

# HYDROGEN SATURATION AND THE THERMAL CONDUCTIVITY OF SUPERCONDUCTING NIOBIUM\*

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## Abstract

The effect of interstitial hydrogen on the magnitude of the phonon peak is examined by subjecting two bicrystal niobium specimens to 300 °C for 1 h in a 75% hydrogen, 25% nitrogen atmosphere at 0.5 atm., and subjecting a monocrystal specimen to a 100 μm uncooled BCP etch. Prior to hydrogen infusion, specimens 1 and 3 were heated to 800 °C for 2 h and 1200 °C for 2 h, respectively. Specimen 2 was heated first to 140 °C for 48 h and later to 1100 °C for 4 h prior to the hydrogen infusion. Both specimens exposed to the 300 °C heating displayed a 25% reduction in the phonon peak due to the additional hydrogen, independent of their crystal orientations and heat treatment histories. The uncooled BCP etch resulted in a 15% reduction in the phonon peak for specimen 3. An 800 °C vacuum heating for 2 h was found to be sufficient to recover the phonon peak in specimen 1, while an 1100 °C heating for 4 h was required to recover the phonon peak in one of the grains of specimen 2. A 1000 °C heating for 2 h partially recovered the phonon peak in specimen 3. The results suggest that hydrogen trapped in the niobium lattice will degas when the material is heated to at least the temperature to which it was heated at prior to the hydrogen infusion step. The vacancy concentration is believed to play a role in this phenomenon.

## INTRODUCTION

The thermal conductivity  $k$  of niobium for temperatures below 3 K is dominated by phonon transport. In niobium with sufficiently few lattice imperfections, a maximum in  $k$  occurs at 1.8 K, called the phonon peak. A large phonon peak is desired for improved thermal transport between the RF surface of the cavity and the superfluid helium bath. This reduces potential local hot spots and contributes to an increased cavity quality factor  $Q$  in the mid- and high-field  $Q$ -slope region. The magnitude of the phonon peak is sensitive to SRF cavity manufacturing processes, such as de-

formation, annealing heat treatments, and chemical treatments that may expose the niobium to impurities.

SRF cavity fabrication includes chemical processing steps, such as buffer chemical polishing (BCP) and electropolishing (EP), which introduce interstitial hydrogen into the niobium. Excessive hydrogen can adversely affect the quality factor of cavities by precipitating into hydrides in the niobium [1, 2]. The current standards for cavity processing includes cooling the BCP bath to  $T < 10$  °C to reduce hydrogen uptake. A fast cool down ( $\geq 1$  K·min<sup>-1</sup>) of the niobium cavity [1], especially at  $77 \leq T \leq 170$  K was also identified as a critical measure to prevent the precipitation of hydrogen into hydrides. Specimens mildly etched ( $< 30$  μm) through cooled BCP have shown little effect on the thermal conductivity for  $1.6 \leq T \leq 4.2$  K [3].

This study exposes one mono- and two bicrystal niobium specimens to hydrogen concentrations greater than typical cavity processing, in an effort to identify the worst-case thermal scenario for a cavity accidentally infused with hydrogen.

## EXPERIMENTAL DETAILS

### Hydrogen Infusion

The impermeable niobium pentoxide (Nb<sub>2</sub>O<sub>5</sub>) layer on the surface of niobium needs to be removed in order to infuse the specimens with hydrogen. Two methods are used to infuse hydrogen into the specimens after dissolving the Nb<sub>2</sub>O<sub>5</sub> layer. The first method heats the specimens in a hydrogen rich environment, to temperatures hotter than 250 °C to dissolve [4] the impermeable niobium pentoxide layer, and saturates them for the heating temperature. The second method simulates a cavity processing incident, by performing a heavy BCP etch in an uncooled acid bath. Recovery heat treatments are identified for each of the specimens.

Two bicrystal, specimens 1 and 2, and one monocrystal, specimen 3, niobium specimens with different heat treatment histories were subject to hydrogen infusion. Prior to hydrogen infusion, specimens 1 and 3 had been heat treated at 800 °C for 2 h and 1200 °C for 2 h, respectively in a custom built high-temperature, high-vacuum furnace [5]. Specimen 2 was first heat treated at 140 °C for

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Table 1: Hydrogen Specimen Histories

Spec.	Est. RRR before H <sub>2</sub>	Heat Treatment (HT)				Hydrogen Treatment		Recovery Heat Treatment (HT)			
		First HT		Second HT		Hot infusion	Uncooled BCP	First HT		Second HT	
		T <sub>h</sub> (°C)	t (h)	T <sub>h</sub> (°C)	t (h)			T <sub>h</sub> (°C)	t (h)	T <sub>h</sub> (°C)	t (h)
1	100	800	2			✓		800	2		
2	190	140	48	1100	4	✓		800	2	1100	4
3	110	1200	2				✓	1000	2		

48 h, and subsequently heated to 1100 °C for 4 h prior to the hydrogen experiment. The thermal conductivities of the specimens were measured in their as-received state, after each heat treatment, and after hydrogen infusion. The as-received state thermal conductivities of the specimens displayed no phonon peak due to thermal strain-induced dislocations from ingot production [3, 6, 7]. The conductivity was unaffected after the 140 °C for 48 h heating for specimen 2 [3, 7].

Hydrogen was infused into the bicrystal specimens 1 and 2 by heating them to 300 °C for 1 h in a 75% hydrogen, 25% nitrogen environment at 0.5 atm. in a brazing furnace. Monocrystal specimen 3 was infused with hydrogen by performing a 100 µm, uncooled BCP etch. Subsequent to the hydrogen infusion, the thermal conductivity of the specimens were measured. Later, specimens 1 and 2 were heat treated at 800 °C for 2 h to degas hydrogen. Based on the results from the degassing heating, specimen 2 was heated again to 1100 °C for 4 h, and specimen 3 was heated to 1000 °C for 2 h. The histories of the specimens are summarized in Table 1.

Using the temperature of heating and the partial pressure of hydrogen, the equilibrium concentration of hydrogen in niobium for specimens 1 and 2 were estimated to be 41.2 at. % hydrogen. At room temperature, this is close to the  $\alpha+\beta$  and the  $\beta$  phase interface in the niobium-hydrogen phase diagram [8, 9]. At cryogenic temperatures, the system is close to the  $\alpha + \epsilon$  and the  $\epsilon$  phase interface. Based on the thickness of the specimens and the diffusion distance for hydrogen in niobium, the specimens heated to 300 °C for 1 h were saturated with hydrogen [3].

### Thermal Conductivity Estimation

The thermal conductivities of the specimens were estimated using a novel technique described in [3, 10]. This technique estimates thermal conductivity from temperature gradient measurements along the length of the specimens, and a parameter estimation algorithm that uses all of the temperature and heat flux data simultaneously. A temperature gradient is obtained by applying a finite electrical power on one end of the specimen while cold sinking the other. The temperature gradient is measured using four calibrated carbon resistors, and yield three thermal conductivity curves for each specimen corresponding to the three

temperature sensor pairs.

## RESULTS

### Saturated Hydrogen

The thermal conductivity curves for specimens 1 after the 800 °C for 2 h heating (open symbols), after hydrogen infusion through the 300 °C for 1 h heating (half filled symbols), and after the 800 °C for 2 h degassing heating (solid symbols) are illustrated in Figure 1. The infusion of hydrogen into the specimen, on an average, led to a 25% reduction in the phonon peak, with no change in the conductivity for  $T > 3$  K. The 800 °C for 2 h heating is observed to be sufficient to recover the phonon peak by degassing hydrogen from the material.

The conductivity curves for the 1100 °C heat treated specimen 2 after its initial 1100 °C for 4 h heat treatment (open symbols), after hydrogen infusion through the 300 °C heating (half filled symbols), after the 800 °C for 2 h degassing heating (red solid symbols), and after the 1100 °C for 4 h degassing heating (dark yellow solid symbols) are illustrated in Figure 2. In addition to the 25% reduction in the phonon peak after hydrogen infusion, similar to specimen 1, specimen 2 displayed a 10% reduction in the thermal conductivity at 4.2 K. The 800 °C for 2 h degassing heating was insufficient to recover the thermal conductivity, while the 1100 °C for 4 h degassing heating was sufficient to recover the phonon peak in grain 2 of the specimen, with no effect on grain 1.

### Hydrogen via Uncooled BCP

Specimen 3, unlike specimens 1 and 2, was infused with hydrogen through a more realistic uncooled BCP 100 µm etch, simulating an error during cavity processing. The conductivity curves for specimen 3 after the 1200 °C for 2 h heating (open symbols), after the uncooled BCP hydrogen infusion (half filled symbols), and after the 1000 °C for 2 h degassing heating (solid symbols) are illustrated in Figure 3. The excess hydrogen in the bulk lead to a 15% reduction in the phonon peak, with no change in conductivity for  $T > 3$  K. The hotter 1000 °C for 2 h hydrogen degassing heat treatment lead to nearly complete recovery in the phonon peak.

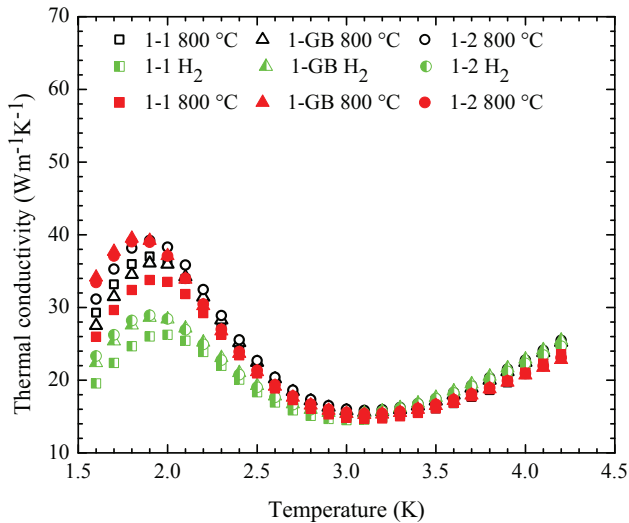


Figure 1: Thermal conductivity curves for specimen 1 after the 800 °C for 2 h heating (open symbols), after hydrogen infusion through the 300 °C for 1 h heating (half filled symbols), and after the hydrogen degassing heat treatment at 800 °C for 2 h (solid symbols). On an average, a 25% reduction in the magnitude of the phonon peak was observed due to the additional hydrogen. The 800 °C for 2 h degassing heating was sufficient to recover the phonon peak to its before hydrogen infusion condition.

### DISCUSSION

Hydrogen from both infusion methods resulted in reduction of the phonon peak. The estimated concentration of 41.2 at. % of hydrogen in niobium, for the specimens heated at 300 °C, is sufficient to form hydrides that scatter phonons and reduce the phonon peak by 25%. Additionally, a 100 μm BCP etch in an uncooled acid bath also introduces sufficient hydrogen to reduce the phonon peak by 15%. The 800 °C for 2 h heating in a high vacuum furnace has been thought to degas all hydrogen [11]. While the response of specimen 1 to the 800 °C degassing heating supports this, the conductivity curves from specimens 2 and 3 do not support it. One important difference between the specimens, in addition to the differences in their RRR, is the temperature of heat treatment prior to the hydrogen infusion. Specimen 1 was heated to 800 °C for 2 h prior to the hydrogen treatment, which is the same as the hydrogen degassing heat treatment. Specimens 2 and 3, though, had been heated at temperatures hotter than 800 °C, *i.e.*, 1100 °C for 4 h and 1200 °C for 2 h, respectively. This indicates that heat treatment history prior to hydrogen infusion plays an important role in determining the temperature of heating required to degas the hydrogen.

This phenomenon may be explained by considering the vacancy concentration of the specimens. The equilibrium vacancy concentration in niobium is exponentially propor-

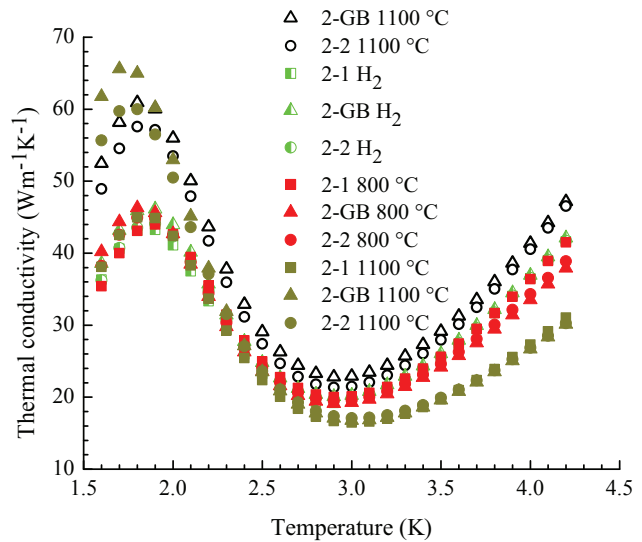


Figure 2: Thermal conductivity curves for specimen 2 after the 1100 °C heat treatment (open symbols), after hydrogen infusion (half filled symbols), after the hydrogen degassing heat treatment at 800 °C for 2 h (red solid symbols), and after the 1100 °C for 4 h hydrogen degassing (dark yellow solid symbols). Similar to specimen 1, the excessive hydrogen lead to a 25% reduction in the magnitude of the phonon peak. In addition, a 10% reduction in the conductivity at 4.2 K was observed. The 800 °C for 2 h hydrogen degassing heat treatment was insufficient to recover the phonon peak, and the subsequent 1100 °C for 4 h degassing heating lead to the recovery of the phonon peak for grain 2 with no change in conductivity for grain 1.

tional to the temperature of heat treatment. The vacancy concentration in the 1100 °C and 1200 °C heat treated specimens would be several orders of magnitude greater than that in the 800 °C heat treated specimen [3]. The additional vacancies may aid in absorbing more hydrogen atoms than that estimated based on the parameters of the infusion, leading to greater concentration of the solid-like  $\beta$  and  $\epsilon$  phases instead of the  $\alpha$  phase. In the  $\alpha$  phase, the hydrogen atoms are disordered like a gas [12, Chapter 2]. In the  $\beta$  and  $\epsilon$  phases, however, hydrogen is ordered like a solid and has well defined spacing [12, Chapter 2]. The mobility of the hydrogen atoms in the  $\beta$  phase has been observed to be two orders of magnitude less than that in the  $\alpha'$  phase [13 - 15]. The reason for the absence of recovery of the phonon peak in grain 1 of specimen 2 even after the 1100 °C for 4 h heating is not yet clearly understood.

The additional hydrogen in specimens 1 and 3 after hydrogen infusion, and before degassing heat treatments, had no effect on the electronic contribution to the thermal conductivity ( $T \geq 3$  K). In specimen 2, the additional hydrogen resulted in only a 10% decrease in conductivity at 4.2 K. Due to the consistently greater reduction in the

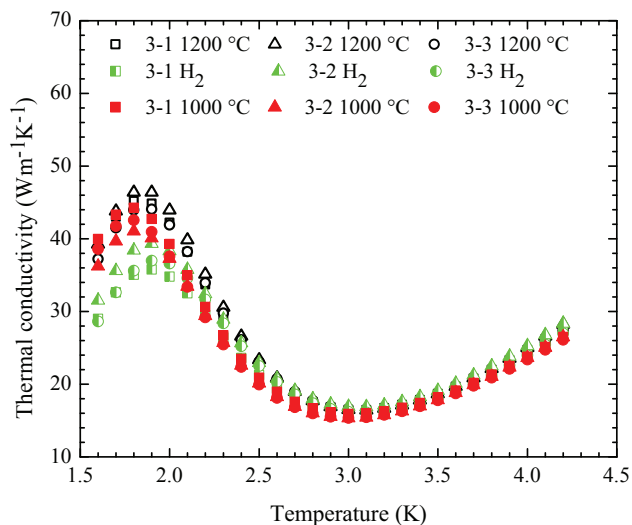


Figure 3: Thermal conductivity curves for specimen 3 after the 1200 °C heat treatment (open symbols), after hydrogen infusion through a 100  $\mu\text{m}$  uncooled BCP etch (half filled symbols), and after the hydrogen degassing heat treatment at 1000 °C for 2 h (red solid symbols). The excess hydrogen in the bulk lead to a 15% reduction in the phonon peak. The hotter 1000 °C for 2 h hydrogen degassing heat treatment lead to nearly complete recovery in the phonon peak.

phonon regime than in the electron regime of thermal conductivity, it may be concluded that phonons are more sensitive to hydrides than electrons, especially in niobium of  $100 \leq \text{RRR} \leq 200$ .

The 25% reduction in the thermal conductivity at 4.2 K after the degassing heat treatment at 1100 °C for 4 h is thought to be due to impurities introduced into the specimen in the furnace, despite using titanium getter.

## CONCLUSIONS

Standard cavity processing steps do not introduce sufficient hydrogen in the niobium to affect the phonon peak. Accidental exposure of a cavity to a heavy BCP in an uncooled acid bath could reduce the phonon peak by 15%. When saturated with hydrogen, the phonon peak is considerably reduced. Following excessive infusion of hydrogen, for complete recovery of the phonon peak by virtue of degassing hydrogen, a heat treatment at a temperature that is at least as hot as the heat treatment prior to the infusion is required.

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