Hydrogen Uptake by High Purity Niobium Studied by Nuclear Analytical Methods

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Abstract. Niobium RF superconducting cavities form the basic component of particle accelerators. The presence of trace amounts of hydrogen in niobium is believed to have a detrimental effect on the mechanical and superconducting properties. We have used prompt gamma-ray activation analysis (PGAA) and neutron incoherent scattering to measure bulk hydrogen content in niobium, and the nuclear reaction method to study hydrogen as a function of depth. The methods were used to study native hydrogen concentrations in the niobium, and to study the effects of vacuum heating and acid treatment on the hydrogen concentration.

INTRODUCTION

Niobium RF superconducting cavities are fast becoming the basic accelerator structures of a new breed of particle accelerators. It is suspected that the presence of interstitial elements in the niobium used to build these cavities may result in degradation of mechanical, thermal, and electrical properties. One such element is hydrogen, which is known to affect materials properties in many materials. Hydrogen is known to cause embrittlement in metals and to change the electrical properties of semiconductor materials. In niobium, the presence of hydrogen and other interstitial elements in the bulk of the metal can lower its thermal conductivity. Hydrogen may also present a problem when present on or near the surface of the niobium cavity. Prior to use, the high-purity niobium must be chemically polished (treated with acid) to remove surface imperfections which could degrade the superconducting properties. This chemical polishing is believed to introduce trace hydrogen on the surface and near surface of the metal. A significant drop in the superconductor's Q-value has been observed if the temperature of the niobium is held at $75 \text{ K} \leq T \leq 130 \text{ K}$ for more than about an hour before being returned to its superconducting state below 9 K, and has been attributed to hydride precipitation of interstitial hydrogen.[1] Therefore, in order to optimize the performance of the cavities, hydrogen in both the bulk of the niobium and near the surface needs to be minimized. Bulk hydrogen and other interstitial elements need to be minimized to improve the thermal conductivity of niobium so that at higher gradients and not so high Q-values the cavity can run stably. The surface hydrogen concentration needs to be reduced so that the Q-value of the cavities is high.

Unfortunately, definitive measurements of hydrogen in niobium have been hampered by a lack of techniques yielding reliable quantitative measurement below H mass fractions of 100 mg/kg.

Nuclear analytical methods have proven useful for the measurement of hydrogen in materials. Jefferson Laboratory, which is responsible for building the accelerator that is the heart of the Spallation Neutron Source, recently began a collaboration with NIST and SUNY Albany to study hydrogen in niobium metal by nuclear techniques. Two techniques that have been developed at NIST to measure bulk hydrogen in materials are prompt gamma-ray activation analysis (PGAA) and neutron incoherent scattering (NIS). In PGAA, the sample is irradiated with a beam of neutrons, inducing nuclei of most elements to undergo neutron capture and emit prompt gamma rays upon de-excitation. The gamma rays are then measured using a high-resolution germanium detector. Comparison with standards yields quantitative multielemental analysis. The measurement is nondestructive, chemically specific, matrix independent, and because both neutrons and gamma rays are penetrating, the entire sample is analyzed. Furthermore, because the measurement arises from a nuclear reaction, the results are independent of the chemical form of the element being determined. The presence of hydrogen is indicated by the appearance of a 2223 keV gamma-ray.

NIS takes advantage of the anomalously high incoherent scattering cross section for hydrogen ($\sigma_{bound} = 80$ b). The sample is placed in a neutron beam, and neutrons scattered from the sample are measured using a ^{3}He detector. Because the neutron scattering cross section for hydrogen is much larger than the absorption cross section ($\sigma_\gamma = 0.3$ b), the NIS technique achieves a higher sensitivity and more rapid detection of hydrogen than PGAA. The disadvantage is that the signal is not specific to hydrogen, hence a reliable blank (same matrix as the sample but containing no hydrogen) is needed to account for neutron scattering by other elements. Nevertheless, we have found NIS to be a useful complementary tool to PGAA for hydrogen measurement.

Nuclear reaction methods have been used to measure hydrogen occurring on or near the surface of materials. Such methods make use of reactions which occur when a surface is bombarded with a beam of heavy ions. Using the method developed at SUNY to study hydrogen, the sample is bombarded with a beam of ^{15}N ions, inducing the nuclear reaction $^{15}\text{N} + {}^1\text{H} \rightarrow {}^4\text{He} + {}^{12}\text{C} + \gamma$. The method takes advantage of the fact that the reaction cross section at the resonance energy ($E_r = 6.385$ MeV) is four orders of magnitude larger than the cross section just outside of this energy region (resonance width, $\Gamma = 0.0018$ MeV). When the sample is bombarded by ^{15}N ions at the resonance energy, the gamma-ray yield is proportional to the amount of hydrogen on the surface. Bombardment of the sample by ions above the resonance energy induces negligible reaction with surface hydrogen, but as the ^{15}N ions penetrate and lose energy, they reach the resonance energy at some depth. The gamma-ray yield is then proportional to the amount of hydrogen present at that depth. Thus, by measuring the gamma-ray yield as a function of beam energy, a hydrogen depth profile (concentration vs. depth) is determined.

EXPERIMENT

Measurement of Bulk Hydrogen

In this investigation we initially set out to answer two questions: Does the acid treatment of the niobium introduce a measurable amount of hydrogen into the material, and can the hydrogen be removed by vacuum heating? Initial measurements were made on five rectangular slabs of ultrapure niobium, each weighing approximately 10 g, with dimensions 1.95 cm x 1.45 cm x 0.41 cm.^{2} Prior to acid treatment, the niobium samples were degassed at Jefferson Laboratory by heating in a high temperature vacuum furnace to remove as much hydrogen as possible. The temperature and duration of this heating for each sample is given in Table 1, column 1. Measurements made on the degassed samples were meant to serve as a baseline for comparison with measurements made after acid treatment.

The degassed samples were sent to NIST for measurement of bulk hydrogen. PGAA measurements were made using the cold neutron PGAA instrument located at the NIST Center for Neutron Research (NCNR). The instrument (shown in Figure 1) has been described previously.[3-6] Each sample was irradiated for at least 6 hours with a 1 cm collimated neutron beam inside an evacuated sample chamber. Thin disks of niobium foil and urea (containing 6.67 wt. % hydrogen) were irradiated as standards. A background spectrum was taken of the empty sample holder similarly irradiated. In each spectrum the hydrogen peak at 2223 keV and the niobium peak at 5104 keV were analyzed. Count rates were corrected for background, and the % H atom fraction of each sample was calculated.

After the baseline measurements were completed, the samples were sent back to Jefferson Laboratory for chemical polishing. Samples were polished by subjection to acid treatment, with voltage applied in an attempt to load hydrogen. The duration of the treatment for each sample is given in Table 1, column 3. The samples were returned to NIST where a second PGAA hydrogen determination was performed on each piece. The acid treated samples were also analyzed by NIS using the setup shown in Figure 2.[7-9] Each sample was measured for 360 seconds, to obtain counting statistics of better than 1%. A background run (empty aperture) was also performed, and the background count rate subtracted from each sample count rate to obtain the net scattered intensity from each sample. The count rate was calibrated as a function of hydrogen content using the polypropylene films addition method. [7-9] Each layer of polypropylene film used with the Nb bulk sample represented (21.1 ± 2.0) mg/kg of H in Nb, or (0.194 ± 0.018) % atom fraction of hydrogen (uncertainties are 1s). The uncertainty was estimated based on
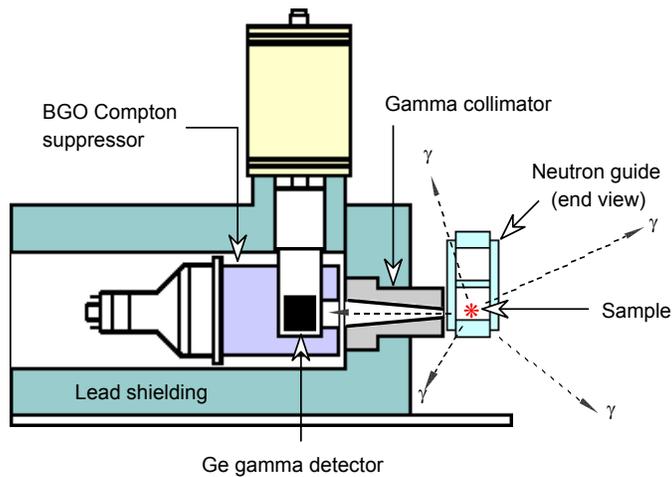
Figure 1. Cold neutron PGAA spectrometer at the NIST Center for Neutron Research
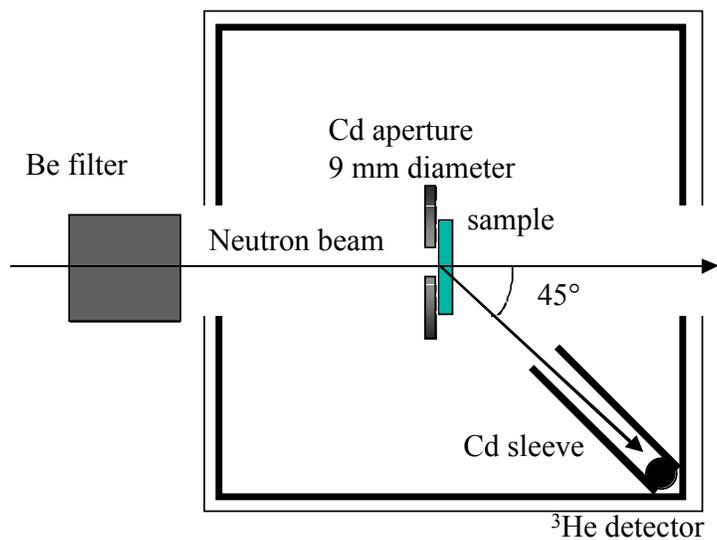
Fig. 2. Schematic drawing for the NIS measurement setup. The calibration using polypropylene films have been carried out using the same setup.

the propagation of uncertainty in the polypropylene film thickness (5.5 µm ± 0.5 µm, with 1s uncertainty), which dominates over the counting statistics.

Because the samples were not measured by NIS before acid treatment, there was no baseline against which to compare the measurements. Therefore, niobium

Table 1. Treatment of niobium samples measured in this investigation.

Sample	Measured as received?	Measured following:	Measured following:	Measured following:	
	(No heating)	Vacuum heating 1	Acid treatment 1 duration (min)	Vacuum heating 2	Acid treatment 2 duration (min)
Nb 2	No	800 °C / 6 h	1	---	---
Nb 3	No	700 °C / 6 h	2	---	---
Nb 4	No	750 °C / 6 h	3	800 °C / 6 h	---
Nb 5	No	600 °C / 6 h	0.5	800 °C / 6 h	5
Nb 6	Yes	----	4	---	---
P1	Yes	800 °C / > 48 h	----	----	----
P2	Yes	800 °C / > 48 h	----	----	----
K1	Yes	800 °C / > 48 h	----	----	----
K2	Yes	800 °C / > 48 h	----	----	----

samples 4 and 5 were returned to Jefferson Laboratory and subjected to a second vacuum heating for 6 hours at 800 ˚C, in order to remove the hydrogen. Sample 5 was then again subjected to hydrogen loading via acid treatment with applied voltage. Both samples were returned to NIST and again measured by both NIS and PGAA, in order to discern whether the hydrogen content of the two samples differed.

Additional baseline measurements for PGAA were performed on two samples each of two batches of niobium metal (labeled P and K). Each of these samples weighed 2.7 g, with dimensions 1 cm x 1 cm x 0.32 cm. All four samples were measured by PGAA "as received" (without vaccuum heating), and again after being vacuum heated at 800 ˚C for > 48 hours.

Hydrogen Depth Profiles

Hydrogen depth profiles were measured using the ^{15}N nuclear reaction method.[9] Measurements were made on the samples Nb 4 and Nb 5 after the second vacuum heating and second acid treatment respectively. Measurements were also made on samples of the niobium P and K metal. All samples were analyzed under (as nearly as possible) identical conditions. Each was first exposed to a small ^{15}N dose to get the "surface H profile" (6.4 to 6.5 MeV) and then each was exposed to a larger ^{15}N dose (6.5-6.65 MeV) to measure the concentration in the "subsurface".

RESULTS AND DISCUSSION

Bulk Hydrogen

While the relative change in the amount of hydrogen in the samples before and after each treatment can be easily determined by both PGAA and NIS, the absolute amount of hydrogen at any stage is not well defined. The principle difficulty in the determination of the absolute amount of hydrogen by either technique is the lack of a definitive blank. Such a blank is necessary for NIS, because neutrons scattered from the sample by hydrogen cannot be distinguished from neutrons scattered by niobium or other elements in the sample. For measurement of hydrogen at very low levels by PGAA, a blank is also necessary for some materials due to the possibility of spectral interferences. Although current prompt gamma-ray compilations do not list a niobium peak at 2223 keV that would interfere with hydrogen measurement, it is unlikely that all prompt gamma-rays lines in the niobium spectrum have been catalogued. Due to the high density of neutron capture levels for many elements, PGAA spectra often consist of thousands of peaks, the tiniest of which are not listed in prompt gamma-ray compilations. Figure 3 shows the spectrum of Nb sample 4 after the first vacuum heating, and again after acid treatment. Both spectra show a peak at 2223 keV, which, if due to hydrogen, yields the equivalent of ~ 0.3 % atom fraction of hydrogen. However, without a well defined niobium blank (known to contain no hydrogen), it is difficult to determine whether this peak is indeed entirely due to hydrogen, or whether there is an underlying niobium interference peak at this same energy. Furthermore, since a peak at 2223 keV in excess of the hydrogen background count rate was observed
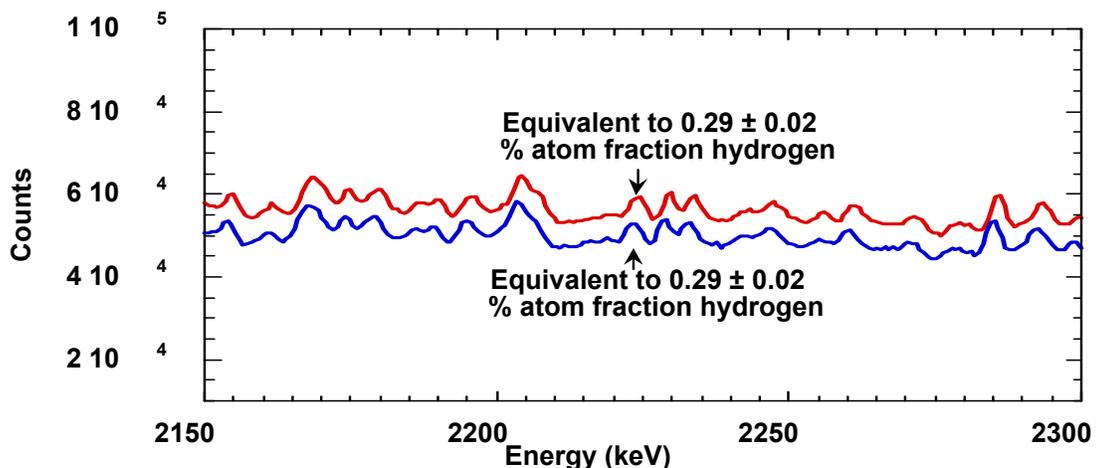
Figure 3. PGAA spectrum (H energy region) of Nb sample 4 after first vacuum heating (top), and then after acid treatment (bottom).
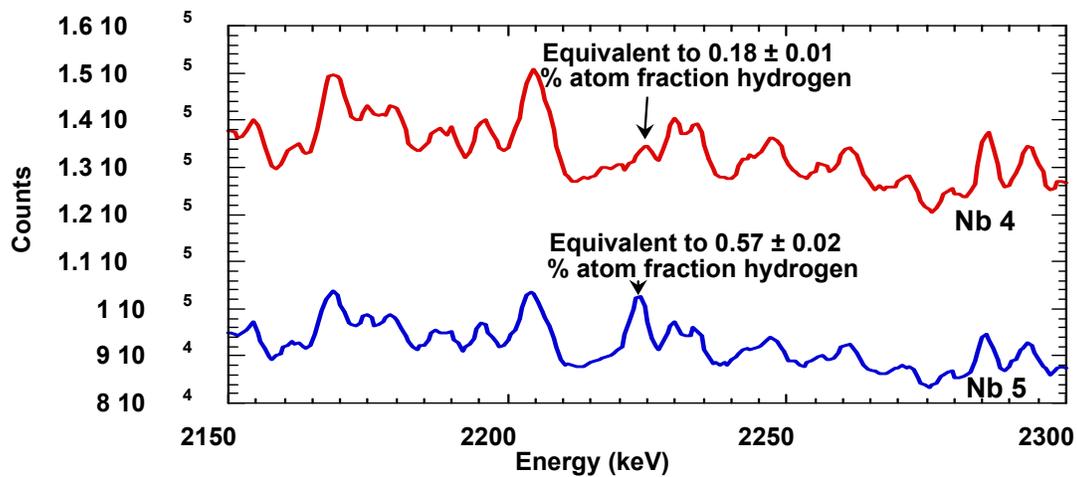
Figure 4. Top: PGAA spectrum (H energy region) of Nb sample 4 after the second vacuum heating. Bottom: PGAA spectrum of Nb sample 5 after second degassing and second acid treatment.

in every PGAA spectrum taken of these samples, it is impossible to say that any of the samples achieved zero hydrogen content after vacuum heating.

Figure 4 shows the PGAA spectrum of Nb sample 4 taken after the second vacuum heating. This spectrum shows a much smaller signal at 2223 keV than previously observed for this sample, indicating that significantly more hydrogen was removed than in the first vacuum heating. Of all measurements made on the initial set of samples, this measurement yielded the lowest hydrogen signal for both PGAA and NIS. Moreover, the 2223 keV signal observed in this measured was identical within experimental uncertainties to that observed for the P and K niobium samples after vacuum heating for > 48 h at 800 ˚C. These measurements yielded an equivalent H concentration of 0.19 ± 0.01 atomic %, in agreement with that measuremed for the twice degassed Nb 4. The results indicate that either residual hydrogen is extremely difficult to remove from niobium, even at high temperatures and long heating times, or that the residual 2223 keV peak observed in the material after this degassing is due to niobium, not hydrogen. If we assume the latter to be true, we can use the twice degassed Nb 4 sample and the long degassed P and K samples as blanks, and establish a detection limit for H in Nb by PGAA equal to 3s of the uncertainty of the signal observed for the blank material, or ≤ 0.03 atomic %.

Table 2 shows hydrogen fractions in the niobium samples calculated relative to the blank. For most measurements, hydrogen fractions determined by PGAA are in agreement with those determined by NIS. For four of the five samples, no measurable hydrogen gain was noted between the first vacuum heating and the first acid treatment. The PGAA measurements indicated an increase in the hydrogen content of sample 2 after acid treatment, however this increase was not confirmed by the NIS measurements. However, both techniques measured a significant increase in hydrogen content for sample 5 after the second acid treatment (see Figure 4). The hydrogen content of the P and K samples also showed a small decrease after vacuum heating.

Table 2. Hydrogen fractions measured in the niobium samples with blank correction. PGAA uncertainties are 2s based on propagation of counting statistics and uncertainties in element sensitivities, NIS uncertainties are 2s based on the propagation of uncertainty in the polypropylene film thickness.

Sample	% atom fraction hydrogen (determined relative blank)					
	As received	After vacuum heating #1	After acid treatment #1		After vacuum heating #2 (Nb 4) and acid treatment #2 (Nb 5)	
		PGAA	PGAA	NIS	PGAA	NIS
Nb 2	---	0.138 ± 0.025	0.257 ± 0.041	0.153 ± 0.032	---	---
Nb 3	---	0.156 ± 0.026	0.169 ± 0.028	0.167 ± 0.034	---	---
Nb 4	---	0.122 ± 0.028	0.114 ± 0.027	0.083 ± 0.020	≤ 0.03	≤ 0.03
Nb 5	---	0.107 ± 0.025	0.107 ± 0.025	0.113 ± 0.024	0.396 ± 0.037	0.352 ± 0.070
Nb 6	0.126 ± 0.027	---	0.140 ± 0.028	0.150 ± 0.032	---	---
P1	0.03 ± 0.02	≤ 0.03	---	---	---	---
P2	0.03 ± 0.02	≤ 0.03	---	---	---	---
K1	≤ 0.04	≤ 0.03	---	---	---	---
K2	0.03 ± 0.02	≤ 0.03	---	---	---	---

In summary, the bulk hydrogen measured in the first set of niobium samples after the initial vacuum heating did not show a correlation with the time or temperature of degassing, nor did hydrogen content after the initial acid treatment correlate with duration of the treatment. However, the results obtained for samples 4 and 5 after the second vacuum heating and acid treatment respectively indicate that both processes can affect the hydrogen content of the niobium. Therefore, the answers to the two questions we set out to ask are "no" for the first cycle of treatment but "yes" for the second cycle. One possible explanation for the significant gain in hydrogen by sample 5 is that heat treatment at 800 ˚C causes removal of strongly bound hydrogen, thereby activating sites where hydrogen can be picked up by the niobium upon subsequent acid treatment. The removal of this strongly bonded hydrogen during the heat treatment may also be responsible for the observed changes in the mechanical properties of the niobium.[1] Additional measurements are necessary in order to fully understand these processes.

Depth Profiles

Hydrogen depth profiles for all samples measured appear in Figure 4. Apart from the fact that the H charged sample (Nb 5) was observed to contain less hydrogen than the vacuum degassed sample (Nb 4), no correlation was observed between the bulk H content of the samples and their H depth profiles. Note that the nuclear reaction method is capable of measuring hydrogen with background at levels around 100 atomic ppm, which is comparable to the hydrogen concentrations measured by PGAA and NIS.
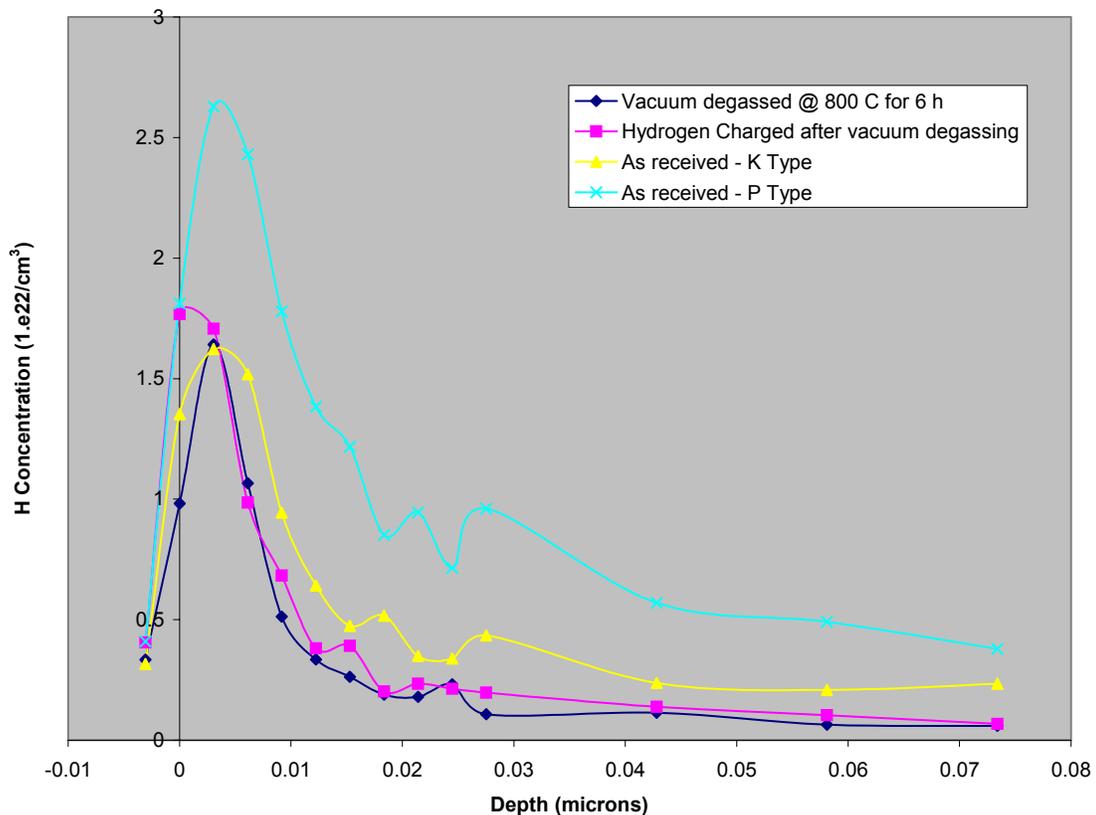
Figure 3. Hydrogen depth profiles for Nb samples measured using the nuclear reaction method.

Nature of chemical bonding

One key piece of information not yielded by any of the techniques used above is the nature of the hydrogen bonding in the niobium. In order to fully understand how hydrogen and other trace elements affect the properties of niobium,

it is important to distinguish between bound and interstitial elements. It may be feasible to study the nature of the hydrogen bonding in the samples by NIS. The current NIS measurements were carried out at room temperature. In theory the nature of the hydrogen bonding can be distinguished by measuring the scattering cross section as a function of H concentration.[11] Likewise, dependence of other factors such as temperature should give the same information. Between a free atom and a rigidly bound atom, the hydrogen can behave like a lattice gas or like an anisotropic harmonic oscillator. At temperatures sufficiently low where H in Nb precipitates, the temperature dependence of the scattering cross section can be a tell-tale indicator of these behaviors. Preliminary NIS experiments on H-Ti systems cooled to liquid nitrogen temperature and warmed freely to room temperature, with data collected every 30 s, indicated differences in temperature dependence of the scattered intensity for the three different H concentrations.[12] There are dedicated neutron scattering instruments (inelastic and quasi-elastic scattering) to study the nature of the hydrogen bonds, but at these low concentration levels the measurements are difficult. The total scattering technique we employed has the advantage of rapid data collection even with these sample sizes and concentrations.

Interstitial elements in niobium and other metals may also be studied using damping or internal friction techniques.[13] In these experiments, Debye peaks are observed whose magnitude depends on concentration of the interstitial responsible for the peak with a temperature or frequency depending on the kinetics of the mechanism of interaction. In a preliminary study, one of these techniques was used to examine interstitial oxygen contents in niobium samples since the hydrogen-dislocation interaction (Snoek) peak is expected to occur at a temperature below current testing capabilities (40-60 K). Similar methods have been used to study hydrogen, oxygen, nitrogen, and carbon in Nb[14-16] and to study of the efficacy of treatments to outgas hydrogen from vanadium.[17] The results of this preliminary study indicate that this technique can be used to estimate interstitial content and to evaluate concentration changes with different treatments. Future plans include using this method to measure hydrogen in niobium and other materials and to combine PGAA, NIS, and these studies to help understand the behavior of interstitial hydrogen in niobium.

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