

USE OF PRECISE X-RAY DIFFRACTION, INTERSTITIAL GAS ANALYSIS AND SQUID MEASUREMENTS TO INVESTIGATE CVD- AND BULK-NIOBIUM SAMPLES*

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Abstract

Niobium produced by chemical vapor deposition is compared to a bulk niobium sample (RRR=500). We report our measurements of impurity concentrations, values of T_c and magnetization vs. H near H_{c1} . X-ray measurements, taken before and after vacuum furnace annealing, indicated a greater reduction in the lattice constant (due to annealing) of the CVD sample than for the bulk sample. Secondary Ion Mass Spectroscopy (SIMS), in combination with x-ray diffraction revealed the CVD sample had approximately 3 at. % hydrogen; seven times more hydrogen than the bulk sample. After annealing, the impurity concentrations in the bulk sample were measured by commercial interstitial gas analysis (IGA). A precise comparison of nearby x-ray Bragg reflections with known single crystals of silicon and sapphire revealed several unsuspected features of these samples, including a possible dependence of the lattice constant on depth within a few microns of the surface and significant surface damage.

Magnetic moment measurements in the superconducting state indicate sharp NC-SC transitions with $T_c=9.26$ K for the bulk sample and $T_c=8.88$ K for the CVD sample. The difference of 0.38 ± 0.03 K persisted after annealing the CVD sample. At 1.9 K, H_{c1} (CVD) was equal to H_{c1} (bulk) or even perhaps slightly higher, while H_{c2} was 5100-6200 Oe for CVD and 3950 Oe for the bulk sample (as expected for pure Nb). The impurity content in the CVD, as inferred from comparative SIMS and IGA analysis of the bulk sample would not account for these differences, which are conjectured to be due to permanent defects caused by cooling the high hydrogen content of the CVD sample initially.

MOTIVATION

The use of chemical vapor deposited (CVD) niobium can lead to the elimination of a number of the procedures presently driving the cost of SRF cavity fabrication. This technology also holds some promise for improving both reproducibility and performance (Q vs. E curves.)

The advantages of using iodide process CVD will include: *use of reactor grade niobium* to replace the requirement of 500 tons of high RRR niobium for the ILC, *seamless construction* (avoiding mass production of electron beam welded cavities), and, finally, to better control over the niobium surface in order to reduce oxides and hydrogen contamination by *eliminating BCP and EP treatments*.

However, there has been no study of the SRF application for CVD niobium comparing it with conventional cavity-grade bulk niobium. The best test would be to construct a single cell SRF cavity using the CVD process. As a first step, we have used the facilities of the Cornell Center for Materials Research (CCMR) in order to compare both the metallurgical and DC superconducting properties of a sample piece of CVD niobium and a similar sample of high RRR bulk material.

PREPARATION AND CHARACTERISTICS OF CVD AND BULK NIOBIUM SAMPLES

The CVD sample was supplied by Ultramet[2]. It was on the outside of a solid molybdenum mandrel, which was about the size of a hockey puck. Figure 1 below shows this mandrel, which was covered with small crystals of niobium.



Figure 1: CVD Nb-Coated Mo Mandrel

As shown in the figure, a piece was removed with a diamond saw and placed in a room temperature bath of aqua regia. Vigorous bubbling occurred (it was probably hydrogen) until most of the molybdenum was dissolved. All gas evolution had stopped after 16 hours. X-ray diffraction and WDS [3] analysis showed that an alloy of niobium and molybdenum existed in a layer at least several microns thick, so that there was no detectable diffraction from pure niobium underneath the alloy layer. After further treatment in 1:1:2 BCP, x-ray analysis showed that only pure niobium was left. EDS[4] analysis

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confirmed this, showing no detectable impurities and no trace of molybdenum.

This piece was then mechanically polished [5], along with the DESY bulk niobium. (Henceforth referred to as “CVD” and “RRR” respectively.) After polishing both pieces were subjected to a 10 second etch in a 1:1 mixture of nitric acid and 40% hydrofluoric acid.

Figure 2 below shows the optical microscopy of the CVD piece at this stage.

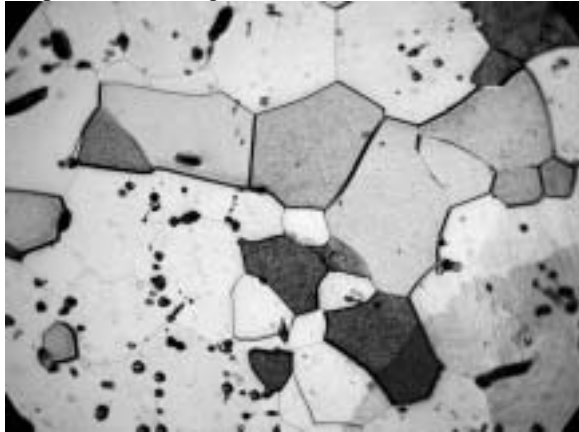


Figure 2: CVD Surface After Polishing and Light Etch

Grains of 100-500 microns in size are visible, plus numerous small black spots, which we assume are etch pits from surface defects. We looked further at one of these etch pits using an SEM. This is shown in Figure 3.

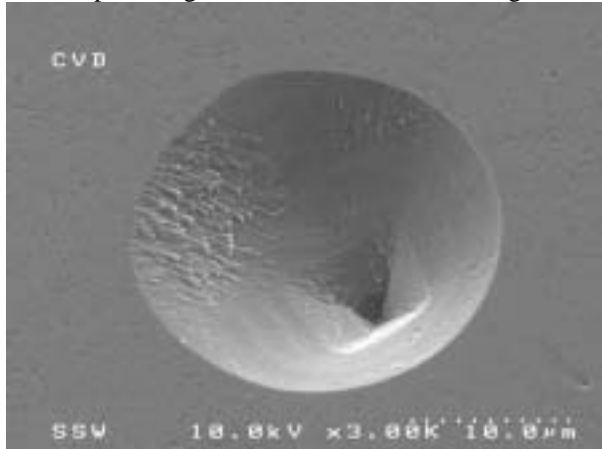


Figure 3: CVD Etch pit, magnified 3000x

The unusual square shape of this and other etch pits suggest that, perhaps, a microcrystal of some more easily etched foreign material was embedded in the niobium. Although some etch pits were visible in the RRR sample, they were less numerous and did not have the shape visible in Figure 3.

The RRR sample from DESY had been annealed in a UHV furnace for at least 4 hours at 1400 C. The grain size in this sample was 2-3 times larger than the CVD grain sizes.

EBSD data [6] was taken on both samples. The CVD results are shown in figure 4 below. Different colors correspond to different grain orientations.

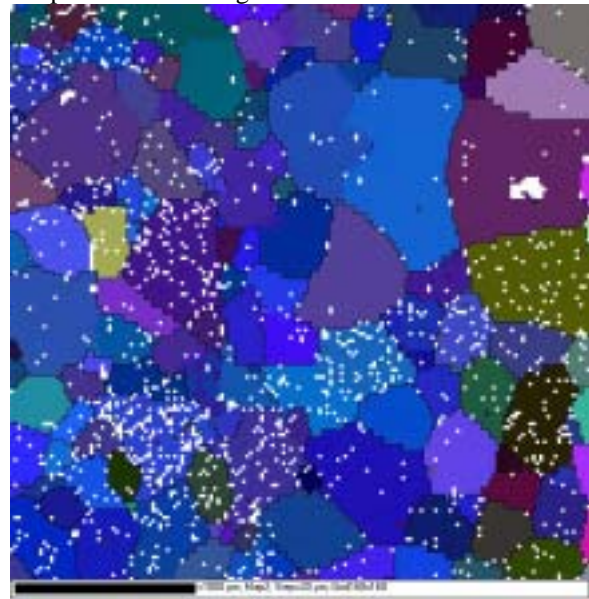


Figure 4: CVD EBSD Map (3.2 mm x 3.2 mm)

From these data, a pole figure plot could be constructed. The results, shown in figure 5 below, indicate that most of the grains are oriented with the 100 planes parallel to the surface of the sample.

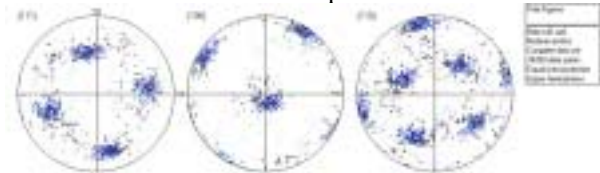


Figure 5: CVD Pole-Figure (EBSD)

This is apparent from the center plot of figure 5. The RRR sample showed mostly random orientation, with some texture due to rolling.

There is much more information available from EBSD about the grains, grain boundary angles, etc.

RESULTS OF COMMERCIAL ANALYSIS OF BULK SAMPLE

Analyzing the level of interstitial impurities contaminating the RRR sample was straightforward. A commercial firm [7] did the analysis for N, O, C, and H. The results for RRR, after the anneal at 1000 C at Cornell were:

Element	ppm wt.	atomic. %
N	6.7	.004
C	14	.011
O	32	.019
H	115	1.07

Table 1: RRR Chemical Analysis

X-ray diffraction evidence suggests that this sample actually gained hydrogen during the 1000 C anneal in a relatively poor vacuum (10^{-6} Torr). The numbers in Table I were taken after this annealing.

Analysis of the CVD sample was indirect, because not enough material was available, and the sample would be destroyed in the process of analyzing it. Before the anneal at 1000 C, both samples were investigated with SIMS [8]. A general scan over all elements revealed no significant impurities present except the interstitial elements in Table I. With SIMS, at a depth where asymptotic values had been reached, we obtained ratios of O, C, and H to niobium for both samples. By taking ratios of these ratios we estimated the relative amounts of O, C, and H in CVD from the measured concentrations in RRR. (The sensitivity of SIMS to N is too low to use this method for nitrogen.)

The results of the SIMS comparison are given in Table II below.

Element	RRR	CVD	CVD/RRR (error)
O/Nb	0.27 +/- .04	0.44 +/- .03	1.6 (17%)
C/Nb	0.42 +/- .05	0.07 +/- .03	0.2 (45%)
H/Nb	0.43 +/- .02	2.9 +/- .2	6.8 (9%)

Table 2: SIMS ratios and CVD/RRR ratios

Unless matrix effects are better understood, we cannot directly use the ratios in columns 2 and 3 above to determine concentrations. But it is believed that the CVD/RRR comparison should be a valid one [9].

The two samples have comparable oxygen levels. The hydrogen level in CVD is much higher than for RRR. By using x-ray data taken before and after the 1000 C anneal, we estimated 3 at.% H in CVD was present before the anneal took place. The solubility limit of the α phase (lattice gas) is 4% at room temperature.

SQUID MAGNETOMETER T_c MEASUREMENTS; MAGNETIZATION VS. H, NEAR H_{C1}

	DESY	CVD
Length(mm)	5.5	5.9
Width(mm)	5.6	4.9
Thickness(microns)	1100	382
Volume(cm^3)	.0354	.0110
Weight(gm)	.3038(2)	.0943(2)

Table 3: SQUID Sample Characteristics

The extreme sensitivity to changes in magnetic flux allows the SQUID [10] to measure the magnetic moments of these samples with a short-term repeatability of 10-30 ppm (.001-.003%), for magnetic moments in the range of .01-.02 emu.

The DESY sample in the SQUID measurements was a RRR=282 sample, also obtained from the TESLA group at DESY.

SQUID TEMPERATURE SCAN FOR T_c

The SQUID measured the magnetic moment in a field $H=10$ Oe, while the temperature was varied from 2.0 K to 9.5 K. The Meissner effect causes the magnetic flux to be expelled when $T < T_c$. $4\pi M = B-H$. There is a dramatic change in M, the magnetization, as T increases above T_c .

With the SQUID, it is possible to use small sample sizes and still have high accuracy. Each point was measured three times in succession. An average and a standard deviation are computed for each temperature.

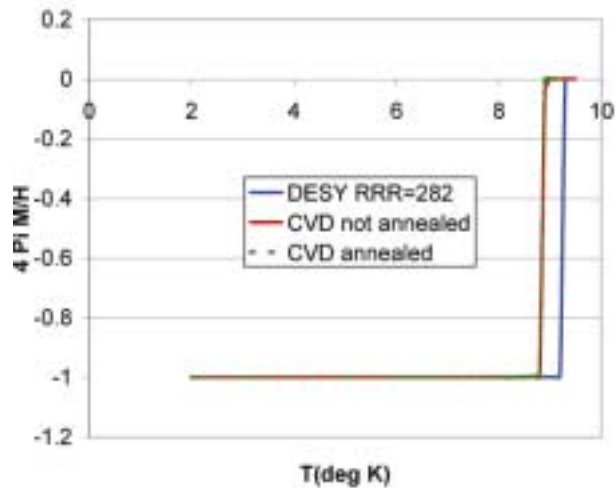


Figure 6: Relative magnetic moment vs. temperature

No change was observed in T_c (CVD) after the 1000 C annealing. The before and after curves are virtually indistinguishable so hydrogen is not the direct cause of the shift observed in T_c between CVD and RRR.

The numerical results are summarized in the table below.

Sample	T_c [observed]	ΔT_c
DESY RRR=282	9.24 +/- .02 K	≤ 0.1 K
CVD	8.86 +/- .02 K	≤ 0.1 K
T_c (DESY)- T_c (CVD)	0.38 +/- .03 K	

Table 4: Results for T_c and ΔT_c

A correction of +.023 K has been applied to get the numbers in the abstract from the data. The observed shift between the two samples could be caused by 0.42 at.% oxygen contamination. But this is more than an order of

magnitude greater than what we have measured, and appears very unlikely. We suspect that permanent defects created on the initial cool-down, when 3% hydrogen was in the lattice, may be the cause [11].

Magnetization vs. H at 1.9 K

This temperature was chosen because it is close to the operating temperature of SRF cavities.

The high precision of the SQUID allows us to take a very close look at the “linear” part of the magnetization data. We first fit a straight line to the data for $M(H)$ from zero to 500 Oe and thus obtain the slope of this line. In both cases, the data are indistinguishable from this fitted line. We then assume this slope of the linear part represents the effect of an average depolarization, so that the internal H field is increased by this factor. In the case of the DESY sample this means $H_{\text{internal}}=1.20 H$. For the CVD sample, $H_{\text{internal}}=1.05 H$. We assume the deviation from 1.0 is caused by a small tilt away from parallel H field relative to the sample surface. We currently lack a good numerical simulation of the magnetization for these geometric shapes, so must treat them as infinite slabs. We then plot the data for $4 \pi M+H_{\text{internal}}=B$ vs H_{internal} . A perfect fit to the Meissner effect would give zero up to H_{c1} , with a rapid increase above H_{c1} due to the creation of vortices penetrating the samples. The experimental results are shown in the figure below.

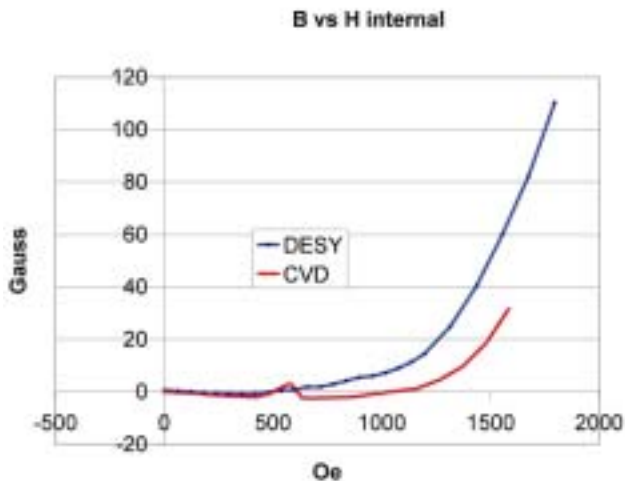


Figure 7: Average “B” vs H_{internal}

We see that the point at which B becomes non-zero is about 1150 Oe for the CVD sample and 650 Oe for the DESY sample. It is surprising that the flux penetrates at a point far below the nominal H_{c1} for pure niobium [12] especially in the case of the DESY sample, but this can happen because, for the rectangular slab geometry, the internal field is enhanced at the corners of the slab. Hence flux penetration begins there first, at values of H considerably lower than H_{c1} .

Even so, and perhaps coincidentally, these curves could be converted to a Q vs. E curve for comparison with rf measurements on real cavities. In a TESLA cavity, the maximum H_{rf} field is 43 Oe/MV/m, so 1150 Oe corresponds to an accelerating gradient of 26.7 MV/m, for

example. Flux penetrates our sample in a DC field at about the same applied H field that the rf magnetic field penetrates the surface of a cavity. There seems to be no way to prove if this intriguing result has any significance, however, so it remains a curious coincidence.

There is clear evidence for irreversible behavior at H fields as low as 100 Oe. The cause of this flux penetration in very small amounts is unknown. Perhaps it, too, could be caused by field enhancement at the corners of the sample or in grain boundaries.

The main conclusion from the SQUID $M(H)$ measurements is that CVD and RRR are not very different where flux penetration is concerned.

X-RAY RESULTS: PRECISION LATTICE CONSTANT MEASUREMENTS

Our intent was to develop a method for non-destructively measuring hydrogen content by precision determination of the lattice constant.

It is known that the presence of interstitial hydrogen expands the lattice [13]:

$$\Delta a/a = (4.72 \pm 0.25) 10^{-4} \% \text{ H/Nb.}$$

If we wish to measure the hydrogen concentration with a precision of 0.1%, we will need to measure the lattice constant to an absolute accuracy of better than 50 ppm. Of course, other interstitial elements also expand the lattice. Oxygen and nitrogen are about twice as effective as hydrogen, but are generally present in such small amounts as to offer small, almost negligible corrections. Strain also affects the lattice, but with enough x-ray reflections, the effect of strain can be distinguished from isotropic expansion

In order to carry out this determination, we must know the lattice constant a of hydrogen-free niobium. The best experiment we can find in the literature is the one reported by R.L. Burns of Bell Labs [14], who measured $a = 3.300208(2)$ angstroms at 25 C, a relative error of 0.6 ppm. This value is not in agreement with the standard value(s) in the Hanawalt tables [15], nor does it agree with the even smaller value measured by Taylor and Doyle [16]. We give more credibility to the Burns value because of his careful sample preparation, and because he simultaneously measured the hydrodynamic density, comparing it to the x-ray density. The two agreed to 1 part in 3000, giving a defect density (not affecting the lattice constant) consistent with expectations from thermodynamic equilibrium of defect formation.

Our samples were prepared by embedding them in plastic, along with three standards: a sapphire single crystal in 110 orientation, a silicon single crystal in 311 orientation and a silicon crystal in 400 orientation. These reference materials have Bragg reflections very close to the 110, 200, and 211 reflections of niobium, respectively.

X-ray scans were taken in continuous scan mode. A step size of 0.0025 degrees was used. About 1 degree was scanned. Our initial intent was to scan all three reflections, and compare to the nearby reference peaks. However, due to the fact of large grain size, not all three

peaks were accessible on either RRR or CVD samples, even with relatively large rocking angles. In the end, the RRR sample had only the 110 and the 211 peaks accessible, and the CVD sample showed only 200, and 211 peaks. This meant that the two samples could only be compared at the 211 peaks, which is not enough for precise lattice constant determination by eliminating the effects of strain, etc. Nonetheless, it may be worth recounting the procedure and quoting the results for all the peaks studied, since they reveal possible problems with the method. The raw uncorrected results are given in separate tables for CVD and RRR below.

Sample	hkl	Measured 2θ (degrees)	FWHM L/R (degrees)
niobium	200	56.6518	.0463/.0557
silicon	311	56.1169	.0424/.0447
niobium	211	69.7632	.1160/.0882
silicon	400	69.1379	.0776/.0959

Table 5: CVD X-ray Data

A split Pearson VII fit was used to fit the data. This type of fit [17] gives two values for the FWHM of the peak. If they are not equal, it measures the asymmetry of the peak. Since the CVD sample had a mostly 100 orientation, it was necessary to rock (add to the incident angle, and subtract from the exit angle) to see the 211 peak. The signal had to be increased by widening the slits. The wider slits were also used for the silicon reference. No correction for the rocking was applied. It may be noted that this peak was relatively asymmetric.

Sample	hkl	Measured 2θ (degrees)	FWHM L/R (degrees)
niobium	110	38.4415	.2542/.2048
sapphire	110	37.7730	.0394/.0394
niobium	211	69.7028	.1495/.0948
silicon	400	69.1207	.0490/.0511

Table 6: RRR X-ray Data

The heights of the reference standards relative to niobium were measured in each case by using a non-contact profilometer, to an accuracy of <2 microns. The error was calculated from internal consistency of the measurements. A small correction was applied (the maximum height difference was 13.1 microns). This then made it possible to compare reference and niobium directly. However, two additional corrections were applied, one for transparency and the other for refraction. A number of geometric corrections [18] were not applied, but were assumed to be the same for the niobium and the reference standard, which peak was almost at the same angle as for the niobium.

In making the transparency correction we used a penetration depth in niobium for copper Kα1 x-rays of 8 microns. The actual depth sampled by the x-rays depends

geometrically on 2θ. For the 110 reflection, it is 1.3 microns, and for the 211 reflection a portion of the sample from the surface to 2.3 microns beneath the surface is probed. Although the RRR sample was etched with BCP, it may be that not all of the surface damage from machining was removed, as the very large widths may also suggest. The effect of rocking was not sufficiently investigated, as well.

The positions of the reference peaks all agreed with calculation from the accepted lattice constants for these materials to .01 degrees, which is excellent agreement. Geometric aberrations common to both niobium and reference samples may account for this small difference between measured and calculated reference peaks.

We cannot determine a lattice constant from a single peak. Furthermore the lattice constant results from CVD(200) and RRR(110) are not consistent with the 211 results for either sample.

If, nevertheless, we do compare the 211 peaks, which have the deepest penetration into the sample, we find

RRR: a = 3.30105(13) angstroms

CVD: a = 3.29933(13) angstroms

If these very preliminary results were to be taken at face value, they would correspond to 1.10 +/- 0.15 at % more hydrogen in the RRR sample, which was known from chemical analysis to have 1.07% hydrogen.

More work is needed to develop a reliable method, but it seems possible that this could be done. In particular, the effect of rocking on peak widths and positions needs study.

CONCLUSION

We strongly urge [20] starting a vigorous ILC R&D program to produce single cell SRF cavities by a CVD process. If even only some of the motivating factors listed earlier are realized, it will be worthwhile.

In the most optimistic scenario, we can move the ILC to a new (higher) gradient in the cost vs. gradient curve, thus reducing the cost. To do this will require improving both Q and Eacc.

ACKNOWLEDGEMENTS

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With the help of Gary Good, we used the SIMS facility at the Surface Science Western Laboratory, located at the University of Western Ontario, London, Ontario, Canada.

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REFERENCES

- [1] Cornell Center for Materials Research
- [2] Ultramet, Pacoima, CA 91331. See www.ultramet.com/rhenium2.htm, for more details. The CVD sample investigated here was supplied to us without any information about the process by which it was made. However, its high hydrogen content suggests the process using hydrogen reduction of the pentachloride. For SRF applications, the iodide process, thermal reduction of the pentiodide [19], may be a more promising candidate. The CVD niobium studied here was in no way optimized for RF cavity applications. The part supplied was a remnant from a production part unrelated to RF cavity applications.
- [3] Wavelength Dispersive Spectroscopy is a technique for measuring electron-induced x-ray fluorescence.
- [4] Energy Dispersive Spectroscopy is similar to WDS, except for a different x-ray measurement technique.
- [5] Polishing was done on a Struers Roto-Pol polishing machine, using a sequence of gradually decreasing grit sizes. The final stages were diamond (3 micron, then 1 micron), followed by an oxide polish with colloidal silica.
- [6] EBSD stands for Electron Backscattered Diffraction. It can map the Euler angles of the normals to the Bragg planes for each grain, down to a resolution of 1 micron, using electron diffraction. The white areas are where the computer failed to index the orientation, possibly due to defects.
- [7] Shiva Technologies, Inc., Syracuse, NY. See www.shivatec.com.
- [8] SIMS stands for Secondary Ion Mass Spectroscopy. A 10 KeV Cs⁺ beam was used, with a current of 3 nA.
- [9] Gary Good, Surface Science Western, private communication.
- [10] We used a Quantum Design MPS commercially built SQUID magnetometer.
- [11] See ref. 13 below, *Hydrogen in Metals II*, page 49, Figure 2.34 and accompanying text.
- [12] Hc1(pure niobium, 1.9 K) is 1765 Oe, according to K. Saito, SRF2003 Workshop, invited talk.
- [13] T. Shober, H. Wenzl, *Hydrogen in Metals II*, pg. 15, vol **29**. Primary references include the Springer Series on Topics in Applied Physics: *Hydrogen in Metals I: Basic Properties*, ed. by G.Alefield and J.Voelkl, Springer-Verlag 1978; *Hydrogen in Metals II Application-Oriented Properties*, ed. by G.Alefield and J.Voelkl, Springer-Verlag 1978. (These are volumes 28 and 29 of that series.)
- [14] R.L. Barns, J. Appl. Physics, **39**, 4044-4045 (1968). The hydrodynamic density was measured to be 8.5754(10) gm/cm³.
- [15] For example, one of the two accepted values in the Hanawalt tables for niobium is $a = 3.30332(13)$ angstroms. It is based on a 1982 publication, NBS Monograph 25- section 19. The calculated x-ray density disagrees with the hydrodynamic density by 1 part in 857. No description of the impurity analysis and surface preparation of the niobium appears in this monograph. Niobium in powder form is unavoidably contaminated with oxygen.
- [16] A.Taylor and N.J. Doyle, Journal of the Less Common Metals, **13**, 313-350 (1967), measured $a = 3.2986(1)$ angstroms for zone refined, degassed niobium. They also measured the lattice expansion due to oxygen and nitrogen impurities.
- [17] *The Rietveld Method* (R.A. Young, ed.), Chapter 7, pp 111-131, Oxford University Press, Oxford, 1993.
- [18] See *X-ray Diffraction Procedures, Second Edition*, H.P. Krug L.E. Alexander, Wiley Interscience 1974.
- [19] This process is based on the same general principle as halogen lamps. It was discovered in 1927 by de Boer and van Arkel. See the book *Iodide Metals and Metal Iodides* by Robert F. Rolsten, John Wiley & Sons, Inc. 1961.
- [20] L.N. Hand, *Informal Talk*, TF-SRF Conference, Jefferson Lab, Newport News, VA, July 17, 2005.