reabsorbed in niobium after UHV outgassing by storage in air or by immersion in etchants. This is confirmed by weighing the samples and cross-checked by the proton NMR measurements.

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I. INTRODUCTION

The metal-hydrogen systems are very interesting both from a theoretical and a practical point of view. The physical and chemical properties of these systems have been extensively studied for many years in relation to the problems of low-temperature behavior of metals like hydrogen embrittlement. Because hydrogen represents the simplest possible impurity in metals, the systems offer advantages for the understanding of basic problems like metal-interstitial solid solutions, phase transitions, diffusion, and electronic properties of solids. Very recently hydrogen in transition metals like Nb, Ta, V, Ti, and Zr has become an object of special interest because hydrides of these metals can be economically used to store hydrogen without danger. Niobium is a good material for nuclear reactors as its absorption cross section for neutrons is very small. On the other hand hydrogen is a most effective moderator for thermal neutrons. Hydrogen concentration in some metals is almost twice as that in liquid hydrogen.¹ Consequently the study of material properties of refractory metal-hydrogen systems is very important for designing the moderator for neutron facilities.

Among many refractory metals, niobium has been given a special interest because it also shows the best superconducting property as a simple element. Much effort has been given to the study of its property in relation to the superconducting rf cavities²⁻⁴ of linear accelerator,⁵ synchrotron,^{6,7} and rf particle separator^{8,9} used in high-energy physics. Niobium is also useful for superconducting resonators used for low-temperature material characterization,^{10,11} stabilized oscillators,^{12,13} filters¹⁴ and antennas for gravity-wave detection.^{15,16}

The superconducting rf properties are very sensitive to the surface treatment and surface conditions,¹⁷ as the penetration of rf field is limited to a depth only between a few hundred and a few thousand Å in thickness. In order to obtain a stable niobium surface with a small rf loss, a large number of studies is being continued, for example, niobium surface with a coating of niobium oxide Nb₂O₅,¹⁸ niobium nitride NbN,^{19,20} Nb₃Sn,²¹⁻²⁴ or other metals¹⁵ which are

formed by anodizing, sputtering, or by heat treatment.

There is, however, still much room for improvement as to large-scale applications of these techniques.

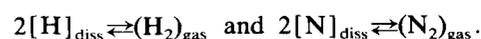
Recently the study has been also done on the formation of niobium oxide by oxidization and its detrimental effect on superconducting critical temperature T_c ,²⁵⁻²⁸ electrical breakdown,²⁹ and rf properties.^{30,31} However, hydrogen can also have a detrimental effect on these properties. This work has been carried out to examine the effect of hydrogen on the superconducting property and the electric resistivity of niobium. Unless otherwise mentioned, the same thin foil samples of niobium were used for all the different measurements. The effects of hydrogen on rf superconducting properties of niobium surface will be reported elsewhere.

II. SAMPLE PREPARATION

The starting material was reactor-grade cold-rolled niobium foil which was obtained from Tokyo Denkai Co., Ltd. and originally from Wah Chang Co., Ltd. It was 50 μm thick and the analyses of the supplier listed 40 ppm by weight O, 30 ppm C, 10 ppm N, 3 ppm H, 600 ppm Ta, 30 ppm W, 20 ppm Mo, and other metallic impurities being less than 10 ppm. It was cut to strips 35 mm × 100 mm. Another sample was high-purity niobium polycrystalline wire 1 mm in diameter.

In order to degas the materials and anneal out work damage and mechanical stress which were introduced by cold working, the samples were vacuum annealed at 1300 °C for 20 h and at 1800 °C for 5 h in a UHV induction furnace. They were threaded with a niobium wire and suspended within a niobium cylinder which heated the samples indirectly as a susceptor. The combination of a 1000-l/sec sputter-ion pump and a titanium sublimation pump was used. The pressure in the furnace at elevated temperatures was below 1×10^{-8} Torr and ultimate pressure after cooling was about 1×10^{-9} Torr.

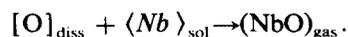
Under these conditions gaseous contaminants like N and H are completely outgassed through the reactions



Oxygen and carbon can be desorbed as the volatile carbon monoxide through the reaction



At elevated temperatures ($> 1750^\circ\text{C}$), however, residual oxygen is mainly desorbed through the dissociation of volatile niobium monoxide following



As the equilibrium vapor pressure of NbO is very low, it condenses on the cold surface of the furnace chamber, and oxygen in Nb is irreversibly decreased.

As the furnace is the induction type and has low thermal inertia, samples can be rapidly cooled to room temperature by switching off the induction current. A fast cooling process prevents the recontamination of the samples mainly by hydrogen. After the annealing–outgassing treatment, pure nitrogen gas of 1 atm, which was free from oxygen and hydrogen, was introduced into the furnace and samples were stored in an ethyl alcohol bath soon after the extraction. It was found that the samples had recrystallized and their grain size increased to about $5\text{ mm} \times 5\text{ mm}$. In the case of a wire sample, a small amount of pure oxygen of 10^{-6} Torr was injected into the UHV furnace prior to the introduction of nitrogen gas in order to passivate the niobium against the hydrogen absorption.³² Foil samples, on the other hand, were taken out without the passivating process.

In order to study the effects of hydrogen on the electrical and superconducting properties of pure niobium, hydrogen was deliberately introduced into the outgassed samples. Hydrogen loading was done by cathodically charging in a 10% sulphuric acid solution using a stainless-steel anode. During the loading a current density of 270 mA/cm^2 on the sample surface and a charging potential of dc 30 V were used. The time required for loading varied from 20 s to 17.5 min. Following the loading, all samples were aged for several hours at room temperature to homogenize the hydrogen concentration throughout the samples. Since the room-temperature diffusion coefficient of hydrogen in niobium is very high ($D \approx 6 \times 10^{-6}\text{ cm}^2/\text{s}$ at 20°C),³³ good uniformity of hydrogen concentration in the samples is expected by this aging process.

The final concentrations of hydrogen were determined by weighing the samples before and after loading. They were also cross-checked by NMR techniques after the foil samples were cut to fine pieces of about $1.5 \times 1.5\text{ mm}^2$ squares. Measurements of critical temperature were made by dc and ac methods on both foil samples and fine pieces, respectively.

III. EXPERIMENTAL METHODS

A. Resistance measurements

The normal-state electrical resistance was measured on individual foil samples at the temperatures 285 K, 77 K, and 9.5 K, just above the superconducting critical temperature, by a dc four-terminal method. Measurements were made both before and after the hydrogen loading, and the value before hydrogenation was used as a standard. A careful handling of the samples was needed because of the embrittlement of the highly doped samples, which eventually caused

spontaneous fracture. The effective dimension of the sample foils were $40 \times 90 \times 0.05\text{ mm}^3$. For the measurements at 9.5 K, however, smaller samples were used and correction of size difference was taken into account. The measuring current which was applied on samples ranged from 10 to 110 mA.

Measurements at 77 K were performed soon after quenching, in which samples were rapidly immersed in liquid nitrogen from room temperature. As has been well known, however, the diffusivity of hydrogen in refractory metals is not small enough even at liquid-nitrogen temperature. Hydrogen can precipitate as a β -phase hydride at 77 K after long-term storage and again dissolve into niobium interstices as α solid solution after being heated to room temperature. Since 77 K is not low enough as a quenching temperature, some hysteretic effects were introduced into the resistance data by low-temperature aging.³⁴ Cooling and warming between room temperature and 77 K yielded slightly different results. In this experiment we adopted the data of the first cooling as the values for 77 K.

B. Measurements of critical temperatures

Superconducting critical temperature of the foil samples was measured in two different ways: (1) dc resistance measurement, (2) ac self-inductance measurement. In dc resistance measurement sample foils were sectioned into small size of about 50 mm length by 5 mm width and set in a thermally insulated copper massive container. The container holding the samples was first immersed in liquid nitrogen and then in liquid helium. It was then drawn up from the liquid-helium level. A slow and uniform rate of change in temperature with time was obtained by allowing the container to warm by natural heat leaks. The temperature of the samples was measured by a calibrated carbon resistance thermometer (Allen Bradley, $51\ \Omega$). The usual four-terminal method was used to determine the resistance change across the superconducting to normal transition.

For the NMR measurements which will be mentioned in Sec. II C the original sample foils were cut to the smaller pieces of about $1.5 \times 1.5\text{ mm}^2$ squares. The ac measurement was conducted on these small samples pieces. Samples were packed in insulated thin wall bobines with 2500 turns of magnet wire 0.1 mm in diameter. Three bobines were firmly mounted in a cylindrical copper cavity which served as a sample container. The container was precooled by liquid nitrogen and then immersed in liquid helium soon after pre-cooling. The superconducting critical temperature T_c was determined from the inductance change of the 2500-turn solenoid which was excited at a frequency of 1 or 100 kHz.

As a superconductor is a perfect diamagnet, the flux is excluded below the critical temperature. Then the solenoid inductance shows a discrete change when the sample in it undergoes a transition from superconducting to normal conducting or vice versa. Since in the dc method there is a possibility of a continuous region of low resistance short-circuiting a region of higher resistance, it is considered that the ac inductance method is more sensitive to material composition.

C. NMR measurement

The technique of nuclear magnetic resonance has been applied to study the structure of the Nb-H samples where the mole fraction of hydrogen varied from 0.018 to 0.67. It covers the α phase of solid solution and the mixed phase of $\alpha + \beta$ at room temperature.

Steady-state NMR absorption measurements were made by using a broad-line NMR unit JNM PW-60 in order to identify the proton signal in the Nb-H system. The resonant field was 14.092 kG (proton Larmor frequency = 60 MHz), and a field modulation of 1 G at 35 Hz was used. In order to suppress the eddy current which would be induced in the sample, foil samples were cut to fine pieces of about $1.5 \times 1.5 \text{ mm}^2$ squares. The sample thickness of 50μ was less than the rf skin depth, which was estimated to be larger than 200μ for 60 MHz. The S/N ratio was increased by tightening the sample pieces with a TFE plug and suppressing the hopping movement in the glass sample cylinder 10 mm in diameter.

Pulsed NMR measurements were also performed with a FT NMR spectrometer, JNM-FX60. The relative hydrogen concentration in charged samples was cross-checked and the unknown concentration in the unweighable sample such as the electropolished one was determined by numerical integration of NMR absorption signals. Pulsed free induction decay signals were accumulated 1000 to 20000 times and recorded by a Fourier transform method. The area under the absorption curve, which is proportional to the number of ^1H in the sample, was measured and normalized with respect to the sample quantity. The proton Larmor frequency was externally locked to 59.80 MHz (the external field = 14.1 kG) by an adjacently positioned deuteron sample. A sequence of 90° pulses of $38 \mu\text{s}$ duration was periodically applied with a repetition rate of 2 Hz.

In addition to measurements at room temperature, the bulk of the experiments were done at 150°C (423 K) in order to avoid the complexity of the coexistence of precipitated β -phase hydride. The proton linewidth is motionally narrowed at this higher temperature and in the plateau region, where

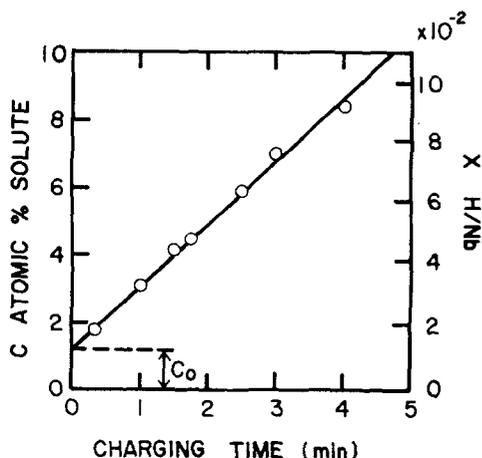


FIG. 1. The concentration of hydrogen absorbed in Nb foils as a function of charging time.

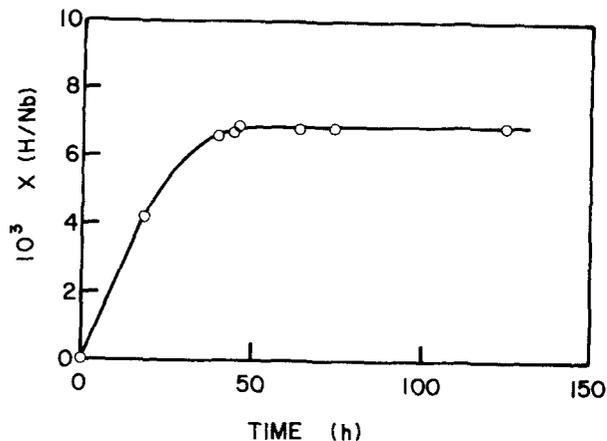


FIG. 2. The increase of weight of a degassed Nb wire sample which was left exposed to the air at room temperature.

the linewidth ceases narrowing and levels off to a value which is determined by a field strength, as described by Zamir and Cotts.³⁵ It eases the determination of the linewidth and the integration of the absorption signals.

IV. EXPERIMENTAL RESULTS

A. Hydrogen absorption

A niobium surface which has been stored in atmosphere is usually covered with a layer of niobium monoxide NbO and traces of water. Although niobium, like most group-V_B metals, can dissolve a substantial amount of hydrogen in equilibrium at room temperature, the reaction rate of it with hydrogen near room temperature is rather low as the oxide layer works as surface barrier and suppresses the hydrogen absorption. Once, however, niobium surface is activated by activation pretreatment, namely, high-temperature annealing in UHV or prior heating in hydrogen atmosphere, or by chemical etching, a considerable amount of hydrogen can be absorbed due to the removal of oxide surface layers. For well-annealed and outgassed samples hydrogen can be deliberately introduced by cathodically charging.

For our foil samples a linear relationship was obtained between hydrogen concentration and charging time with a fairly good approximation below 8 at. % solute. The straight line shown in Fig. 1 does not go through the origin. The small intercept (about 1.2 at. % solute) on the axis of solved quantities may be interpreted as the quantity of hydrogen which was absorbed in the sample during storage in air between outgassing and charging treatments. As the foil samples were taken out from the furnace without passivating by oxygen, hydrogen was dissolved in the samples with no intentional doping.

The solubility of hydrogen in niobium at temperature above 1000°C is very small. And the relation $C \propto (p_{\text{H}_2})^{1/2}$ holds (Sievert's law) for dilute solid solution at high temperatures, where C is the hydrogen concentration and p_{H_2} is the hydrogen gas pressure.³⁶ Consequently, hydrogen removal should not provide any difficulties in a high-vacuum outgassing process at comparatively low temperatures. Hydrogen, however, is easily reabsorbed at low temperatures

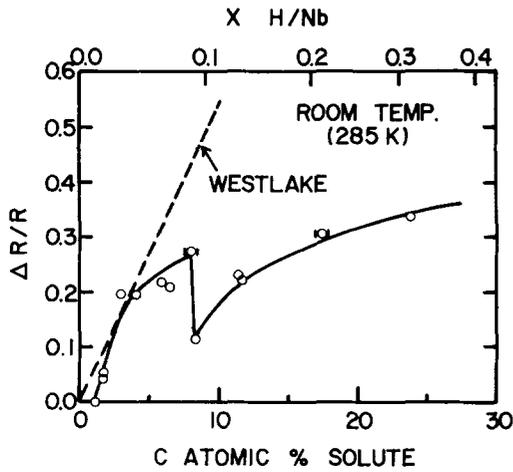


FIG. 3. The fraction of the resistance increase ΔR versus unchanged resistance R as a function of hydrogen concentration at 285 K.

following purification^{32,37} because niobium, like most group-V_B metals, dissolves hydrogen exothermally and the solubility increases with decreasing temperature. Even relatively small gas pressure leads to solid solutions with high hydrogen concentrations. The relative partial molar enthalpy at infinite dilution, $\Delta\bar{H}^\infty$, equals -0.33 eV/H.³⁸

Although hydrogen absorption is hindered by a surface oxide layer which can be formed by intentionally introducing oxygen into the furnace after high-temperature degassing,³² a small amount of absorption was proved to be inevitable. The small increase of weight could be detected as shown in Fig. 2 for a degassed Nb wire sample which was left exposed to the air at room temperature. Although the saturated level was still lower (about 0.68 at. %), hydrogen was absorbed in Nb wire even after the passivating process. If the purified sample was left in air without forming the oxide barrier, a much larger amount of hydrogen would be reabsorbed either from the atmosphere or from adsorbed water vapor as indicatively shown by the intercept C_0 in Fig. 1. There is a danger that an unexpected amount of hydrogen is absorbed in niobium up to the saturated value after long-

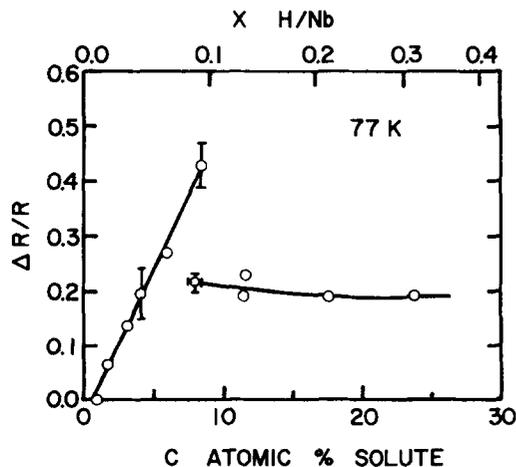


FIG. 4. The same as Fig. 3 except at 77 K.

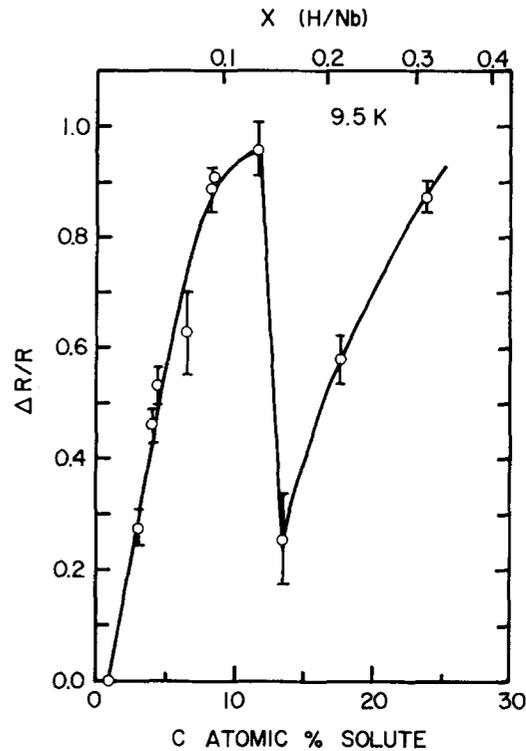


FIG. 5. The same as Fig. 3 except at 9.5 K.

term storage at room temperature. This fact has been also found in another type of experiment such as the flow stress measurement by Ravi.³⁹ The flow stress of outgassed Nb was increased by aging for periods of 2–6 weeks at room temperature. The main reason of this behavior can be considered to be the same.

B. Change of electric resistivity

The fractions of the resistance increase ΔR versus uncharged resistance R are illustrated in Figs. 3–5. The electrical resistivity increases up to concentrations of about 8 at. % H for 285 and 77 K and 12 at. % for 9.5 K. Resistivity then abruptly decreases and gradually increases again at 285 and 9.5 K or holds nearly constant at 77 K as the concentration is increased. The initial slope in Fig. 3 shows the close agree-

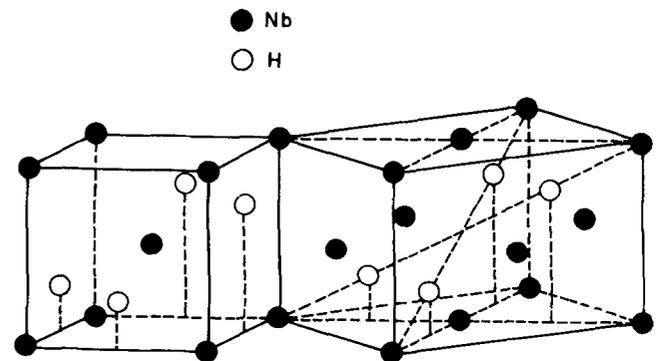


FIG. 6. The ordered orthorhombic superlattice structure of the niobium hydride (β) phase (after Langeberg *et al.*, Ref. 45).

ment with the results of other works.^{40,41} The dotted line corresponds to the slope value of $0.655 \mu\Omega \text{ cm/at.}\%$ by Westlake.

Hydrogen first enters into niobium bcc lattice cells as interstitial solutes (α phase) and deforms the lattice structure. The excess resistivity is due to the scattering of the conduction electrons of the metal by interstitial hydrogen atoms which disturb the periodic variation of potential within the metal lattice. The parabolic, approximately linear, relation observed in the α solid-solution region is the behavior usually expected for disordered alloys.⁴²

The initial slope of the excess resistance versus concentration at 285 K is roughly the same as that at 77 K, although the steeper relation is observed at 9.5 K. The temperature independence and the parallelism of the curves in the α solid-solution region are concluded from the Mattiessen's rule which have been observed in Ta-H, Ta-D,^{43,44} and also in Nb-H (Ref. 37) systems. At room temperature, in the concentration range NbH_{0.09}-NbH_{0.70} two phases coexist: the α phase, a solid solution with a niobium base, and the β phase, hydride with a base of NbH. Only the β phase is present at concentrations greater than NbH_{0.70}. The abrupt decrease of the excess resistivity at about 8-12 at. % solute shows the precipitation of the niobium hydride (β) phase. According to recent studies this phase is considered to be the ordered orthorhombic superlattice structure, with only slight deviation from bcc symmetry⁴⁵ as shown in Fig. 6. It was determined from neutron diffraction studies,^{46,47} x-ray studies,^{48,49} and both x-ray and neutron scattering techniques.⁵⁰ This phase transition was also found by NMR linewidth and intensity measurements of the Nb-H system. According to Refs. 35 and 51, for the Nb-30 at. % H alloy the orthorhombic unit cell has lattice parameters of 4.82, 4.85, and 3.4 Å, and the coexisting α phase has a parameter of 3.31 Å.

Because of the rapid hydrogen diffusion, the hydride precipitates as needles instead of classical eutectoid microstructures as a result of the $\alpha \rightarrow \beta$ phase transformation. The habit plane of the niobium-hydride plates is $\{100\}$ and the growth direction changes at the grain boundary. Especially at hydrogen concentrations of approximately 0.2 H/Nb atom ratio and lower, needles form a Widmanstätten structure which was identified by Paxton *et al.*⁵² and extensively investigated by optical microscopy,⁵³ and thus can be expected to form in our foil samples.

As the hydride (β) phase has a more ordered lattice structure than the α phase, it shows a lower resistance value. The needle structure of the β phase short-circuits the foil sample, which probably corresponds to both the sharp dip of the excess resistivity of our foil sample and the small difference from the behavior which has been reported for small filament samples.³⁷ The trough value of the resistivity for ordered hydride phase is almost near the absolute value for original pure niobium. It can be explained as follows. Electrons from added hydrogen mainly fill the d -band levels of the parent metal, leaving the s states almost unchanged. Since the light s electrons predominately participate in electrical transport, the resistance of the ordered Nb-H compound and of the pure Nb are practically the same. The excess resistance again increases with hydrogen content

especially at 9.5 K beyond the dip. It can be explained by the fact that the region of a disordered hydrogen solid solution stretches its area in the precipitated hydride.

C. Dependence of T_c on hydrogen concentration

Figure 7 shows the dependence of the superconducting transition temperature (T_c) of our niobium strip samples on hydrogen concentration. The transition temperature was obtained by the dc method. The value ΔT_c indicates the temperature width of the transition (full width). Although T_c and ΔT_c initially show a slight decrease and increase, respectively, they remain almost constant for the hydrogen concentrations between 2.5 and 24 at. % solute. These results coincide with those reported in reference which indicated that there were no detectable changes in T_c .⁵⁴⁻⁵⁶ In the literature, however, there has been another contradictory result which showed that T_c decreased monotonically with the increase of hydrogen.⁵⁷⁻⁵⁹ These contradictions can be ascribed to the difference of sample form, purities of starting materials, and measurement methods. Samples which were reported to have shown the T_c decrease were fine powders^{57,59} or fine strips⁵⁸ measured by an induction method rather than a dc resistance method. The induction method on such sample forms would be more sensitive to composition than a resistance method since in the latter method there is a possibility of a continuous region of low resistance short-circuiting a region of higher resistance.

We made T_c measurements by the ac induction method on the same foil samples which were cut to small pieces after dc measurements. The suppression of the current passing through the remaining superconducting phase of Nb-H was not sufficient, but there is a slightly enhanced initial decrease of T_c as shown in Fig. 8. The value of T_c , however, remains almost constant for the hydrogen concentrations above 1.8 at. % solute.

The remarkable change obtained by induction method is a two-steps R -vs- T character found for a few samples as shown in Fig. 9. On the other hand, highly doped (above 40 at. % H: β or ϵ phase) samples showed no normal to super-

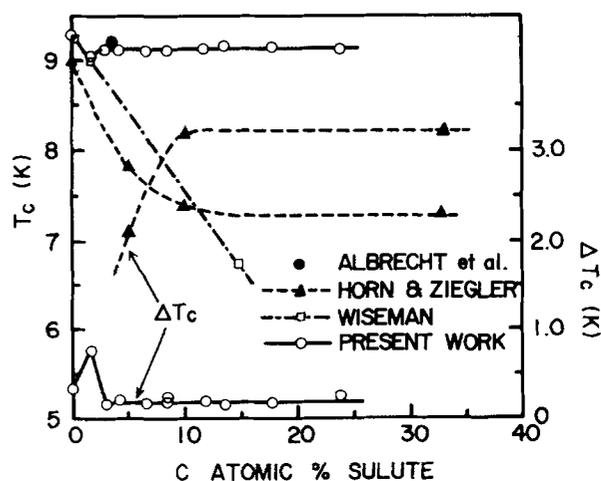


FIG. 7. The dependence of T_c on hydrogen concentration. The T_c was measured by the dc resistance method.

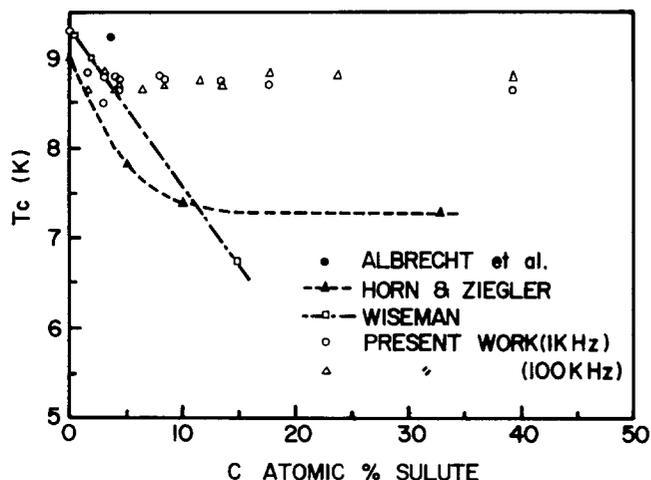


FIG. 8. The dependence of T_c on hydrogen concentration. The T_c was measured by the ac induction method.

conducting transition above 1.3 K, which was also in good agreement with other reports.^{56,60,61} These results indicate the real presence of mixed structures of two phases of high and low T_c values in our Nb-H samples.

In general the addition of interstitial gaseous impurities distorts the crystal lattice structures of the parent metal. Lattice distortion affects the local lattice strain field which reduces to the bulk change in electron volume and the consequent change in electron-phonon coupling constant, namely, the change of transition temperature. For example, oxygen in interstitial solid solution in bcc Nb is known to markedly reduce the T_c of Nb, almost linearly by 0.93 K per at. % O.

The hydrogen atom can interstitially enter in both octahedral and tetrahedral positions of niobium bcc cells [Figs. 10(a) and 10(b)]. It also stretches the crystal lattice parameter of the parent niobium metal. Wiseman found the monotonous decrease of T_c by addition of hydrogen into purified Nb samples.⁵⁸ The relationship between transition temperature and interstitial hydrogen, however, has been rather uncertain. Niobium hydride phase (β or ϵ), on the contrary, shows the obviously decreased transition temperature. It can be accounted for by the decrease of electron-phonon coupling constant, which determines the values of the transition temperature. The slight decrease of T_c in our samples by adding small amounts of hydrogen may be due to the slight decrease of T_c in interstitial niobium-hydrogen phase or due to the proximity effect by niobium-hydride second phase (β or ϵ) of low T_c values.

D. Results of NMR measurements

The room-temperature NMR spectra of ^1H from two samples A and B are shown in Figs. 11(a) and 11(b). These are derivative signals of steady-state NMR absorption measurements with a broad-line NMR unit at 14092 G. The separation of the derivative maxima corresponds to 1 and 1.3 G, respectively. Although hydrogen was deliberately loaded to a concentration of about 10 at. % in sample A, it was not doped in sample B, which had been only electropolished and

immersed in a solution of 89.5% (by volume) of concentrated H_2SO_4 and 10.5% of 40% HF. In the setup of the electropolishing the electrochemical potential in the electrolyte is rather inversely loaded against the hydrogen doping. The proton spectra of Fig. 11(b) shows, however, that a large amount of hydrogen can be picked up in the Nb sample during immersion in an electropolishing bath because it is a hydrogen-rich electrolyte. The concentrating effect of hydrogen in Nb by thinning may also exist as reported by Westlake *et al.*⁶²

There are several methods for determining the hydrogen content in niobium metal. The direct measurement of weight changes before and after loading, as has been also performed in this work, is the simplest one. However, this method cannot be applied to the determination of protons in the unweighable sample, such as sample B. Care must be taken for heavily doped samples as they become brittle and easy to induce weight loss. The vacuum-extraction technique is one of the most common methods, but it makes samples useless for subsequent measurements. Another method using the technique of neutron interferometry⁶³ in one used the fact that the hydrogen content changes the neutron average coherent scattering length is rather simple and accurate, but it is suited for determination of a smaller quantity than 10 at. % as is also the case with the internal friction method. In this work the quantitative determination of protons was carried out by integrating the absorption signals of pulsed NMR measurements at 150 °C.

Figure 12 summarizes the results of the H concentration obtained from the cross-check between NMR and weight measurements. One of the samples is chosen as a standard and its hydrogen concentration is calibrated with that from weight measurement. Hydrogen concentration of other samples by NMR measurement is expressed in a value relative to this standard. In a fairly good approximation a linear correspondence is obtained as shown in Fig. 12. The main error comes from the ambiguity of the base line of the NMR absorption spectrum which extends almost full width of the magnetic field sweep. From the NMR measurement proton concentration in sample B could be determined to be 4 at. % solute. This fact means that a large quantity of hydrogen can be absorbed in niobium during immersing in etchant and electropolishing processes.

The dependence of the proton linewidth on the hydrogen concentration at 150 °C is illustrated in Fig. 13. At room temperature hydrogen is in a heterogeneous system consist-

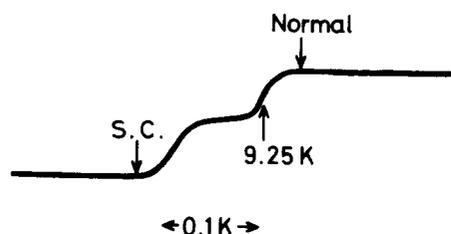


FIG. 9. Two-steps R -vs- T character found for a niobium sample containing hydrogen.

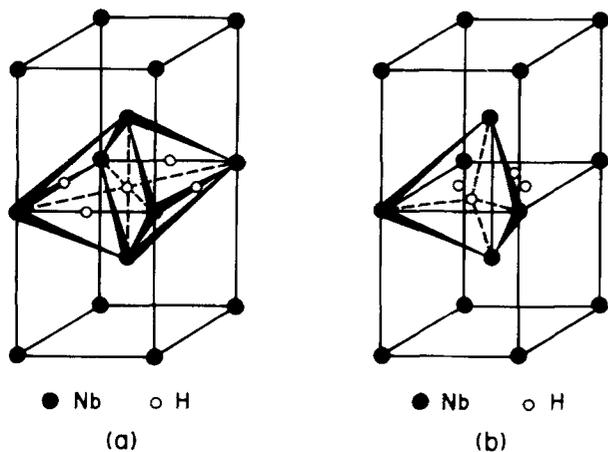


FIG. 10. Hydrogen atoms interstitially entered in niobium bcc cells. (a) Octahedral positions; (b) tetrahedral positions.

ing of two phases, α and β . At 150 °C (423 K), however, hydrogen in niobium can be considered to form a lattice gas with a gas (α phase)–liquid(α' phase) phase transition.⁶⁴ At higher temperatures the proton linewidth is motionally narrowed due to thermally activated rapid self-diffusion of the protons. At low temperature (for example, below 77 K) the proton second moment in the NbH_x system is rather concentration independent since the Nb–H interactions are on the average larger than the H–H interactions and the Nb environments are equivalent across the concentration range. At temperatures above the onset of the plateau which was reported by Zamir and Cott, however, proton linewidth depends on the hydrogen concentration.

Although data in Fig. 13 are very much scattered and broadened, we can conclude as follows. The linewidth slightly increases up to the concentration between 20 and 35 at. % and again seems to decrease at the higher concentration (α' phase). The initial increase corresponds to the increase of the activation energy E_a and the gradual stiffening of the hydrogen motion.⁶⁵ The low-concentration phase (cubic α phase) shows rather narrow width which corresponds to the fact that hydrogen occupies the various interstitial sites at random and diffuses rather freely with higher jump frequency

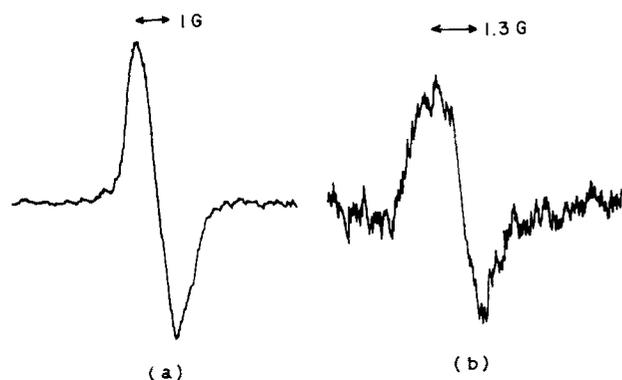


FIG. 11. Room-temperature NMR spectra of ¹H. (a) Sample A; hydrogen concentration about 10 at. %. (b) Sample B; electropolished in hydrogen-rich etchant.

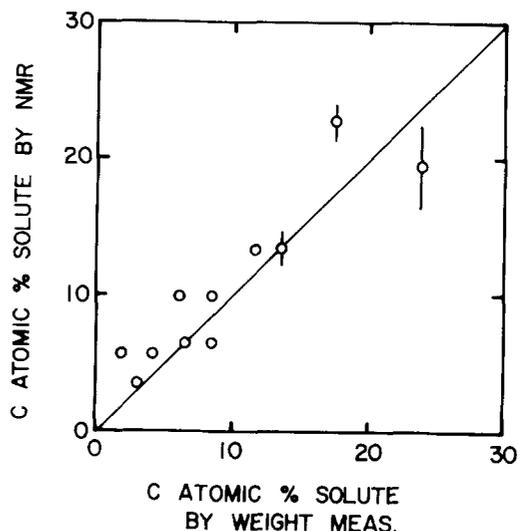


FIG. 12. Comparison of H concentration obtained from NMR and weight measurements.

ν_c and with lower activation energy E_a .^{33,35,51} The values ν_c and E_a are related as

$$\nu_c = 1/\tau_c = \nu_{0c} \exp(-E_a/RT), \quad (1)$$

where τ_c is the correlation time and R is the gas constant. The decrease at the higher concentration is partly due to the decrease of the volume magnetic susceptibility^{35,66,67} χ_v or due to the difference in sample shape, which is thinner and finer at the higher concentration because of the brittleness. The concentration for the linewidth maximum at 150 °C roughly corresponds to the critical concentration of the (α)–liquid(α') phase transition,⁶⁴ which has been found to be 24.8 at. % H at about 445 K (Ref. 68) by the solubility measurements and by the Gorsky effect and to show the phenomenon called “critical slowing down.”^{69,70}

V. DISCUSSION

The group-V_B metals in the periodic table (Ta, Nb, V) have a high solubility limit for hydrogen at ambient temperatures. Hydrogen is easily reabsorbed in niobium which has been activated by the UHV outgassing process. Absorption is taking place exothermally and solubility increases with decreasing temperature. Our foil samples, which were outgassed and not covered with oxide barrier, dissolved in a short time about 1.2 at. % hydrogen with no intentional doping (Fig. 1). Oxide barrier formed on the surface can remarkably retard and oppose the penetration of hydrogen. In the absence of a barrier, however, hydrogen is dissolved in the metal up to the equilibrium content determined by a solubility limit at this temperature. The solubility limit C_α of hydrogen in the α phase is temperature dependent and can be characterized by

$$C_\alpha = C_\alpha^0 \exp(-H_p/kT) \quad (\text{H/Nb}), \quad (2)$$

where $C_\alpha^0 = 5.35$ and precipitation enthalpy $H_p = 0.12$ eV/H = 2.77 kcal/mol H.⁷¹

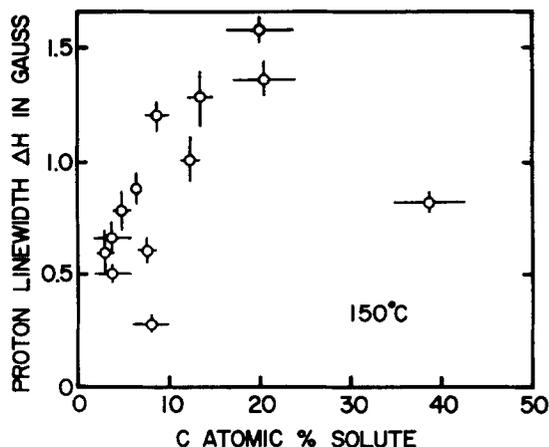


FIG. 13. The dependence of the proton linewidth on the hydrogen concentration at 150 °C.

Makrides *et al.*⁷² found that hydrogen absorption by vanadium and tantalum is remarkably promoted by coating the activated surface of these metals with a sputtered film of palladium. Palladium, which is selectively pervious to hydrogen, protects the surface against the oxide barrier formation and promotes the hydrogen dissolution. Also in the case of niobium, hydrogen dissolution is suppressed to a lower saturated level by a passivating process. From the weight change of the degassed wire, however, it was made clear that a small (but unignorable) amount of hydrogen (about 0.68 at. %) can be still absorbed in Nb even after thin oxide barrier formation (Fig. 2). The weight increase by hydrogen absorption from air, ceases after about 40 h. The saturated level of hydrogen contamination is still smaller as compared with the solubility limit at room temperature owing to the oxide barrier on surface. It was also clarified by the NMR technique that a large amount of hydrogen can be absorbed in Nb only by immersion in hydrogen-rich etchant and even through the electropolishing process in which voltage is inversely applied against hydrogen doping.

Sieverts first showed that the metal niobium is capable of absorbing hydrogen to compositions approaching the stoichiometric ratio NbH. By electrochemical charging or by mixing with zinc in hydrochloric acid, up to the composition of NbH₂ (δ phase) can be obtained. According to the phase diagram of the Nb–H system which is shown in Fig. 14,^{71,72} hydrogen is absorbed at room temperature up to a composition NbH_{0.04~0.07} as a solute in the bcc lattice of Nb (α phase).⁷³ Above this concentration niobium hydride (β phase) precipitates by a bainitic transformation.⁷⁴ The solubility limit, however, is drastically reduced when the temperature is lowered, e.g., $x \sim 5 \times 10^{-6}$ at $T = 100$ K. The α phase becomes an almost pure niobium phase and stably coexists with the hydride phases, called ζ or ϵ , which corresponds to the composition Nb₄H₃.

A hydrogen atom lying in α solid solution deforms the lattice by repelling the neighboring niobium atoms which, in turn, displace the next niobium atoms. Consequently, a long-range displacement field arises in Nb that declines as $1/r^2$ away from the included hydrogen atom. The lattice constant

of niobium is found to be stretched by $\Delta a/a = 7 \times 10^{-4}/\text{at. \% H}$.⁵⁴ The strain field produces an excess resistivity due to the scattering of the conduction electrons. According to our experimental results, the resistance increases at temperatures of 285, 77, and 9.5 K are approximately linear to the hydrogen concentration up to 8–12 at. %, which corresponds to the linear increase of lattice constant in the α phase. The concentration corresponding to the trough value of the resistance is almost independent of temperatures (8–12 at. %) and a little higher than the room-temperature phase boundary between α and $\alpha + \beta$, which is found to be 5–6 at. %. It may be considered that the room-temperature lattice structure of Nb–H was quenched to lower temperatures by rapidly cooling the samples. In general diffusivity of hydrogen in niobium is very high. The temperature dependence of its jump frequencies was found to be in good accord with the quantum-mechanical model of Flynn and Stoneham.⁷⁵ At low as 77 K the hydrogen atom is more mobile as observed in some hysteretic behaviors in resistance measurements between 285 and 77 K. It may be possible that hydrogen remains mobile even at 0 K due to quantum-mechanical tunneling processes. That is, the hydride may be formed by a transformation involving the rapid diffusion of hydrogen atoms even at lower temperature.

However, in our experiments cooling from room temperature to 77 K or to 9.5 K was very fast and the time between cooling and resistance measurement was of the order of several minutes. Even if the hydrogen diffusion and rearrangement are fast, it would take about a few hours or, strictly speaking, a few days. A possible explanation for the increase of the excess resistivity up to 8–12 at. % at 77 and 9.5 K could be that the phase structure at room temperature was quenched by rapid cooling and hydrogen remained in the α phase up to oversaturated concentrations. On top of that, in our sample preparation, niobium may be contaminated by other interstitial impurities like oxygen or nitrogen after out-gassing process. It is now established experimentally that these impurity atoms act as traps and strongly reduce the diffusivity D , forming H–N and H–O complexes.^{40,76,77}

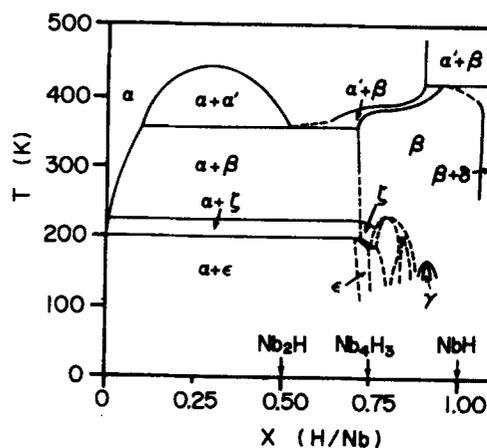


FIG. 14. The phase diagram of the Nb–H system (after Wenzl and Welter, Ref. 71, and Chandler and Walter, Ref. 72).

Springer assumed for this process a two-step model which applies to low trap concentrations.⁷⁸ The diffusing hydrogen alternates between a "free state" where it diffuses freely during an average time τ_1 and a "trapped state" where it stays for a time τ_0 in the average. Substitutional impurity such as Ta may also retard the hydrogen precipitation.⁷⁹

The reasons why the trough of excess resistivity is shifted toward the higher concentration may be considered as follows. (1) The solubility limit C_α of hydrogen and precipitation enthalpy H_p in Eq. (2) are impurity-sensitive values. The substitutional impurity such as Ta or dissolved interstitials like C, N and O may not only reduce the diffusivity but also push up to the $(\alpha + \beta)$ phase boundary. (2) In our electrochemical doping process, we used a charging potential of 30 V_{dc} which was much higher than the equilibrium voltage for the hydride. It raised the bath temperature and equilibrium concentration which corresponded to higher temperature than room temperature might be formed. Concentrated hydrides might be formed near the surface and raise the net value of hydrogen concentration. (3) Efficiency of doping also depends on sample shape. If the aging time after doping was not long enough, the homogeneity of the hydrogen content was not assured. Small discrepancy observed in data at different temperatures may be due to this lack of homogeneity.

Some of the data in Figs. 3–5 are summarized as a function of $1/T$ in Fig. 15. Here, only the hydrogen-induced increase of the resistivity is plotted logarithmically. The dashed line in Fig. 15 indicates the experimental values which were measured for nitrogen-free niobium in the presence of precipitations by Pfeiffer and Wiph.⁴⁰ Although our data points are rather scarce, a difference can be observed in the temperature behavior of the hydrogen-induced resistivity increase, $\Delta\rho_H$, when compared with that of the litera-

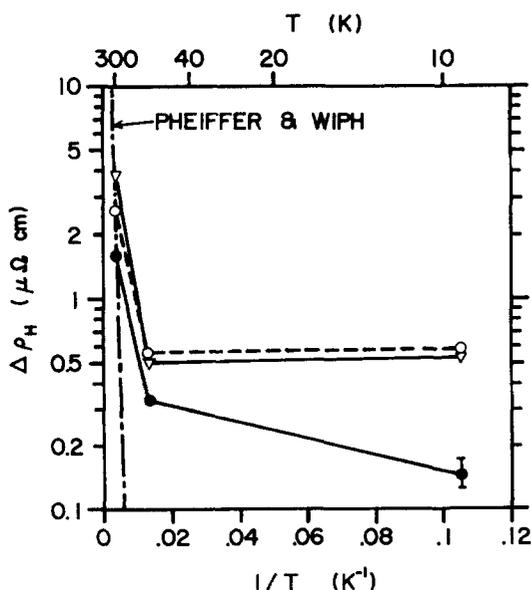


FIG. 15. The values $\Delta\rho_H$ at temperatures of 285, 77, and 9.5 K as a function of $1/T$. Hydrogen concentration of NbH_x is as follows. (∇) $x = 0.31$ (24 at. %), (\circ) $x = 0.13$ (12 at. %), (\bullet) $x = 0.03$ (3.1 at. %).

ture.⁴⁰ The values $\Delta\rho_H$ of our relatively highly doped samples decrease much more slowly when the temperature is lowered than that of the lightly doped samples of the literature. The departure is mainly due to the difference of sample preparation. In the measurements by Pfeiffer and Wiph, data points were reported to be obtained after an aging time of two or three days at the lower measuring temperatures. On the other hand, our samples were cooled rapidly from room temperature to 77 or 9.5 K in several minutes. The different behavior observed in Fig. 15 may be evidence to support our above-mentioned view that in our measurements the structure at room temperature was quenched to 77 or 9.5 K by rapid cooling. The values of resistivity ratio, $R_{285}/R_{9.5}$, of our hydrogen-free original samples are between 20 and 30. These values are relatively low in comparison with other measurements. This fact indicates the existence of other interstitials or substitutionals which may affect the resistivity and diffusivity as also mentioned above.

When the hydrogen molecule H_2 dissociates at the niobium surface forming two adsorbed atoms, they lose their bound electrons and are dissolved in the bcc niobium lattice. Hydrogen may exist in niobium in three different forms; bare proton with plus charge, anion with minus charge, and neutral atom. The possibility that the hydrogen exists as a neutral atom, however, can be discounted because the presence of single bound electrons would give rise to an enormous hyperfine field. Such a field would prevent the measurement of the NMR spectra which have been observed by us for foil samples and by several researchers for powdered samples. On the other hand, the electron momentum distributions predicted by the protonic and the anionic models differ radically.

From low-energy electron diffraction (LEED) and inelastic electron scattering (IES) experiments by Hass,⁸⁰ however, it appeared that hydrogen was chemisorbed onto niobium (110) surfaces at room temperature involving the dissociation of hydrogen into atoms. The hydrogen molecule dissociates at the surface, forming two adsorbed atoms. It is decided that the adsorbed atoms lose their bound electron and are dissolved in niobium lattice as protons on tetrahedral sites. Recently Pattison, Cooper, and Schneider⁸¹ made Compton profile measurements on deuterium in $\text{NbD}_{0.6}$ and obtained the conclusion also supporting the protonic model in which the electrons from the deuterium fill empty states in the conduction band of the host Nb metal.

If the dissolved hydrogen atoms are present in the form of protons, their extra electrons are added to the metallic electrons in the conduction band and are distributed according to Fermi-Dirac statistics. The charge of the resulting bare proton is screened by a cloud of conduction electrons, and the proton itself remains mobile. Various experiments⁵⁶ suggest that the density of states of the electrons near the Fermi surface in pure niobium ($N(\epsilon_F) \sim 0.9$ states/eV atom) is depressed roughly by the factor of $\frac{1}{2}$ in the hydride phase and the niobium Knight shift is also decreased.³⁵ The decrease of $N(\epsilon_F)$ is due to the fact that electrons from hydrogen fill the d band of the niobium, which makes the fundamental contribution in the transition metals to $N(\epsilon_F)$. The d

band then comes to lie below the Fermi surface and $N(\epsilon_F)$ sharply diminishes.

The decrease of $N(\epsilon_F)$, however, does not directly mean the decrease of T_c expected from the formula by the BCS theory which is written in the form

$$T_c = 1.14\theta_D \exp[-1/N(\epsilon_F)V], \quad (3)$$

where θ_D is the Debye temperature of the metal and V is the interelectronic binding constant. In real metals the critical temperature T_c can be more effectively expressed as⁸²

$$kT_c = \hbar\omega_D \exp\left(\frac{-(1+\lambda)}{\lambda[1 - (\langle\omega\rangle/\omega_0)\mu^*] - \mu^*}\right), \quad (4)$$

where ω_0 is the maximum phonon angular frequency, $\langle\omega\rangle$ is its average, λ is the electron-phonon coupling constant, and μ^* is the Coulomb pseudopotential, which expresses the electron-electron repulsive interaction and for most superconductors is a very small quantity of the order of 0.1–0.2. Applying the phonon spectrum of Nb to expression (4), McMillan showed the expression for T_c as follows.⁸²

$$T_c = \frac{\theta_D}{1.45} \exp\left(-\frac{1.04(1+\lambda)}{\lambda(1-0.62\mu^*) - \mu^*}\right). \quad (5)$$

As has been noted empirically by McMillan and theoretically corroborated by Hopfield,⁸³ electron-phonon coupling constant λ for many transition metals is practically independent of the density of states of electrons at the Fermi surface.

As the hydrogen is added, however, the niobium changes from a metal having d electrons to a metal having almost free s electrons. The decrease in the constant λ of niobium is considered to involve a decrease in the matrix element for electron-phonon interaction, which results in a depression of T_c of the niobium hydride. According to Schröder⁶¹ niobium hydrides and deuterides whose concentrations were $\text{NbH}_{0.88}$, $\text{HbH}_{0.99}$, and $\text{NbD}_{0.79}$ and $\text{NbD}_{0.80}$, did not become superconducting above 1.94 K. Horn and Zielger⁵⁷ reported that the β phase did not show superconductivity. Furthermore, according to Maksimov, no signs of superconductivity had been observed in niobium hydride down to a temperature of the order of 0.1 K.⁶⁰ In our work, either, hydride phase (about 48 at. % H) shows no normal to superconducting transition above 1.3 K. The absence of superconductivity in niobium hydride is, however, frequently not found because nearly the pure solid-solution phase, which coexists with hydride, short-circuits the samples.

The relationship between transition temperature T_c and interstitial hydrogen in the α phase, however, has been rather uncertain. The thoroughly aged sample in the equilibrium state consists of nearly pure niobium phase (α phase) and $\text{NbH}_{0.7}$ hydride phase, and the former frequently short-circuits the latter concentrated phase. In this work, however, samples could dissolve hydrogen up to a concentration of 8–12 at. % by fast quenching. The initial slight decrease of T_c which has been found for our foil samples by the ac induction measurement may indicate the depression of T_c in α solid solution, although it may be also due to the effect of other impurities such as O. The data by Wiseman⁵⁸ which showed a monotonous decrease of T_c in concentration below 14 at. % might be explained by the quenching of hydrogen rich solid

solution. Anyway, the problem of superconductivity of the α solid-solution phase of the Nb–H system still requires further investigations.

VI. CONCLUSION

The excess resistivity due to the hydrogen in niobium shows a monotonous increase in α solid solution up to a concentration of 8–12 at. % which is almost independent of temperatures. The structure at room temperature or above is quenched to 77 to 9.5 K by relatively rapid cooling. The abrupt decrease of resistivity is observed, which corresponds to the formation of the ordered orthorhombic hydride phase.

The superconducting transition temperature of niobium is rather insensitive to hydrogen concentration in the α solid-solution phase, although a slight decrease can be observed by ac induction measurement. The niobium hydride phase, however, shows no sign of superconductivity down to the temperature below 1.3 K. It is found that hydrogen can be easily reabsorbed in niobium after UHV outgassing both by storage in air and by immersion in hydrogen-rich etchant. Electropolishing treatment also increase the hydrogen concentration in niobium. These are observed by weighing the samples and cross-checked by NMR measurements. Hydrogen concentration which is determined by the integration of pulsed NMR absorption signal is consistent with that from direct weighing measurement. The width of the NMR signal shows a gradual increase below 20 at. %, which corresponds to the stiffening of the proton motion with hydrogen concentration. Hydrogen in the low-concentration phase can diffuse rather freely with higher jump frequency and with lower activation energy.

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¹G. G. Libowitz, *J. Nucl. Mater.* **2**, 1 (1960).

²H. Pfister, *Cryogenics* **16**, 17 (1976).

³M. Kuntze, *Proc. 9th Int. Conf. on High-Energy Accelerators*, SLCA, Stanford, California, 1974, p. 115 (unpublished).

⁴A. Septier and Nguyen Tuong Viet, *J. Phys. E* **10**, 1193 (1977).

⁵P. B. Wilson, *Linear Accelerators*, edited by A. Septier and P. Lapostolle (North-Holland, Amsterdam, 1970), p. 1107.

⁶J. Kirchgessner, H. Padamsee, H. L. Phillips, D. Rice, R. Sundelin, M. Tigner, and E. von Borstel, *IEEE Trans. Nucl. Sci.* **NS-22**, 1141 (1975).

⁷H. Padamsee, J. Kirchgessner, M. Tigner, R. Sundelin, M. Banner, J. Stimmell, and L. Phillips, *IEEE Trans. MAG-13*, 346 (1977).

⁸A. Carne, in *Ref. 5*, p. 587.

⁹J. R. Aggus, W. Bauer, S. Giordano, H. Hahn, and H. J. Halama, *Appl. Phys. Lett.* **24**, 144 (1974).

¹⁰W. H. Hartwig, *Proc. IEEE* **61**, 58 (1973).

¹¹S. Isagawa, *Jpn. J. Appl. Phys.* **15**, 2059 (1976).

¹²S. R. Stein and J. P. Turneaure, *Proc. IEEE* **63**, 1249 (1975).

¹³J. Bénard, J. J. Jimenez, P. Sudraud, and Nguyen Tuong Viet, *Electron. Lett.* **8**, 117 (1972).

¹⁴C. W. Alworth and C. R. Haden, 1972 *Applied Superconductivity Conf., Annapolis* (IEEE, New York, 1972), p. 679.

- ¹⁵G. J. Dick and H. C. Yen, in Ref. 14, p. 684.
- ¹⁶D. G. Blair, J. Mills, and R. E. Rand, *IEEE Trans. Magn. MAG-13*, 350 (1977).
- ¹⁷M. Strongin, *J. Appl. Phys.* **42**, 4105 (1971).
- ¹⁸H. Diepers and H. Martens, *Phys. Lett. A* **38**, 337 (1972).
- ¹⁹P. B. Wilson, Proc. of the 1972 Proton Linear Accelerator Conf., Los Alamos, New Mexico (unpublished); SLAC-PUB-1134, 1972.
- ²⁰S. Isagawa, Y. Kimura, Y. Kojima, S. Mitsunobu, and Y. Mizumachi, in Ref. 3, p. 147.
- ²¹B. Hillenbrand and H. Martens, *J. Appl. Phys.* **47**, 4151 (1976).
- ²²P. Kneisel, H. Küpfer, W. Schwarz, O. Stoltz, and J. Halbritter, *IEEE Trans. Magn. MAG-13*, 496 (1977).
- ²³G. Arnolds and D. Proch, *IEEE Trans. Magn. MAG-13*, 500 (1977).
- ²⁴H. Padamsee, J. Kirchgessner, M. Tigner, R. Sundelin, M. Banner, J. Stimmell, and L. Phillips, *IEEE Trans. Magn. MAG-13*, 346 (1977).
- ²⁵H. Padamsee, M. Banner, and M. Tigner, *IEEE Trans. Nucl. Sci. NS-24*, 1101 (1977).
- ²⁶W. DeSorbo, *Phys. Rev.* **132**, 107 (1963).
- ²⁷H. Hahn and H. J. Halama, *J. Appl. Phys.* **47**, 4629 (1976).
- ²⁸C. C. Koch, J. O. Scarbrough, and D. M. Kroeger, *Phys. Rev. B* **9**, 888 (1974).
- ²⁹G. J. Sayag, Nguyen Tuong Viet, H. Bergeret, and A. Septier, *J. Phys. E* **10**, 176 (1977).
- ³⁰S. Giordano, H. Hahn, H. J. Halama, C. Varmazis, and L. Rinderer, *J. Appl. Phys.* **44**, 4185 (1973).
- ³¹H. A. Schwettman, J. P. Turneaure, and R. F. Waites, *J. Appl. Phys.* **45**, 914 (1974).
- ³²K. Faber and H. Schultz, *Scr. Metall.* **6**, 1065 (1972).
- ³³G. Schaumann, J. Völkl, and G. Alefeld, *Phys. Status Solidi* **42**, 401 (1970).
- ³⁴O. Buck, D. O. Thompson, and C. A. Wert, *J. Phys. Chem. Solids* **32**, 2331 (1971).
- ³⁵D. Zamir and R. M. Cotts, *Phys. Rev. A* **134**, 666 (1964).
- ³⁶J. A. Pryde and C. G. Titcomb, *J. Phys. C* **5**, 1293 (1972).
- ³⁷J. A. Pryde and C. G. Titcomb, *Trans. Faraday Soc.* **65**, 2758 (1969).
- ³⁸R. B. McLellan and C. G. Harkins, *Mater. Sci. Eng.* **18**, 5 (1975).
- ³⁹K. V. Ravi, Ph.D. thesis, Case Western Reserve University, 1969.
- ⁴⁰G. Pfeiffer and H. Wipf, *J. Phys. F* **6**, 167 (1976).
- ⁴¹D. G. Westlake, *Trans. Metall. Soc. AIME* **245**, 287 (1969).
- ⁴²N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford, 1936), p. 286.
- ⁴³J. A. Pryde and I. S. T. Tsong, *Acta Metall.* **19**, 1333 (1971).
- ⁴⁴K. Poulter and J. A. Peyde, Proc. of the 4th Intern. Vacuum Congress, 1968, p. 111 (unpublished).
- ⁴⁵J. C. Langeberg, R. B. McLellan, *Scr. Metall.* **7**, 301 (1973).
- ⁴⁶V. A. Somenkov, A. V. Gurskaya, M. G. Zomlanov, M. E. Kost, N. A. Chernoplekov, and A. A. Chertkov, *Fiz. Tverd. Tela* **10**, 1355 (1968).
- ⁴⁷V. A. Somenkov, M. G. Zemliamov, M. E. Kost, H. A. Chernoplekov, and A. A. Chertkov, *Akad. Nauk SSSR* **181**, 56 (1968).
- ⁴⁸W. Albrecht, W. Goode, and M. Mallett, *Battelle Memorial Institute Report No. BMI-1332*, 1959.
- ⁴⁹C. Wainwright, *Bull. Instrum. Metals* **4**, 68 (1958).
- ⁵⁰M. A. Pick, Proc. of Intern. Conf. on Hydrogen in Metals, Jülich, 1972, Vol. 1, p. 90 (unpublished).
- ⁵¹H. Lütgemeier, R. R. Arons, and H. G. Bohn, *J. Magn. Resonance* **8**, 74 (1972).
- ⁵²H. W. Paxton, J. M. Sheehan, and W. J. Babyak, *Trans. Metall. Soc. AIME* **215**, 725 (1959).
- ⁵³T. Schober and U. Linke, *Metallography* **9**, 309 (1976).
- ⁵⁴W. M. Albrecht, W. D. Goode, and M. W. Mallett, *J. Electrochem. Soc.* **106**, 981 (1959).
- ⁵⁵G. C. Rauch, R. M. Rose, and J. Wulff, *J. Less-Common Met.* **8**, 99 (1965).
- ⁵⁶J. M. Welter and F. J. Johnen, *Z. Phys. B* **27**, 227 (1977).
- ⁵⁷H. F. Horn and W. T. Ziegler, *J. Am. Chem. Soc.* **69**, 2762 (1947).
- ⁵⁸C. D. Wiseman, *J. Appl. Phys.* **37**, 3599 (1966).
- ⁵⁹K. M. Ralls and J. Wulff, *J. Less-Common Metals* **2**, 127 (1966).
- ⁶⁰E. G. Maksimov and O. A. Pankratov, *Usp. Fiz. Nauk* **116**, 385 (1975) [*Sov. Phys. Usp.* **18**, 481 (1976)].
- ⁶¹V. E. Schröder, *Z. Naturforsch.* **12A**, 247 (1957).
- ⁶²D. G. Westlake and W. R. Gray, *Appl. Phys. Lett.* **9**, 3 (1966).
- ⁶³H. Rauch, E. Seidl, and A. Zeilinger, *J. Appl. Phys.* **49**, 2731 (1978).
- ⁶⁴G. Alefeld, G. Schaumann, J. Tretkowski, and J. Völkl, *Phys. Rev. Lett.* **22**, 697 (1969).
- ⁶⁵R. M. Cotts, *Hydrogen in Metals I*, edited by G. Alefeld and J. Völkl (Springer-Verlag, Berlin, 1978), p. 256.
- ⁶⁶D. Zamir and R. M. Cotts, *Nuclear Magnetic Resonance and Relaxation in Solids*, edited by L. V. Gerven (North-Holland, Amsterdam, 1965), p. 276.
- ⁶⁷R. E. Norberg, *Phys. Rev.* **86**, 745 (1952).
- ⁶⁸G. Alefeld, J. Völkl, and J. Tretkowski, *J. Phys. Chem. Solids* **31**, 1765 (1970).
- ⁶⁹O. J. Zogal and R. M. Cotts, *Phys. Rev. B* **11**, 2443 (1975).
- ⁷⁰H. C. Bauer, J. Völkl, J. Tretkowski, and G. Alefeld, *Z. Phys. B* **29**, 17 (1978).
- ⁷¹H. Wenzl, J. M. Welter, *Current Topics in Materials Science, Vol. 1*, edited by E. Kaldis (North-Holland, Amsterdam, 1977), p. 620.
- ⁷²W. T. Chandler and R. J. Walter, *Refractory Metal Alloys*, edited by I. Machlin, R. T. Begley, and E. D. Weisert (Plenum, New York, 1968), p. 215.
- ⁷³O. Buck, D. O. Thompson, and C. A. Wert, *J. Phys. Chem. Solids* **32**, 2331 (1971).
- ⁷⁴M. Amano and Y. Sasaki, *Phys. Status Solidi A* **19**, 405 (1973).
- ⁷⁵C. P. Flynn and A. M. Stoneham, *Phys. Rev. B* **1**, 3966 (1970).
- ⁷⁶C. C. Baker and H. K. Birnbaum, *Acta Metall.* **21**, 865 (1973).
- ⁷⁷K. W. Kehr, D. Richter, and K. Scroeder, *Proc. of a Symposium on Neutron Inelastic Scattering, Vienna* (IAEA, Vienna, 1978), Vol. 2, p. 399.
- ⁷⁸T. Springer, 3rd Intern. School on Neutron Physics, Alushta, 1978, p. 112 (unpublished).
- ⁷⁹T. Matsumoto, Y. Sasaki, and M. Hihara, *J. Phys. Chem. Solids* **36**, 215 (1975).
- ⁸⁰T. W. Haas, *J. Appl. Phys.* **39**, 5854 (1968).
- ⁸¹P. Pattison, M. Cooper, and J. R. Schneider, *Z. Phys. B* **25**, 155 (1976).
- ⁸²W. L. McMillan, *Phys. Rev.* **167**, 331 (1967).
- ⁸³J. J. Hopfield, *Phys. Rev.* **186**, 443 (1969).