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STUDY OF ANNEALING IN NIOBIUM FILMS

CHESS FEASIBILITY STUDY FS225 PART I

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ABSTRACT

The results of Part I of the CHESS feasibility study FS225 are reported. This was done with 19 KeV x-rays at the F3 beam line. The main goal was a very precise comparison of relative lattice spacings and peak widths for annealed and unannealed niobium films on both sapphire and quartz substrates. Secondary goals were to obtain rocking curves and to study trace impurities. The results of the preliminary run at 10 KeV are also discussed here.

A comparison of the measured sapphire Bragg peak positions with values calculated from the accepted lattice constant did not yield agreement. It is likely that the energy calibration was 60-95 eV off. A method to calibrate the energy is proposed, with a future goal of ± 2 eV. This will allow determination of the absolute Nb lattice constant for films to a precision much higher than the published error of ± 400 ppm for bulk niobium.

Using a "ratio of sines" method, high precision in the energy calibration is not necessary. We were able to measure a 0.069% $\pm$ 0.028% reduction in the normal component of the lattice constant after annealing the film. The figure on page 8 is our main result. Uncertainty about systematic errors prevents us from declaring the method to be established, however. (see Appendix III.)

Finally, we observed that our annealed films had a peak not seen in unannealed films. The intensity was about 0.2% of the Nb 110 peak. The identification of the reflection seen as due to NbO, NbH, screw dislocations or other causes is not yet possible.

Possible improvements in the F3 diffractometer are discussed which can convert it into a high precision instrument. A checklist of suggested improvements is on the last page of this report.

Introduction

This run used an x-ray energy of 19 KeV in order to observe the sapphire substrate through the relatively thick Nb films. At the lower energy of 10 KeV used in the previous run, the substrate Bragg reflections do not penetrate Nb films of this thickness (≥ 4 microns). Appendix I is a summary of the films measured.

The primary goal of this run was to compare the lattice constants of different Nb films. The substrate sapphire lattice constants are assumed to be the same for all films. This is intended to reveal small differences in the niobium lattice spacing which arise when the niobium films are annealed. It is believed that this could be due to loss of hydrogen included when the films are sputtered.

In the first section of this report we compare the predicted Bragg peaks for sapphire with those observed, using the energy calibration described in Appendix II. Our conclusion is that the energy was actually 60-95 eV lower than the nominal calibration value. This problem can be avoided in the future by using a different method of calibration, which is proposed below.

Next, we study the small differences between the annealed and the unannealed films, using the substrate peak as a standard. To do this, we first take the ratio $\frac{\sin\theta_{Nb}}{\sin\theta_{sapphire}}$ for each film, then compare these numbers. This method is completely independent of the x-ray wavelength, and appears to be potentially very precise. When better understood, it will yield a good measurement of the relative lattice constants for the two films. Systematic errors, especially those due to the third harmonic need to be studied further.

The films 13B and 13D measured in the 19 KeV run were fresh films, prepared only a few days previously. Nevertheless, the film 13D showed a small peak at 15.2° , which could be a NbO or NbH peak. (13B also had this same peak, but it was much weaker.) The peaks observed in other, older films in the 10 KeV run were mostly absent, although this same $d = 2.44\ \mathring{A}$ peak did occur for the older films also, and was very strong in some of them.

Finally, we analyze the results of the earlier run at an energy of 10 KeV.

Absolute Peak Angles for Sapphire Substrates

We made two independent measurements of the sapphire Bragg peaks, one for film 13C and the other for film 13D.

The $hh0$ reflections in sapphire obey the simple equation $d_{hh0} = \frac{a}{2h}$. The NIST value for the lattice constant is [1] $a = 4.75919(44)\mathring{A}$ (and $c = 12.99183(17.4)\mathring{A}$). From this, we derive the 2θ angles in degrees for the family of reflections 110,220,330,440, which are tabulated below.

Table I

Predicted Peak Positions (2θ) For Sapphire In Degrees

hkl	E=18.99 KeV thick foil	E=19.04 KeV thin foil calibration
110	15.7702	15.7285
220	31.8494	31.7636
330	48.6058	48.4700
440	66.5623	66.3649

The difference between reflections for the lower energy and reflections for the higher energy varies from 0.05 degrees for the 110 reflections to 0.2 degrees for the 440 reflections. This should be readily observable.

In table II below, we present the measured peak positions for the sapphire 110,220,330,440 peaks. There was some ambiguity, depending on whether the peak or the COM was chosen. We give both values below. The sapphire peaks were measured for both films 13C and 13D. It was not trivial to find them, due to the miscut of the substrates, and the narrow widths of the χ and θ (often called ω) distributions.

Table II

Measured Positions for the Sapphire Peaks in Degrees *

hkl	13C Peak	13C COM	13C FWHM	13D Peak	13D COM	13D FWHM
110	15.8	15.8	.028	15.771	15.779	.012
220	31.935	31.942	.030	31.956	31.961	.015
330	48.775	48.782	.045	48.792	48.798	.034
440	66.76	66.767	.033	66.771	66.773	.031

The peaks were often asymmetric, and in some cases there were two peaks, one larger than the other. In addition, we do not understand the peak widths nor the intensities. The method cannot be said to have worked until these are understood, ultimately in the context of the dynamical theory of diffraction [2]. The peak position in the table above is for the larger of the peaks if two were visible. The COM(center of mass) includes both peaks.

The variations between measurements of 13C and 13D are small compared to the discrepancy between the calculated values in Table I and the measured values in Table II, so we will average the two films and ascribe the difference to the measurement error, which is in all cases smaller than the FWHM of the peak. In almost all cases, the measured angles are significantly larger than the calculated angles, even for $E = 18.99$

* See Appendix III for graphs and more discussion.

KeV.

The 110 peaks were measured with the thick foil Nb absorber in front of the detector, to reduce the intensity. No absorber was used for the other 3 peaks.

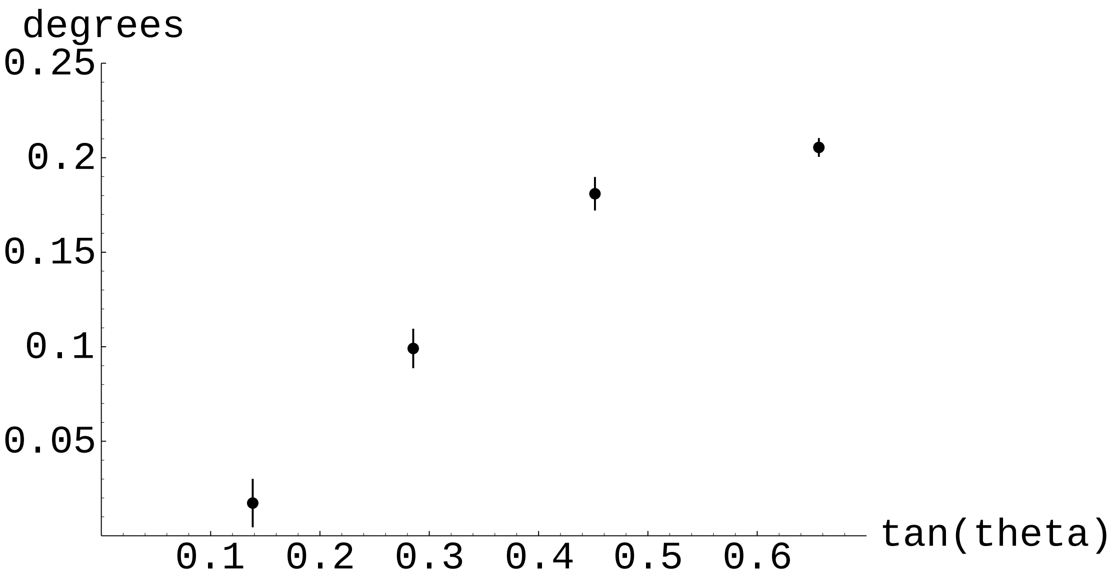
Table III

Average of Sapphire Peak Positions for 13C and 13D

hkl	Average Measured Peak(2θ) in degrees	σ
110	15.788	.013
220	31.949	.010
330	48.787	.009
440	66.768	.005

The "good news" is that peaks are reproducible on the .01° level. But the "bad news" is that the measured angles do not agree with either of the entries in Table I. The discrepancy with the calculated angle for 19.04 KeV is as large as 0.4° for the 440 reflection. It is likely that the energy somehow became even lower than 18.99 KeV. To test the idea that the discrepancy is due to an anomalous low energy, we plot the difference between the measured values (Table III) and the calculated values (Table I for 18.99 KeV) vs. $\tan\theta$. An energy error would give a straight line in this graph. An error in the lattice constant would also be a straight line.

Graph of Discrepancy between Table I(18.99 KeV) and Table III



What can be the reason for this large discrepancy? Could the lattice constant for corundum differ from the lattice constant for synthetic sapphire? The lattice constants in ref [1] apply to a particular sample of

$\alpha-$corundum. We have looked for lattice constants specific to synthetic sapphire, and found one case listing [3] $a = 4.76280$ Å , $c = 13.00820$ Å . This larger lattice constant will predict even smaller larger diffraction angles, in greater disagreement with experiment. The difference is about 0.1%. We will stay with the original NIST values, which also agree with the values for synthetic $\alpha-$corundum in the reference [3].

What about systematic errors in the diffractometer? There is a vast literature on this. We will consider some of the more important ones [4] to see which could make a difference here.

A zero shift of $\leq -.05°$ from the sag introduced by the NaI counter is definitely present. We do not have a precise measurement of this. The actual diffraction angle is smaller than the nominal angle, a correction which is in the right direction, but which does not (we hope) depend much on angle.

A height displacement of s=1 mm gives a 2θ displacement varying from 0.06° to 0.05° over the entire range of angles here. ($\Delta(2\theta) = \frac{s}{R}\ \cos\theta$.) **We must keep this error less than 0.2 mm to achieve no more than a .01° error.** The variation with angle is so slight as to make this error indistinguishable for our case from a zero shift in 2θ .

According to the reference [4], possibly the next most important systematic error is due to sample transparency. If we estimate the absorption length in sapphire to be $\approx \frac{1}{\rho\mu}$ and take $\mu \approx 4$ cm^2/gm, $\rho = 3.9$ g/cm^3, we get $L_{abs} \approx \frac{1}{15}$ cm. The transparency correction to 2θ would be $\frac{L_{abs}}{2R}\sin 2\theta$. This is an overestimate, because the crystal is not infinite but is instead 0.5 mm in thickness. We get $\Delta(2\theta) \leq \frac{\sin 2\theta}{3000}$. This estimate varies from .005° at the 110 reflection to .017° at the 440 reflection. This correction can, at most, account for 10% of the discrepancy between the observed and the calculated values. It has not been made, however.

The "flat sample correction" behaves like the height displacement correction, at least for small θ . The correction for the Lp factor gives a larger angle by a rather small amount which depends on the square of the FWHM. It is in the wrong direction to explain what is seen here.

At least part of the answer could lie in the theoretical calculation of the peak position. The dynamical theory of diffraction must be used [2] to do this correctly. An indication that this is necessary is experimentally visible in the asymmetric peak shapes observed from the substrate. This is characteristic of a dynamical theory where absorption plays a role. (See Zachariasen page 143 [2], which closely resembles the asymmetric shape of some of our sapphire peaks, at least at the 110 reflection.)

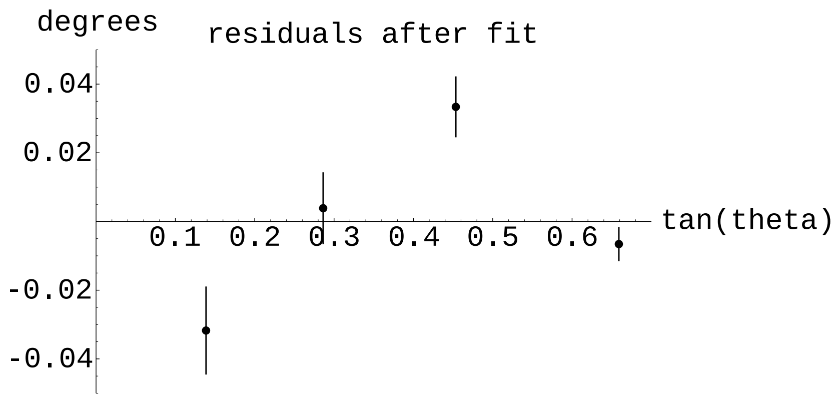
The starting point for our calculation is formula 3-194 in the reference [2]. The correction to be added to the Bragg 2θ to get the observed 2θ is:

$$\Delta(2\theta)(\text{radians}) = \frac{2}{\sin 2\theta}\left(|\psi_0'| \ - \ \frac{\kappa}{|g|}|\psi_H'|\right)$$

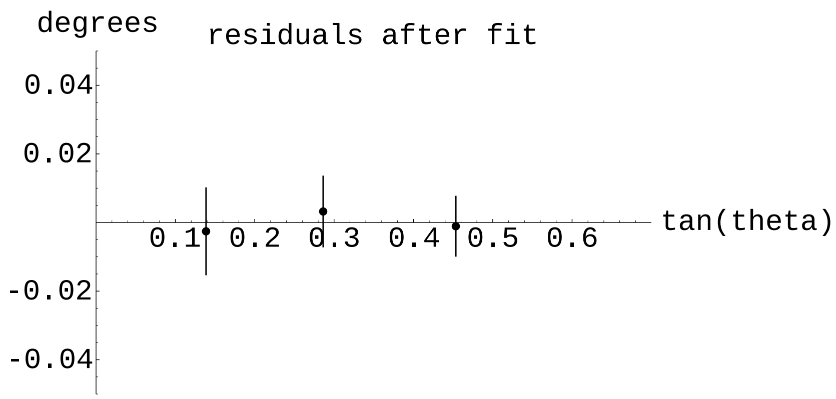
We have simplified things a bit, by taking $b = -1$ (its Bragg angle value) and $K = 1$ (polarization normal to the x-ray scattering plane). The ratio $\frac{\kappa}{|g|}$ is a measure of crystal absorption. We set this equal to zero. For a first estimate and upper limit, we need only ψ_0'. Let us first crudely estimate $|\psi_0| \approx 10^{-5}$. (the value for calcite[2] is 1.7×10^{-5}.) This gives us a correction which varies from .004° at the 110 reflection down to .001° at the 440 reflection—entirely the wrong functional dependence and also much too small. It is probably not worth making a more precise estimate.

Instead, we are forced to conclude that the lattice constant a (i.e. the x-ray energy) should be a fitting parameter. Do we get the literature (NIST) value for a if we do this, and throw in a possible zero shift at the same time? The answer is no. We can fit either all four points, or only the first three. The results are shown in the figures below, and in the table which follows. We have assumed the energy is 19.0 KeV for this purpose.

Fit to all four points:



Fit to first three points:



The table below gives the results of these fits. Using the first three points gives the best fit, with a very low χ^2/dof.

Table IV

Results of Least Square Fit to Sapphire Data

Bragg reflections used in the fit	χ^2_{min}/dof	a Å	zero shift degrees	% shift in a (from NIST a)	max. residual degrees
110,220,330,440	11.1	4.74422	+.0055	-0.31%	.03
110,220,330	0.15	4.73586	-.052	-0.49%	.003

A different lattice constant, almost 0.5% less than the NIST value is unbelievable. We are forced here to the unwelcome conclusion that the energy was really 60-95 eV (0.5%) lower than 19.000 KeV.

Does Annealing Change the Lattice Constant of our Niobium Films?

Despite the mystery surrounding the substrate lattice constant, we can use the ratio of $\sin\theta$ for niobium and sapphire to measure the change in the niobium lattice.

The ratio $\frac{\sin\theta_{Nb}}{\sin\theta_{sapphire}}$ is independent of the reflection order and the wavelength of the x-rays. It can be shown that it equals $\frac{a_{sapphire}}{\sqrt{2}a_{Nb}} = 1.01829(40)$, using the NIST corundum value for $a_{sapphire}$ and the literature value for bulk Nb [5], which is $a_{Nb} = 3.3032(13)\ \AA$. The error on a_{Nb} is 400 ppm. It determines the error on the ratio of sines.

The data taken on this run appears in the table below.

Table V

Nb Film Data for 2θ

hkl	13C Peak	13C COM	13C FWHM	13D Peak	13D COM	13D FWHM
110	16.11	16.185	.068	16.131	16.129	.061
220	32.54	32.533	.092	32.574	32.571	.060
330	49.69	49.687	.132	49.764	49.756	.097
440	68.1	68.116	.135	68.167	68.158(68.163)	.112

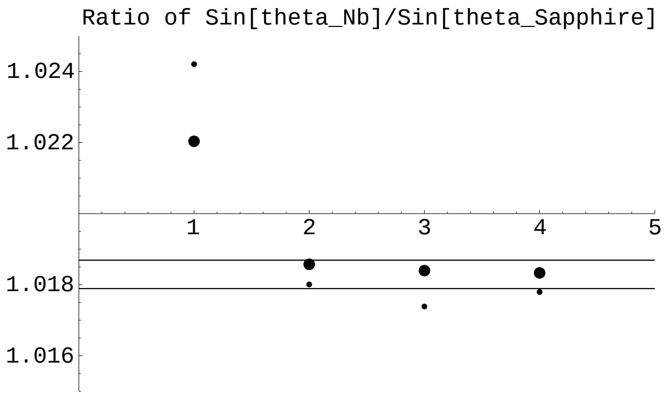
The entry for the COM of the 13D 440 reflection has been increased .005° to 68.163 to allow for the fact that the scan was slightly unsymmetrical.

A hitherto unsuspected systematic error in the 110 reflections is revealed in the plot below of these data. For these reflections only, the 250 micron Nb filter was used. This filter preferentially passes the third harmonic, which may have caused the error. For this reason, we use only the 220,330, and 440 ratios of sines in taking an average. The error is determined internally by calculating the standard deviation of these points in both cases.

Table VI

Results of Ratios of Sines

film	annealed?	$\sin\theta$ ratio	$\frac{a_{Nb,film}}{a_{Nb,bulk}}$
13C	no	1.01773(26)	1.00055
13D	yes	1.01843(10)	0.999859



The horizontal lines indicate the region allowed by using the bulk Nb lattice constant and the error of ± 400 ppm. For the 220,330,440 cases, the upper point belongs to film 13D, and the lower point to film 13C. We suspect the problem with the 110 reflection is due to the presence of third harmonic. The ratio of lattice constants for the unannealed film C to the annealed film D is, fitting only the higher three reflections:

$$\frac{a_C}{a_D} = 1.00069 \pm .00028$$

I.e. the error in determining the relative lattice constant is 280 ppm. We see that in fact, the film does become more dense by about 0.07% when it is annealed.

The films had 20 nm of TaN on the surface, so these results do not have to agree with the earlier results measured at Snee [6], which showed 2-3 times larger shrinkage of the lattice.

This is only a 2.5 σ result. But the method is capable of being improved considerably. More counts on each point are needed. We should be able to reduce the error below 100 ppm, and measure the relative lattice constant with much greater precision in the future. We might attempt to fit the peaks to get greater accuracy on the peak position.

The physical reasons for the shrinkage could be one or more of the following: hydrogen removed, defects annealed, argon trapped in the Nb removed (unlikely). More experiments are needed to tell which of these are actually important. Notice that the peak widths for the annealed film are roughly $\frac{2}{3}$ those of the unannealed film. This indicates more longitudinal coherence—larger grains with fewer intragrain defects [7].

Measurements of Bragg Peaks on the Quartz Substrate Films 13A and 13B

Table VII

Absorber in?	hkl	13A (unannealed) 2θ (degrees)	13B (annealed) 2θ (degrees)
yes	110	16.04(.15)	16.075(.10)
no	220	32.375(.29)	32.436(.19)
no	330	49.41(.40)	49.5(.31)
no	440	67.558(.56)	67.843(.41)

These peaks are all more than a factor of 2 wider than the sapphire substrates for the 110 peaks. This difference increases to a factor of 4 at the 440 peaks. Not only are the crystallites half as large, but the degree of coherence within the crystallites is much less for the films on quartz than for the films on sapphire.

The decrease in the lattice constant upon annealing is evident from the table above. If we take the ratio of sines for the angle θ, we obtain

Ratio $\frac{\sin\theta_{13B}}{\sin\theta_{13A}}$

Table VIII

hkl	ratio of sines
110	1.00217
220	1.00183
330	1.00171
440	1.00372

The average of the above is 1.00236 ± 0.00080. This result is about 3 times the change in the lattice constant observed for the sapphire substrates. The error quoted does not allow for the error in determining the peak position, which may be important for these very wide peaks.

Rocking curves for the quartz films were about 1.5° FWHM.

We take the sapphire/quartz factor of 3 shrinkage in the lattice as an indication that the niobium crystal contains many more dislocations in the case of a quartz substrate than in the case of a sapphire substrate. This conclusion is also consistent with the peak widths being much narrower for the sapphire than for the quartz.

Measurements Below the Nb 110 Peak

One possibly important factor is the detection of the possible presence of NbO and/or NbH after annealing. This was on the 0.2% level after annealing, and was almost 50 times smaller before annealing.

In the sapphire-based film 13 D, a peak with FWHM of .086° was observed at 15.23° . The peak height was 645 counts with 500 units on the ion chamber monitor. For the Nb(110) peak in the same film, also for 500 IC units, we had 21,591 counts for a full width of .061° . The peak location was 16.129° . The absorber was in place for this measurement, so the ratio of peak areas is $\frac{.086}{.061}\frac{645}{20\times 21591} = .002$. We are seeing 0.2% NbO with hkl=111, if that is what is causing the peak. No peak was visible in film 13 C, so we conclude this is a consequence of the annealing. A systematic search was not done for any other peaks. Had it been done, it could have helped identify the presence or absence of oxides. (This could still be done at Snee.)

The only non-Nb peak observed in the measured films was at $2\theta = 15.15°$ for the quartz substrate films 13 A and 13 B. The unannealed film 13A had a very weak peak of 42 counts above a background of 10 counts. Again, the IC=500. This same peak in the annealed film 13B was 1429 counts with a FWHM of 0.11 and IC was 2000. The ratio of intensity to the Nb 110 peak is $\frac{1429/2000}{20\times 10917/500} = 0.0016$.

The near identity of the ratio of the "NbO" peak to the Nb 110 peak in the two cases makes it unlikely that the 15.2° peak arises from decomposition of the substrate. In the quartz films, the strength of this peak increased by a factor of 45 after annealing the film. We do not have a measurement of this increase for the sapphire films, but presume it was similiar.

Candidates for this peak are NbO and NbH. Both of these come in many forms. The table below lists some of the possibilities [8].

Table IX

Possible Sources Of 15.2° Peak Compared to Nb(110) Peak

	hkl	d	calculated 2θ (19 KeV)	comments
Nb	110	2.3357	16.0599	should add .06°
$\alpha-NbH_{0.1}$	110	2.3434	16.0072	expanded lattice!
$NbH_{0.9}$	110	2.4395	15.3723	
NbH	110	2.4204	15.4943	"isostructural with Nb"
NbO	111	2.4307	15.4243	primitive cubic
Nb_6O	110	2.395	15.66	tetragonal
"	101	2.354	15.9343	"
Nb_4O	200	2.35	15.96	tetragonal
"	111	2.3488	15.9699	"
NbO_x	220	2.3494	15.966	"epitaxy with Nb"

The infamous $\beta-NbH_{0.89}$, which is not a superconductor, has an orthorhombic crystal structure with

$a = 4.84, b = 4.90, c = 3.45$. If $hkl = 111$ there is a peak at 15.387° , with $d = 2.4372$. If $hkl = 200$, there is a very close peak at 15.497° , with $d = 2.42$. If $hkl = 020$, 2θ is 15.306° , with $d = 2.45$. Strain on the crystal could possibly shift the $NbH_{0.9}$ cubic phase peak down by .2° , or the $\beta-$hydride peak down by 0.1° . But this is only speculation.

The closest hydride is the $\beta-$hydride. The closest oxides are Nb_nO, with $n = 4$ or $n = 6$.

Nothing on this list perfectly matches the position of the observed peaks. Of course we cannot identify a compound from a single line, we have to look for other lines, which may be very weak. The best place to look is at still smaller angles, and also in the region between the Nb 110 and 220 peaks.

We can only guess what is the origin of this peak. If it is due to oxygen, consider the following: Nb, in a volume of 1 micron x 10 mm x 10 mm contains 5.6×10^{18} atoms. 2.3 nm of Nb_2O_5 , which is the normal surface layer on Nb, contains 1.2×10^{16} oxygen atoms. If dispersed throughout a 1 micron depth of Nb, this is 0.2 at. %. Our films are about 4 microns in thickness, so we expect a factor of 4 less if the surface layer is dispersed by the annealing. Still, the numbers are close enough to give one pause for thought. *If this is the cause, the only cure is to eliminate the surface oxide before putting on the cap layer of TaN, or else never let it form.* Another number to keep in mind: a 1 nm layer of H_2O on the sapphire contains 3.3×10^{15} oxygen atoms and twice as many hydrogen atoms. If as much as 10 nm of water were present on the sapphire surface, our result could be explained, although one would think the 600° C substrate temperature when the film is sputtered would disperse the oxygen before annealing is done. Some water will also adhere to the oxidized Nb surface, too.

0.2 at. % of oxygen (1 O atom in 500 Nb atoms) will give a 10° K resistivity of 0.9 $\mu\Omega$-cm, which is exactly what we observed in film 11D. If oxygen is really there at this level, eliminating it should greatly improve the RRR of annealed films. But there is certainly no proof at this stage that the peak is due to an oxide.

If the peak seen is due to $\beta-$hydride, it could arise from the hydrogen in the vacuum of the annealing furnace. The vacuum is approximately 10^{-6} Torr when the furnace is hot, or sometimes a bit higher. We speculate that this residual gas is primarily hydrogen, and that it is absorbed by the niobium, even though the films are placed face-to-face and surrounded by silicon powder during the annealing process. Presence of this hydride would contradict the conclusion reached in ref. [6].

A table of the measured[9] Bragg reflections for $\beta-$hydride appears below, for future reference.

Table X

β−Niobium Hydride Bragg Reflections

hkl	d(Å)	Relative intensity
200	2.41	100
220	1.72	50
022	1.41	50
311	1.40	50
222	1.22	10
400	1.21	5
113	1.09	100
042	0.99	10
402	0.98	10
151	0.92	100
511	0.91	100
440	0.86	50

A precise mass spectrographic analysis could settle which of these alternatives (or both) is the case. Or else eliminate impurities as the cause of the small peak.

Analysis of the 10 KeV Run

In the earlier run, the energy was set to a nominal 10.207 KeV using a tungsten foil. A NIST corundum standard [1] was measured to check this calibration:

Table XI

Calculated and Measured Peak Positions for NIST Standard

hkl	Calculated 2θ	Measured 2θ (FWHM)	Difference
104	27.5466	27.572(.047)	0.025
208	56.87	56.82 (.053)	−0.05
324	83.9787	83.972(.064)	−0.007

This calibration indicates that errors as large as .05° can be present unless some attempt is made to use a calibration standard in a systematic way to uncover the source of these errors. An error of +.05° changes the apparent lattice constant inferred using the Bragg formula by -.163% at the 110 reflection and -.073% at the 220 reflection.

The results of niobium film measurements are:

Table XII

110 and 220 Bragg Peaks of Various Nb Films

film	110 2θ (FWHM)	$\Delta\chi$	220 2θ (FWHM)	$\Delta\chi$
11B	30.104(.109)	0.49	62.418(.204)	0.72
11D	30.086(.063)	0.88	62.480(.10)	0.49
12A	30.182(.075)	—	62.598(.145)	—
12C	30.163(.059)	—	62.612(.096)	—
8A	30.013(.20)	2.0	62.222(.44)	1.8
8B	30.134(.16)	2.1	62.510(.33)	1.4

These data can be used to find a lattice constant for each angle measured, and take the ratio of this film lattice constant to the lattice constant for bulk niobium (3.3032 Å). The results are given in the table below in the form $\frac{a_{film}}{a_{bulk}} = 1 + \epsilon$. The value of ϵ is given in percent.

Table XIII

film	110 ϵ	220 ϵ
11B	.129	.362
11D	.448	.277
12A	-.124	.107
12C	-.063	.087
8A	.425	.651
8B	.31	.233

It is clear that results are not consistent enough to deduce the lattice constant. Perhaps the 220 numbers are more accurate due to the reduced sensitivity to angle error. Some of the results are interesting though. The very thin film 8A has a clearly much larger lattice constant than 8B. The Nb/Ti films 12 A,C seem to have smaller lattice constants than comparable purely Nb films.

To achieve our goal of accurate lattice constant measurements despite the diffractometer errors, we were driven to take a second run with 19 KeV photons so that the sapphire substrate could be used as a standard. At the shorter wavelength the substrate peaks become visible and also it is possible to observe four reflections instead of two. To be useful as an absolute instrument, the error on the diffractometer should be reduced to .005° or less.

Other Peaks Seen With 10 KeV X-rays

We made a much more thorough investigation of peaks besides the Nb 110,220 during the 10 KeV run than was done during the 19 KeV run. The table below summarizes the results.

Table XIV

Peak, film	2θ	intensity relative to Nb(110)(%)	d (Å)	near to	other
X1, 12C	22.08(.015)	high	3.172	$HNb_3O_8(240)3.1830$	$Nb_2O_5(180)3.140$
X2, 8A	22.038 (.0082)	high	3.178	"	"
A, 11D	27.2	0.08	2.583	?	$NbO_2(222)2.544$
B1, 11D	28.44(.11)	1.6	2.472	$NbH(111)2.4468,(020)2.454$	NbO_2 (440) 2.4210
B2, 12C	28.77(.065)	?1	2.445	$NbO_x(111)$ 2.4306	
B3, 11B	28.83	0.2	2.440	NbH_x 2.45-2.49	
B4, 8A	28.685(.26)	0.5	2.452		$\beta - NbH_{0.89}(200)$ 2.41
SA1, 11D	29.57(.067)	0.2	2.380	$Al_2O_3(110)2.3796$	
SA2, 12C	29.575(.020)	230	2.380	"	
SA3, 8A	29.569(.020)	17.5	2.380	"	
C',11D	29.7	0.04	2.37	"?	
D, 11D	33.41(.18)	0.11	2.113	$NbO(200)2.1055$	
12C	54.49(.075)	5.6	1.327	Nb(211)	
E, 11D	56.0(0.25)	0.05	1.294	?3rd harm.	
F1, 11B	59.44(.49)	0.008	1.225	$NbH(222)1.226,(040)1.2296$	
					$NbO(222)1.2156$
F2, 8A	~ 59.2	0.2	1.225	"	"
SB, 12C	61.259(.089)		1.1921	$Al_2O_3(220)1.1898$	
12C	70.96(.11)	25.1	1.046	Nb(310)	

There is a wealth of information here, but the interpretation is not always clear. The peaks labelled X1 and X2 seem likely to be associated with the substrate due to the very narrow width. But there is no sapphire peak at this location! The identification with the Nb compounds listed cannot be made unless there is a plausible explanation of the width. The peaks A and B seem almost certainly associated with NbH and/or NbO, as are the peaks C', D, F1 and F2. Peak E is unidentified.

Other peaks are easily identified with sapphire peaks or Nb peaks in the case of film 12C, which is not aligned like the other films, due to the Ti layer next to the sapphire. In no other film were the Nb 211 or 310 or other peaks visible. Other features can be explained in terms of the history of the various films, but we will not go into this here. See Appendix I below for a discussion of how these films differ.

Conclusions

We were able to demonstrate the potential viability of the "ratio of sines" method for obtaining very precise lattice constants for niobium films. More work is needed on the systematic errors, including the dynamical theory of diffraction, absorption corrections, and elimination of the third harmonic, which affects mainly the 110 reflections. *How the sapphire peaks depend on experimental conditions must be studied and understood.*

Peak widths and rocking curves proved that films made on A-cut sapphire are superior to films made on quartz substrates. In the future, we hope to obtain films with peak widths which can only be measured at CHESS, due to resolution limitations at Snee. Variations in rocking curves were seen which remain unexplained.

In the future we hope to understand the nature of the small peak at $d = 2.44\mathring{A}$ in the annealed films by using the high intensity beam now available at F3 with the 1% bandpass monochromator.

The film quality now needs to be correlated with the superconducting and normal conducting properties of the films. We also need to make a study of x-ray reflection intensity and O/H contamination vs. time for films which have been exposed to dry air. There is already evidence that the deterioration is significant over a time period of several months. This has serious implications for superconducting rf work.

Future measurements will also include roughness measurements using small angle scattering.

The F3 diffractometer could be improved. See the checklist at the end of this report. Energy calibration should be done with the NIST carborundum standard and not with the K edge. Installation of a detector which has the sensitivity of the NaI detector, but allows a higher counting rate would be desirable. Of course, the third harmonic should be removed, perhaps by installing another mirror or a graphite filter.

Acknowledgements

We are extremely grateful to Dr. Randy Headrick, Staff Scientist at CHESS, for making this run possible. He provided the expertise necessary to set up and run at F3.

Prof. Sol Gruner and the entire CHESS staff deserve credit for a very impressive operation. And of course the CESR operations staff provided the positrons which produced the x-rays.

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[1] NIST lattice constants for corundum standard: Standard Reference Material 676, May 25, 1962.

[2] W.H. Zachariasen, *Theory of X-Ray Diffraction in Crystals*, Dover reprint, 1994, see also *X-ray Diffraction*, B.E. Warren, Dover reprint, 1990

[3] *Crystal Data*, page H-260, [8]

[4] International Tables for X-ray Crystallography, vol. II, page 221

[5] ICDD Powder Diffraction File. The PDF #'s were: $NbO_{0.7} : 47 - 1694, NbO : 43 - 1290, NbO_{1.1} : 47 - 1695, NbO_2 : 43 - 1043, Nb_2O_5 : 43 - 1042$.

[6] L.N. Hand, *Our Niobium Films Contain Hydrogen!*, SRF 000410-06, April 10,2000. Lattice parameter contraction due to annealing was estimated at 0.16% with no error quoted. Films were coated with calcium, protected by a thin outer layer of Pt.

[7] L.N. Hand, *Evaluating the Structure of Niobium Films Using X-ray Diffraction Line Shapes*, SRF 000316-05, March 17, 2000 (internal report).

[8] *Crystal Data Determinative Tables*, Third Edition, vol.2, J.D.H.Donnay,Helen M. Ondik, U.S. Dept.of Commerce, Nat. Bureau of Standards 1973

[9] PDF# 07-0263, Brauer,Hermann, Z. Anorg.Allg. Chem., **274**,11(1953). The quality of these results is unrated. These are the only measurements available. Note that the 111 and 020 reflections were not seen. Perhaps they were unresolved from the 200 reflection.

[10] NIST Standard Reference Data Scientific Databases: X-Ray Form Factor, Attenuation and Scattering Tabulation. On the web, go to "nist.gov/srd/", then search for "x-ray attenuation".

[11] B.D. Cullity, *Elements of X-ray Diffraction*, Second Edition, Addison-Wesley, 1978

Appendix I

Description of Films

Table AI-I

Characteristics of Films Measured in the 19 KeV Run

Batch 13 Film	Date Produced	Nb Thickness microns	Film Structure	Substrate	Comments
13A	5/21/2000	nominal 6 microns	nominal 20nm TaN/Nb	quartz	not annealed
13B	"		20nm TaN/Nb	quartz	annealed
13C	"		20nm TaN/Nb	sapphire	not annealed
13D	"		20nm TaN/Nb	sapphire	annealed

All of these films were sputtered at a substrate temperature of 600° C. The sapphire was A-cut. Annealing was for 8 hours at 750° C.

Characteristics of Films Measured in the 10 KeV Run

The films 8A and 8B were produced in August 1999. Film 8A is 0.94 microns thick, 8B is 6.6 microns thick, as determined by the resistivity.

The films 11B and 11D were produced Jan. 5, 2000. They were nominally 6 microns, but resistivity measurements placed the thickness nearer to 4 microns. After sputtering the Nb, about 1 micron of calcium was evaporated on the films, followed by a very thin Pt layer. These extra top layers of Ca and Pt were removed by scrubbing with nitric acid after 11D was annealed.

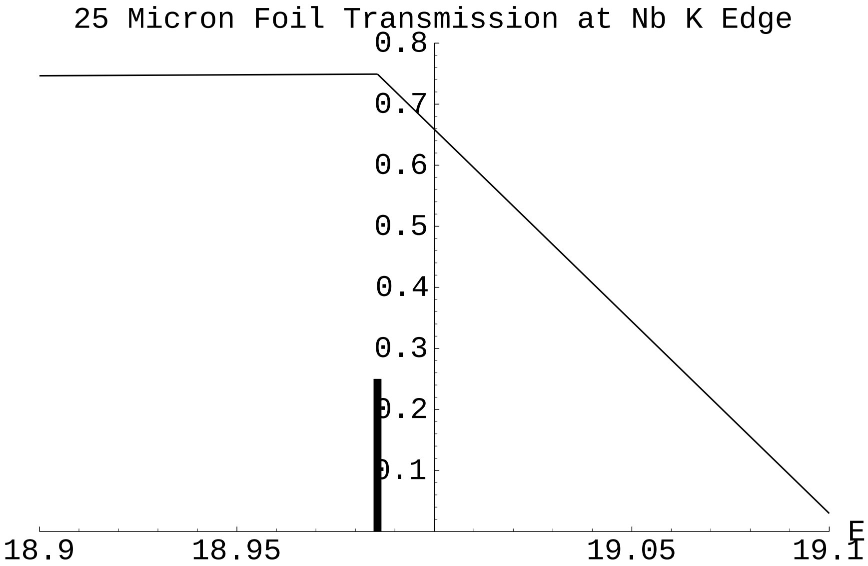
The films 12C and 12D were also nominally 6 microns. They were made April 21, 2000. A 0.25 micron titanium layer was first sputtered onto the sapphire, then the Nb, and finally a 0.2 micron TaN layer. The substrate temperature for the Nb and Ti was 600° C, for the TaN, room temperature. No electrical measurements have been made on these or on the Batch 13 films. Annealing was also 750° C for 8 hours.

Appendix II

Energy Calibration at 19 KeV Using the Nb K Edge

Initially, the energy was calibrated by observing the beam absorption in a 25 micron Nb film. The K absorption edge has a NIST value of 18.9856 KeV [10]. There is some ambiguity in locating the edge, however. We chose to locate this point at the half-way point on the edge, rather than at the point of maximum transmission just below the K edge. The beam energy was then changed to 19.0 KeV *according to this calibration.*

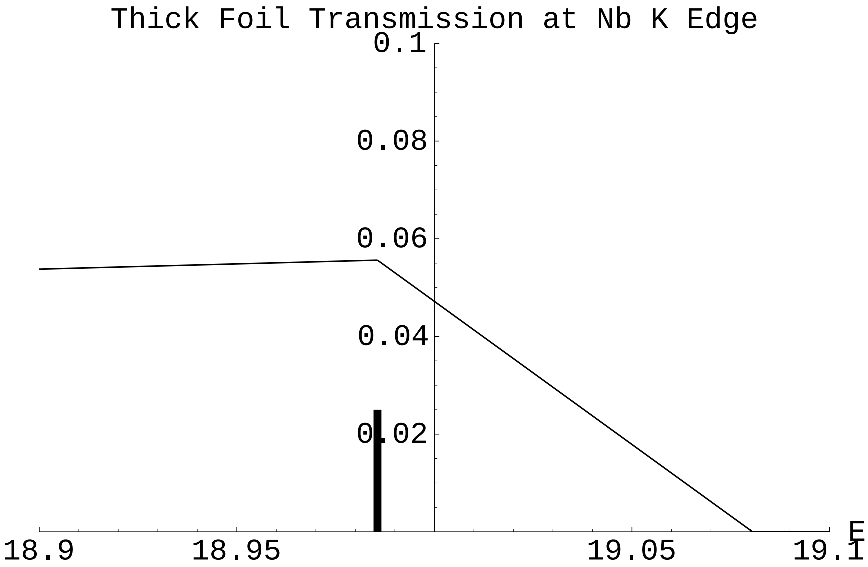
We have used the NIST tabulated attenuation coefficient [10] values near this edge. A plot of the calculated intensity transmitted through a 25 micron Nb film appears below. The short line indicates the position of the edge, using the NIST value. We should have taken the maximum of the transmission curve for the position of the edge. i.e. the minimum in the absorption.



Our (erroneous) assumption was that the edge was halfway down the transmission curve. This energy is estimated by linear interpolation on NIST data to be 19.0331 KeV (Foil transmission 0.38). We mistakenly believed this energy to be 18.986 KeV, when we should have used 19.033 KeV. According to this, we should add 40-50 eV to our nominal energy setting. When later we changed the energy setting to 19.000 KeV, it was actually 19.04-19.05 KeV. This was the value actually chosen for the run. But it is still not correct (see below).

We actually observed a transmission (arbitrary units) which varied from 65000 counts below the edge to 10000 counts at the minimum above the edge, in pretty good agreement with the values calculated from NIST data.

There is another way to check this. We observed that a 250 micron niobium foil inserted in the beam gave an approximate factor of 20 attenuation in the beam. This indicates a value attenuation $\approx$ 14 cm^2/gm. Using the NIST data to estimate the attenuation for $E = 18.967$ KeV, we obtain $\mu(attenuation) = 13.548$, which would give an attenuation of a factor of 18, in agreement with what we observed. This method is fairly sensitive because the attenuating foil is thick, and we are close to the K edge.



Since we did not accurately determine the beam attenuation, it is probably reasonable to assume that the thick foil attenuated beam was at the K edge— the minimum in the attenuation. If the incident beam is set slightly higher, the attenuation will be more than this minimum value. Hence we assume an energy of $E = 18.986$ KeV when the thick foil is placed before the detector. The actual beam energy can be only slightly higher, however. In the future, we might try minimizing the attenuation using the thick foil. This is probably the most accurate method for doing the energy calibration if the K edge is used.

The 25 micron foil transmission midpoint calibration gave an energy of 19.02-19.04 KeV, which we later moved to 19.03-19.05 KeV.

The difference between $19.04 \pm .01$ KeV (thin foil calibration) and 18.986 Kev (thick foil) is 50 eV, a substantial amount. However, these are not necessarily mutually inconsistent. The thick foil filters out the higher energy components of the beam, thus passing a lower average energy than the thin foil does.

The energy of the beam without the thick foil therefore lies somewhat above 18.986 KeV, but not as high as 19.05 KeV. This range of uncertainty can be reduced substantially on subsequent runs. In particular, we should do a fit to the transmission of the 25 micron foil, and compare it to the point at which the transmission by the 250 micron foil has a maximum.

How accurately do we need to define the energy? Let's assume that the energy calibration corresponds to an error of .01° in 2-theta for niobium.

$$\delta(2\theta) = -2\tan\theta\ \frac{\delta E}{E}$$

For .01° ,$\delta\theta = 0.1745$ milliradians, $\theta(110) \approx 8.05°$, $\tan\theta \approx 0.141$, so we have $0.174510^{-3} = 0.282\ \frac{\delta E}{E}$. This gives $\frac{\delta E}{E} = \pm.00062$, or $\delta E(110) \leq 11.7$ eV. For the same equivalent angle error at the 440 reflection, $\tan\theta$ is larger by a factor of 4.77, so the energy error must be less than 2.5 eV. But we do not need the precision in angle at the 440 reflection. In fact the error in lattice constant is just the same as the energy error, so a 11.7 eV error in beam energy is an error of 620 ppm in lattice constant. This is still too high. The literature quotes a published value for the Nb lattice constant which has an error of 400 ppm. But it will be ok for relative comparisons.

The absorption method at the K edge will permit calibrating with an accuracy of < 10 eV, if we fit the entire absorption curve. It has the advantage of being independent of goniometer systematic errors. But the most accurate value for the energy will be obtained by using the NIST 1976 corundum standard, together with a fit to the measured intensity vs 2θ. Using this standard will minimize some of the systematic errors in the goniometer as well, since we will only be comparing measurements with the NIST standard, *provided the sample height is the same.*

Appendix III

Details of Sapphire 2θ Peaks on the 19 KeV Run

Use of the ratio method is dependent on obtaining consistent results for the sapphire 2θ Bragg peaks. Although the COM method gave us peak positions which were consistent for the two films 13C and 13D, we wish to study these peaks here in more detail. Doing this reveals some striking (and disturbing) differences, unexplained variations in peak widths, etc. All this needs to be completely understood if the " ratio of sines" method is to become a useful tool in film analysis.

A detailed study of the four sapphire peaks for film 13C and the corresponding four peaks for film 13D reveals a number of features which show that systematic effects were not under sufficient control. In particular, the choice of absorber to reduce the intensity, and the setting of the piezo control of the silicon monochromator (α setting) were haphazard, and administered in an ad hoc fashion in this first run. It is remarkable that the peak positions in Table II above agreed so well, but if this method is to be seriously used for publishable data, such a cavalier approach must give way to something more systematic and reproducible from one film to the next. The sapphire should be affected neither by the film above it, nor by the annealing process.

We begin by tabulating the conditions in so far as we can determine them from the rather cryptic entries in the data book. The α setting and the choice of absorber affected the ratio of first to third harmonic. It is this which we blame for the very wide variation in observed peak widths. These are significantly wider than the resolution for film 13C.

We must control the third harmonic and the overall beam intensity to compensate for the wide variation in peak intensities. These stem from the LP factor, and absorption corrections plus the Debye-Waller factor and atomic scattering factors. The most rapid variation comes from the LP factor, a table of which is found in Appendix 14 of the book by Cullity[11].

Table AIII-I

Factors Affecting Intensity

hkl	2θ (deg.)	LP factor	D-W Factor	$\frac{\sin\theta}{\lambda}$	f_{Al}^2	Nb Absorption	Product
110	15.8	3.67	.94	.21	77	.36	$\equiv 1$
220	31.9	1.89	.78	.43	38	.60	.35
330	48.8	1.33	.57	.63	16	.71	.09
440	66.8	1.09	.37	.84	7.8	.77	.025

The LP factor is here taken as $\frac{1}{\sin 2\theta}$ ([12], page 44. This is the formula for polarized radiation incident on a single crystal. (The usual factor $1+\cos^2 2\theta$ becomes a constant for radiation polarized normal to the scattering plane.) The Debye-Waller temperature factor is really just a guess, since the Debye temperature and atomic weight of aluminum have been used. The values for the square of the atomic scattering factor are only approximate, since we have neglected anomalous dispersion, taking the values, again only for aluminum from Cullity [11], Appendix 12. Absorption has been calculated assuming a 6 micron niobium film, and using the value $\mu = 13.694\,\mathrm{cm}^2/\mathrm{gm}$ for 18.89 KeV photons in niobium [10]. The final product of four factors tabulated above is our estimated relative intensity. We have normalized so that the 110 Bragg reflection has intensity 1. In addition, we have to consider extinction in the dynamical theory diffraction to accurately predict the line shape, position and intensity. This depends on the degree to which the crystal is bent, making it futile to attempt this calculation. Table AIII-I can give us something to compare with.

Table AIII-II

Details About Data From Sapphire 19 KeV Peaks

		FILM 13C		
hkl	α Setting	Absorber	FWHM(degrees)	Scan #/Page
110	0?	thick Nb	.028	128/15
220	0	Nb+In	.030	115/13
330	13.5	Nb+In	.045	127/16
440	56?	thick Nb?	.033	145/18
”	13	Nb+In	(double peak).05	155/19
		FILM 13D		
hkl	α setting	absorber	fwhm(degrees)	scan/page
110	?	thick Nb	.012	226/34
”	?	”	.012	231/35
220	56	?thick Nb	(double peak).015	194/25
330	”	none	.034	204/27
440	”	”	(saturated).031	208/27

We see immediately that the peak widths for film 13C are twice as broad as for film 13D. There is no physical reason for this, assuming that the annealing had no effect on the sapphire.

Table AIII-III

More Details About Data From Sapphire Peaks

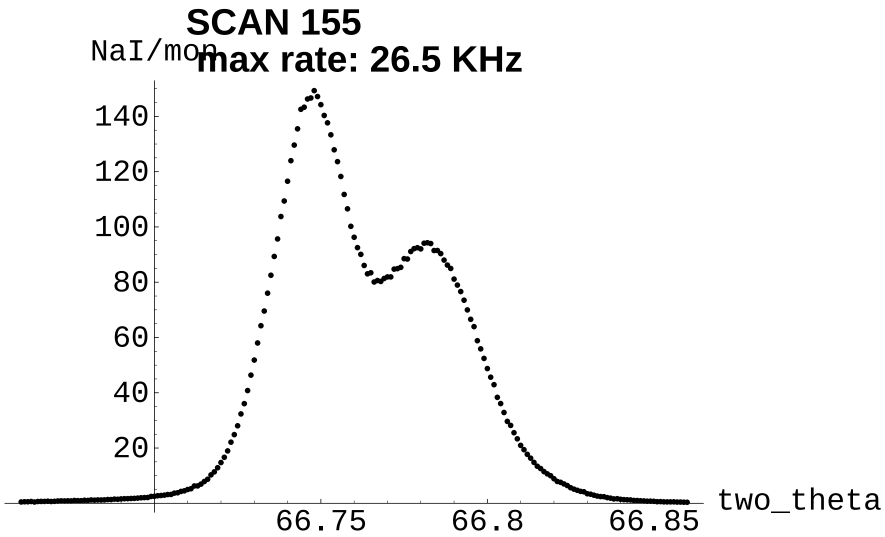
Film/hkl	Scan #	Max. Rate KHz	Peak Intensity counts NaI/1000 IC3	Sum Intensity*$\Delta(2\theta)$ counts NaI $\times$ deg./IC3
13C-110	128	0.33	1540.	.23
220	115	23.2	134000.	3.8
330	127	16.4	72900.	3.3
440	145	10.1	2730.	.11
"	155	26.6	14900.	7.7
13D-110	226	2.72	4910	.096
"	231	3.09	5240	.081
220	194	12.9	67100.	1.5
330	204	18.6	53700.	1.9
440	208	50.9	8080.	.29

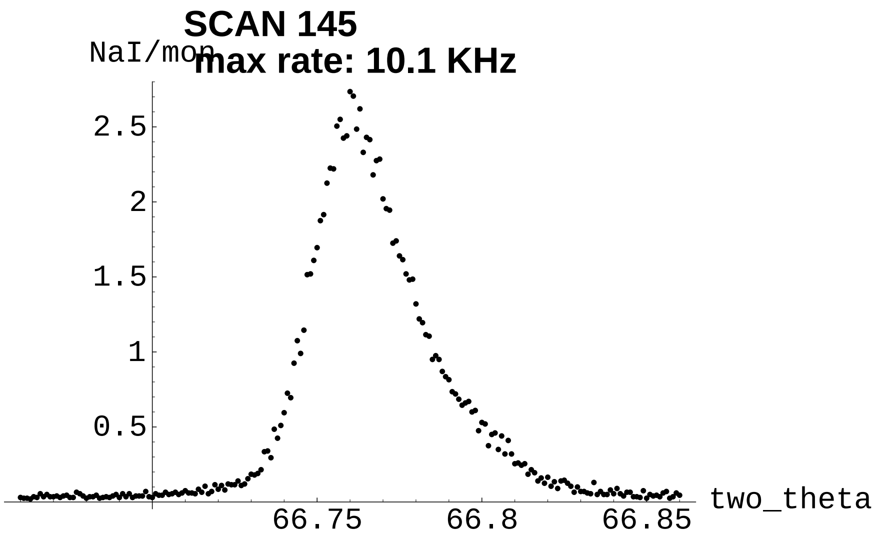
All but the last entry, 13D-440, had data taken at rates which did not seriously saturate the detector. But inspection of the peak shape for 13D-440 indicates it was slightly saturated, probably not enough to shift the peak center significantly. In the future, if the NaI counter is used, we should stay below 20 KHz to avoid this saturation.

The column "Sum Intensity*$\Delta(2\theta)$" is, barring saturation, independent of the beam intensity. It is approximately equal to the area under the peak. But it is affected by the piezo α setting, which controls the amount of third harmonic, and by whatever is used as a beam absorber to reduce the intensity.

These intensities (peak areas) vary all over the map, even for identical Bragg reflections. For example, as an extreme case, consider the two measurements of 13C-440, which vary by two orders of magnitude. We will need to make a study of this until the measurements are reproducible and agree with expectations. A method which uses sapphire peaks as reference standards cannot be used until these peaks are completely understood.

We give the two cases of the 13C-440 measurement to show how different these measurements were. There is a high probability that the double peak in scan 155 is related to the setting $\alpha = 13$. Scan 145 had $\alpha = 56$ (probably) and an unrecorded absorber, which was probably the thick Nb + ?.





The COM of both sets of data was very close—within .004° ! Notice the great difference in intensity. This is due to the use of different absorbers, not to the difference in the setting of the piezo. At the time, we did not realize that use of a thick Nb absorber *enhances* the third harmonic! If the double peak were caused by the third harmonic, the <u>lower</u> scan should have the double peak, not the upper one. So the problem is an unsolved mystery at this time.

Suggested Improvements in the F3 Diffractometer

A Checklist

1. The NaI detector is too heavy. When it replaces the ion chamber, the 2θ arm sags an additional 0.8 mm, an amount which certainly depends on 2θ . The lack of mechanical rigidity of the 2θ arm is probably the cause of the $\pm .05°$ error in 2θ which was observed with the NIST sample on the 10 KeV run where the energy was reasonably well known. The NIST corundum sample can be used to test the geometric integrity of the 2θ arm. Reducing the error to $< \pm .002°$ would be a desirable goal.

2. Also, this same NaI detector cannot handle counting rates above 25 KHz without serious distortion of peak shapes. This counting rate limitation was a problem, since we had no reliable way to attenuate the x-ray beam without enhancing the third harmonic contamination. Also, we had no good way to see that the upper level discriminator was rejecting third harmonic x-rays, and at high rates it was not doing so. All this points to replacing the NaI with a smaller, lighter detector having good energy resolution and capable of rates above 1 MHz (1 μsec dead time). We need a dynamic range of well over 100:1 with no peak degradiation. Counting rates below 1 KHz are too slow.