Physical properties of niobium iodides

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PHYSICAL PROPERTIES OF NIOBIUM IODIDES

by

Pyrtle William Seabaugh, Jr.

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of The Requirements for the Degree of Doctor of Philosophy

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Ames, Iowa

1961
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I. INTRODUCTION

Interest in niobium has been revived recently due to the discovery of large deposits of niobium minerals and the knowledge that it is a potential material for nuclear reactor and aircraft construction. Production of the pure metal is difficult due to the ease of contamination by carbon, oxygen and nitrogen when heated and the difficulty of separating the neighboring element. High-purity niobium, however, has been prepared by Rolsten (26,27) by the Van Arkel-de Boer iodide decomposition process starting with crude metal. Representative analytical results for the metal are: oxygen, 640 ppm; nitrogen, 10 ppm; hydrogen, 8 ppm; and carbon, <10 ppm. Also, McCarley and Tadlock (20,21) have purified niobium metal in a similar manner. Their representative analytical results are: oxygen, 540 ppm; nitrogen, 58 ppm; hydrogen, 4 ppm; and carbon, 220 ppm.

Following preparation of niobium metal, Rose began introductory work on the niobium halides (29,30). Apparently he was able to prepare the pentachloride but obtained indefinite results on the iodides. With the recent revived interest in niobium chemistry, further work has been done on the halides. Particularly, the niobium-chlorine system (5,15,34,35,37,38) seems to be well characterized. Schäfer (34) concluded that the tetrachloride of niobium could be prepared by analogy with vanadium and other neighboring elements. He found that niobi-
um trichloride was produced when the pentachloride was vola-
tilized in hydrogen at 180-190° and the mixture passed through
a tube at 450°. The greenish-black trichloride crystallized
in the hottest part of the tube, while the yellowish crystals
of pentachloride deposited at the coldest. A brown substance
found in the region between the two chlorides proved to be the
tetrachloride. Also, the tetrachloride was prepared by reduc-
tion of niobium pentachloride with niobium metal, iron and
aluminium. Having prepared the tetrachloride, Schäfer and co-
workers (34,35,37) further characterized the properties.

Several groups (5,15,28,34,38) have investigated the pre-
paration of niobium trichloride. Various methods have been
employed in preparing the trichloride, with Roscoe (28), Sue
(38), Schäfer, Göser and Bayer (37), and Brubaker and Young
(5) all using the hydrogen reduction of the gaseous pentachlo-
ride. Other methods (6,34,37) involve the reduction of the
pentachloride with niobium and the disproportionation of the
tetrachloride.

Characterization of the niobium trichloride phase has
been very extensively done by Schäfer and Dohmann (32,36).
Generally, crystalline halides have been considered to be sim-
ple stoichiometric compounds. However, it is known that iron
(III) chloride is homogeneous between FeCl$_3$.000 and FeCl$_2$.9975
and that composition of the solid trichloride phase depends on
the compound of the gas phase (33). It has been shown (32,36)
that niobium trichloride has a surprisingly large homogeneity region. The composition range from $\text{NbCl}_{2.67}$ to $\text{NbCl}_{3.15}$ has been studied by thermal decomposition of $\text{NbCl}_4$, reduction of $\text{NbCl}_5$ with hydrogen and the chemical transport reaction:

$$\text{NbCl}_x(s) + (4-x)\text{NbCl}_5(g) = (5-x)\text{NbCl}_4(g)$$

where $3.15 > x > 2.67$. It is remarkable that the chlorine to niobium ratio is both greater and smaller than three in the homogeneity range. Clearly, the stoichiometric trivalent niobium oxidation state is not particularly stable and this is further evidenced by the absence of niobium(III) oxide (4,16).

Niobium trichloride with composition of the upper limit of the homogeneous region is obtained by disproportionation of niobium tetrachloride. Niobium and the tetrachloride with an excess of pentachloride are placed in a reaction tube with one end at approximately $20^\circ$ and the salt end heated at 270 to 400$^\circ$. The composition of the lower limit is obtained by heating the salt end of the reaction tube to 600$^\circ$.

In the homogeneity region the color of the trichloride phase changes continuously from green ($\text{NbCl}_{2.67}$) to brown ($\text{NbCl}_{3.1}$). It was possible by microscopic examination to estimate the composition and homogeneity of a preparation by its color. Powder patterns confirmed the existence of the variable phase.

Niobium dichloride was also prepared by heating stoichiometric amounts of niobium metal and $\text{NbCl}_{2.67}$ at 800$^\circ$ (36), and
was found to be an essentially stoichiometric compound. No evidence for the existence of niobium(I) chloride was obtained.

Preparation of the lower bromides of niobium have also been reported (5,17). Brubaker and Young prepared NbBr₃ by reduction of the pentabromide with hydrogen at 500°. They found it to be quite similar in inertness to niobium(III) chloride. Gutmann and Tannenberger (17) reportedly prepared NbBr₂ by reduction of NbBr₅ with hydrogen and also noted the formation of NbBr₄ and NbBr₃ during the course of the reaction.

Published results on the niobium-iodide system has been fragmentary. Early attempts at obtaining iodides from the elements at approximately 600° were unsuccessful (22,31). Better results (3) were obtained by reacting hydrogen iodide with the pentabromide of niobium but the product was not free of bromide and was not analyzed or examined further.

Körösy (19) prepared the pentaiodide by heating a niobium wire at 1300 to 1600° in iodine vapor. Niobium pentaiodide was easily dissociated at the sublimation temperature and appeared to be unstable at any temperature above 200°. Recently, Alexander and Fairbrother (1) synthesized the pentaiodide from the metal heated from 800 to 1500° by high-frequency electrical induction currents and iodine vapor at approximately one atmosphere. Several attempts were made to analyze the product
but inconsistent results were obtained owing to the difficulty of separating the product quantitatively from traces of metal and lower iodides and to its sensitivity to air. Apparently pure niobium pentaiodide was prepared by Rolsten (25). He reacted niobium metal with excess iodine in a Pyrex reaction tube at 280 to 290° under a pressure of iodine. The disadvantage of this method is that unreacted metal or impurities may become mixed with the product. Also, the removal of excess iodine involves considerable time. Corbett and Seabaugh (11) prepared pure niobium pentaiodide by the reaction of the metal with a 10 to 15 per cent excess of iodine. The metal and iodine were contained in opposite ends of an evacuated, V-shaped Pyrex tube, and the metal heated to 510° and the iodine to 180°. This method has the advantage that a sublimed product is obtained at the junction of the two furnaces. Synthesis of niobium pentaiodide has also been reported by Niselson and Petrusevich (24). In an investigation of the reaction between \( \text{Al}_2\text{I}_6 \) or \( \text{SiI}_4 \) and \( \text{NbCl}_5 \) to produce \( \text{NbI}_5 \), the halides were mixed in proportions according to the conventional equations:

\[
4 \, \text{NbCl}_5 + 5 \, \text{SiI}_4 \rightarrow 4 \, \text{NbI}_5 + 5 \, \text{SiCl}_4 \\
3 \, \text{NbCl}_5 + \frac{5}{2} \, \text{Al}_2\text{I}_6 \rightarrow 3 \, \text{NbI}_5 + \frac{5}{2} \, \text{Al}_2\text{Cl}_6.
\]

For complete substitution of iodide for chloride a 10 per cent excess of \( \text{Al}_2\text{I}_6 \) or \( \text{SiI}_4 \) was used. Composition of the iodide corresponded to \( \text{NbI}_{4.5} \) to 4.8.

Dissociation of \( \text{NbI}_5 \) to give the lower iodides \( \text{NbI}_3 \),
and Fbgl-JY has been reported (19), but there is no reliable information on them. Recently there has been more substantial evidence for existence of the lower iodide. Thermal decomposition of NbI₅ in a "hot-cold" tube results in the formation of the tetraiodide and triiodide (11). If the decomposition is carried out at 270° the residue obtained is pure, grey NbI₄ while decomposition at 430° gives the black NbI₃.

Preliminary single-crystal X-ray studies of NbI₄ by Dahl and Wampler (12) show it to be orthorhombic with space group Cmc2₁. The lattice constants are a = 7.67 Å, b = 13.28 Å, and c = 13.93 Å. This compound is the first known structure of its configuration which consists of infinite chains parallel to the a axis formed by NbI₆ octahedra sharing two opposite edges. Pairs of niobium atoms are shifted from the centers of the octahedra of iodine atoms by the interaction of the unpaired electron on each niobium atom to form a metal-metal bond.

Chizhikov and Grin'ko (10) prepared lower niobium iodides by the reaction of iodine vapor with the hot metal. The composition of the product depended on the metal temperature and method of treatment. Formulas of NbI₅, NbI₄ and NbI₃.₂ were indicated by analysis and the authors suggested that range of solid solutions was evidenced by X-ray diagrams of samples near NbI₃.₂. By heating niobium and iodine in proportion corresponding to NbI₃, the triiodide was formed at 580° to 600°.
It was sublimed at 600° and condensed as acicular crystals. Further work on the triiodide indicated that it can be prepared by heating mixtures of Nb$_2$O$_5$ and Al$_2$I$_6$ at 230 to 300° for 24 to 48 hours. Chaigneau (8) obtained a mixture of NbI$_3$, iodine, NbO$I_3$ and Al$_2$O$_3$ which were separated by fractional sublimation. Iodine and NbO$I_3$ sublimed first and finally the less volatile triiodide. It was suggested by Chaigneau that the pentaiodide formed first and then dissociated to iodine and triiodide. Purity of the products was apparently good but the method of analysis was not given. Following the work on the triiodide, he prepared the diiodide by hydrogen reduction of NbI$_3$ (9). The formula NbI$_2$ was indicated by the analysis of the product, but no physical evidence was cited (e.g. powder pattern).

Although several iodides of niobium have allegedly been prepared, there has been little work done on the properties of these compounds. Even some of these methods do not lend themselves readily to preparation of pure products and leave doubt as to the actual composition. Niobium trichloride (32,36) is known to be a compound of variable composition and conceivably NbI$_3$ might exhibit this property, although no cited evidence justifies this conclusion.

Due to the general lack of information on the niobium-iodine system it has been of interest to study the phase relationship of these iodides. Furthermore, the phase diagram
permits identification of the actual composition of these compounds. A phase diagram not only relates the different phases but in a very concise form contains much of the chemistry of the system and was employed for the characterization of these niobium iodides.
II. EXPERIMENTAL

A. Preparation of Niobium Iodides

Preparation of niobium(V) iodide (\(\text{NbI}_5\)) preceded that of other iodides since they were obtained by decomposition of this material. All samples were transferred in an argon-filled dry box. Argon used for flushing the box was dried by flowing through \(-80^\circ\) trap, and the box atmosphere was continuously circulated through Linde Molecular Sieve Type 4A.

1. Niobium(V) iodide

Niobium pentaiodide was prepared by the reaction of the metal with a 10 to 15 per cent excess of iodine. The niobium metal was obtained through the courtesy of Dr. R.E. McCarley of this Laboratory. Representative impurities were: oxygen, 610 ppm; nitrogen, 403 ppm; carbon, 956 ppm; and hydrogen, 5 ppm. Iodine (J.T. Baker Reagent) was first purified by sublimation in vacuo at ca. 80\(^\circ\). Usually 20 gram "batches" of \(\text{NbI}_5\) were prepared by heating the metal and iodine in opposite ends of an evacuated, V-shaped Pyrex tube to 500 and 180\(^\circ\) respectively. Generally the reaction was completed in 24 to 36 hours, during which time the product sublimed to the junction of the two furnaces. At the finish, the metal end of the tube was cooled to within 70\(^\circ\) of the iodine reservoir and then both ends were cooled uniformly to room temperature. Analysis of the resulting product gave iodine to niobium ratios of 4.95 or
greater.

Salt for determination of the melting point was prepared by taking the above product and resubliming it in an iodine atmosphere \( \text{i.e. salt at } 450^\circ \text{ and iodine at } 180^\circ \). Iodine to niobium ratios of \( 5.00 \pm 0.01 \) were obtained.

2. Niobium(IV) iodide

As previously described \((11)\), samples of NbI\(_5\) were transferred in the dry box to glass tubes equipped with ball joints for evacuation. Because of the extreme sensitivity of NbI\(_5\) to moisture, the containers were evacuated and flamed before being taken into the box. After being filled, they were re-evacuated and sealed off.

Niobium(IV) iodide was prepared by thermal decomposition of NbI\(_5\) at 270\(^\circ\) for 48 hours, collecting the evolved iodine in the other end of the tube at about 35\(^\circ\) (v.p. of I\(_2\) = ca. 0.8 mm).

3. Niobium(III) iodide

Triiodide was prepared in a similar manner by heating niobium pentaiodide to 400\(^\circ\) for two days.

B. Analyses

1. Ignition

Samples were transferred in the dry box to a small weighing bottle and the ground joint lightly greased. After weighing this in air, the salt was poured into a porcelain crucible,
the bottle quickly recapped, and the weight of the sample determined by difference (corrected for buoyancy). Since only niobium and iodine were presumed present, the analysis was carried out by ignition to Nb₂O₅.

2. Wet method

Since samples with iodine/niobium ratios between 4.0 to 5.0 are readily dissolved in water they were used to check the reliability of the ignition method. Niobium was precipitated from these solutions by addition of ammonium hydroxide, then filtered off and ignited. To the filtrate, a small amount of sodium sulfite was added to reduce any iodine to iodide. Iodide was determined by titration with standard silver nitrate using as the indicator, Eosin Y in a 50% solution of Polyethylene 400 in water (14). The solutions were acidified with five ml of 10% acetic acid.

3. Analytical accuracy

Material balance on samples used to check the ignition method were 100 ± 0.02%. Iodine/niobium ratios are considered to be ± 0.02 except when otherwise stated.

4. X-ray powder patterns

Diffraction patterns were obtained on samples contained in 0.1 to 0.05 mm capillaries that had been filled in the dry box. An 11.46 cm Philips camera was used with Ni-filtered CuKα radiation; absorption corrections were not applied. NBS tables (23) were used to convert θ to distances. Values for
the iodides are listed in the Appendix.

C. Measurements

1. Construction of the phase diagram

Differential thermal analysis, thermal analysis and equilibrations were employed for the phase diagram determination. Although thermal analysis does detect heat effects associated with the particular system of interest, ascertaining the nature of these breaks is not necessarily forthcoming. Consequently other means, physical or chemical, should necessarily accompany thermal analysis in constructing a phase diagram.

For thermal analysis, the apparatus shown in Fig. 1 was employed. Since all the iodides have a definite iodine pressure above them, metal containers are undesirable so that cooling curve cells were constructed from 15 mm Pyrex or Vycor tubing depending on the temperature needed. A small section of 3 mm tubing was sealed into and fused to the bottom of the cell for the thermocouple well. These cells were equipped with ball joints for evacuation. For the actual process, the sample was placed axially in a vertical 16" Marshall tube furnace and held in position by binding the cell to the thermocouple wire that hung on a support above the furnace. That part of the #28 gauge chromel-alumel thermocouple extending into the furnace was in an alundum shield. Convection baffles of transite were placed in the top and bottom of the furnace.
Fig. 1. Cell for thermal analysis
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THERMOCOUPLE WELL

50 mm

2 mm.

15 mm
Temperature was regulated by a Brown proportioning controller with its thermocouple in contact with the inside wall of the furnace. Generally, cooling and heating rates were approximately 5°/min although in specific cases the rates were <1°/min. Thermocouple potentials were recorded on a Bristol Model 560 Dynamaster strip chart, two-pen recorder. This recorder is equipped with a variable, 2 to 10 millivolt range with 0 to 40 millivolt zero suppression and fixed millivolt range for the differential thermocouple. By impressing a known potential from a Rubicon potentiometer into the input of the instrument, the range and amount of zero suppression could be established at the desired values. In the same manner, the recorded thermal halts were measured with the potentiometer by lining up the pen with the recorded break. Positioning of the differential pen was controlled by a variable voltage box. Corrections for the measuring thermocouple were established by standardization against National Bureau of Standards sample of lead.

For the determination of thermal halts, approximately 20 to 25 millimoles of salt were transferred in the dry box to the cells. Because of the sensitivity of samples to moisture (especially those with iodine/niobium >3), cells were evacuated and flamed before being taken into the box. Before running the first heating curve on any particular sample, the sample was equilibrated for several hours at a relatively low temper-
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ature (280 to 300°) to ensure equilibrium.

2. Determination of dissociation pressures

Dissociation pressure measurements were obtained with the aid of a null-type, Pyrex diaphragm gauge (Fig. 2) similar to that described by Daniels (13). The typical gauge had a sensitivity of about \( \frac{1}{2} \) mm deflection per mm pressure differential with the null point invariant to >480°. When viewed with a 15X telescope, the reproducibility of the pointer movement was comparable to that with which the manometer could be conveniently read (0.25 mm). This manometer, including other features of the all-Pyrex measuring apparatus, is shown in Fig. 3. Pressures were measured visually on a meter stick that had been compared to a precision cathetometer.

The cell was positioned axially in a vertical, 12" Marshall tube furnace with transite covering at the top and bottom of the furnace. One thermocouple was positioned in a small indentation in the bottom of the cell to measure the sample temperature. A second thermocouple, parallel and in contact with the cell wall was used to measure the temperature gradient along the cell. A gradient of 5 to 7° at 300° was used with the top of the cell being hottest. Shunts on the furnace taps were used to adjust the temperature at any point to ±0.5°. A Rubicon potentiometer permitted direct measurement of the sample and gradient temperature to ±0.3°. The furnace temperature was regulated by a Brown proportioning
Fig. 2. Pyrex diaphragm gauge for determination of dissociation pressures
Fig. 3. Apparatus for dissociation pressure measurements
controller with its thermocouple in contact with the inside wall of the furnace.

Before bringing the cell into the dry box, it was evacuated with a diffusion pump and baked out approximately 12 hours at 400°C. After being filled, the cell was re-evacuated for 5 hrs at room temperature and sealed off. Then pressure measurements were made in 5 to 10°C intervals with sufficient time between measurements for the system to reach equilibrium. Checks were made to ensure equilibrium condition by holding the sample at a given constant temperature over an extended period of time (i.e. 24 to 48 hrs) and periodically measuring the pressure.
III. EXPERIMENTAL RESULTS

A. Niobium-Iodine System

The interest and importance of the investigation of this system lies in the determination not only of the conditions for stable existence of compounds formed, but also conditions for chemical combination that may occur among these compounds. In addition to compounds reported earlier (11), a lower iodide with an iodine/niobium of 2.67 is formed. A summary of these iodides with some of their properties is found in Table 1.

Table 1. Niobium iodides

<table>
<thead>
<tr>
<th>$\frac{I}{Nb}$</th>
<th>Temperature of heat effect</th>
<th>Process</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>400°C</td>
<td>melting</td>
<td>brassy</td>
</tr>
<tr>
<td>4.00</td>
<td>503°C</td>
<td>incongruent melting</td>
<td>dark-grey,</td>
</tr>
<tr>
<td></td>
<td>417°C</td>
<td>phase transformation</td>
<td>metallic-</td>
</tr>
<tr>
<td></td>
<td>348°C</td>
<td>phase transformation</td>
<td>appearing</td>
</tr>
<tr>
<td>3.00</td>
<td>526°C</td>
<td>disproportionation</td>
<td>black</td>
</tr>
<tr>
<td>2.67</td>
<td>(&gt;790°C)</td>
<td>(melting)</td>
<td>black</td>
</tr>
</tbody>
</table>

As shown in Fig. 4, the tetraiodide occupies an important position in the phase diagram for this system. Existence of a phase corresponding to an approximate composition of NbI$_4$ was established by observing thermal halts on samples with I/Nb ratio near 4.0. Because of limitations in detecting thermal halts, more accurate composition determinations of the phase
Fig. 4. Phase diagram of the niobium-iodine system
were afforded by other methods (e.g., equilibrations below). When a cooling curve is run on a NbI$_4$ sample, the temperature at which the disproportion reaction

\[ \text{NbI}_4(\gamma) \rightleftharpoons \text{liquid} + \text{NbI}_{2.67} \]

takes place is 503° and in addition, a larger, flat halt is seen at 410 to 415°. The second halt occurs at the temperature of the phase transformation:

\[ \text{NbI}_4(\gamma) \rightleftharpoons \text{NbI}_4(\phi) \]

Further cooling to room temperature failed to reveal any new temperature effects. Similarly, heating curves showed only two halts under usual conditions although prior evidence for some change near 340° had been obtained from iodine dissociation pressure measurements. However, when the sample is equilibrated at 300° for 12 hours, a small heat arrest can be detected at 348° by differential thermal analysis on heating. Rapid cooling and heating rates were avoided because of possible complete suppression of this solid state transformation; nevertheless, even with cooling rates <1°/min. the halt was not observed. After cooling the sample below the transformation temperature, heating curves run immediately to several hours later did not show any halt at or near 348°. Only when the sample had been equilibrated for a period of 10 or more hours did the 348° halt appear on heating. This halt was found on samples with iodine/niobium ranging from 2.94 to 4.70.
The rapid temperature transformation between NbI$_4$(\(\alpha\)) and NbI$_4$(\(\phi\)) only on heating is not readily understood. Furthermore, careful examination of X-ray powder patterns for samples equilibrated above and below 348° failed to reveal any evidence for a phase change. Rapid quenching (either in ice water or by taking the sample out of the furnace and letting it cool in air) of samples from temperatures above 348° also produced negative results. Apparently the transformation:

\[
\text{NbI}_4(\phi) \rightleftharpoons \text{NbI}_4(\gamma)
\]

involves a large heat effect; accordingly is the largest break of the three observed. Supercooling is noted on cooling curves, but the break is consistently at 417° on heating curves. Unlike the \(\phi\) form of NbI$_4$, the \(\gamma\) form gives a powder pattern dissimilar to that of the \(\alpha\) form. Although heating and cooling curves indicate rapid reversibility of the \(\phi\) to \(\gamma\) transformation, quenching the \(\gamma\) form to room temperature in air or ice water presents no difficulty.

In determination of the disproportionation temperature of \(\gamma\) NbI$_4$, heating curves proved to be inadequate. Apparently, the incongruent melting process is sluggish, since the heat effect as detected by differential thermal analysis is observed over an extended temperature range (10 to 20°) as a very small continuous change in slope. Possibly experimental factors such as temperature gradient and variations in heat supply contributed, although care was taken to minimize these
effects. However, cooling curve breaks were sharp and well-defined.

Sublimed NbI\(_4\) was prepared by heating the decomposition product of a higher iodide (2.6< I/Nb<4.00) above 526° (for reasons to be given later), cooling below 503°, and then subliming the NbI\(_4\). The procedure followed in this preparation was to place the sample in an evacuated quartz tube provided with a thermocouple well, and heat to a temperature<526° in a Marshall furnace. Then the sample was cooled below the disproportionation temperature of NbI\(_4\) and the temperature gradient adjusted. (Usually a small gradient of 3 to 10° was used with the hotter end of the sample tube being that with the bulk salt.) After adjustment of the gradient, the sample was heated for 24 to 48 hours at temperatures that ranged from 430 to 490°; thus, a sublimate of \(\sqrt{3}\)NbI\(_4\) was obtained at the cooler end of the tube as a solid crystalline mass. The sublimation can be carried out more rapidly by using a temperature just below the disproportion temperature and a relatively large gradient (e.g. 20 to 30°). Analysis and powder patterns confirmed that the sublimed product is NbI\(_4\).00±0.01. Qualitative examination of magnetic properties by the Gouy method indicated all three forms are diamagnetic; however, the samples were contained in Pyrex tubes and conceivably a weak paramagnetism may have been masked. The inhomogeneous field had a maximum intensity of approximately 12,000 gauss. In light of the \(\alpha\)NbI\(_4\) structure (12), the metal-metal bonds
must be retained in all forms for them to exhibit diamagnetism. Moreover, powder patterns of mixtures from NbI$_{4.3}$ to NbI$_{3.7}$ showed no measurable expansion in the distances for any form, indicating absence of solid solutions or a range of composition.

The apparent position of NbI$_3$ in the phase diagram was not readily understood. As shown in Fig. 4, the triiodide disproportionates at $526^\circ$ according to the reaction

$$\text{NbI}_3 \longrightarrow \text{NbI}_{2.67} + \text{liquid},$$

and cannot be recombined.

If cooling curves are run on samples with compositions approximately NbI$_3$, no thermal halts other than those corresponding to the tetraiodide are observed and these are obtained with samples of compositions as low as NbI$_{2.76}$. Likewise, heating curves run on samples after they have been heated above $526^\circ$ reveal no halts other than those of the tetraiodide phase. A more extensive investigation by differential thermal analysis revealed, however, that the first heating curves show thermal halts at $511^\circ$ and $526^\circ$ if iodine/niobium $>3.00$ and $526^\circ$ if iodine/niobium $<3.00$. In view of this behavior, a series of careful measurements was made on NbI$_{3.07}$. The first heating curve, which followed an overnight equilibration at $300^\circ$, showed only one break at $526^\circ$. Equilibrations at $515^\circ$ (overnight), $490^\circ$ (2 hrs), and $310^\circ$ (46 hrs) failed to show any evidence of recombination to
the triiodide as judged by the absence of a thermal effect at 526° on heating. Cooling curves on this sample revealed only halts associated with the tetraiodide phase.

As a check on identification of the triiodide phase at different temperatures, X-ray patterns were employed. Choosing NbI2.94 as a typical example, patterns were taken of samples equilibrated at 400, 450, 490 and 514°. No evidence was found for any phase other than that of the triiodide as long as the temperature was below 526°. However, when the sample was annealed above 526°, only the pattern corresponding to NbI2.67 was obtained. The sample was quenched to room temperature (25°) either in air or ice water. Effort to recombine this sample by equilibration at 510 and 450° for 24 hours failed as only the NbI2.67 phase could be detected. Consequently it is concluded that NbI3 disproportionates at 526° as an irreversible process and accordingly is not an equilibrium product, as indicated by the phase diagram. Qualitative magnetic measurements indicate the triiodide to be diamagnetic.

Niobium triiodide can be prepared other than as the residue of the thermal decomposition of a higher iodide. Sublimed NbI3 was obtained in a manner similar to that described for sublimed NbI4, heating a decomposition product (2.67 < I/Nb < 3.00) of a higher iodide in a sealed, evacuated tube at 400 to 490° with a temperature gradient of 9 to 14° for 48
hours. Both powder pattern and analysis confirm that the product is $\text{NbI}_3.00 \pm 0.05$. Also, reaction of $\text{NbI}_4$ with metal gives the triiodide. Finely divided $\text{NbI}_4$ (900 mg) in a sealed, evacuated tube with 254 mg of metal was heated at $411^\circ$ for 8 hours. Examination of the bulk salt revealed it to be composed of unreacted $\text{NbI}_4$, Nb and, visually, black $\text{NbI}_3$. The metal was separated by hand and a few small pieces of the black substance were picked out of the bulk salt for powder pattern samples. Analysis of the bulk material indicated an I/Nb ratio of 3.43; the powder pattern corresponded to that of triiodide.

Compositions of residues from exhaustive $\text{NbI}_4$ sublimations were determined to have I/Nb ratios of 2.67, 2.67 and 2.70. This compound was first prepared by heating a sample of $\text{NbI}_3.08$ to 765$^\circ$ to decompose the triiodide, quenching in air to 25$^\circ$, and washing the bulk salt with cold water several times to dissolve $\text{NbI}_4$ and $\text{NbI}_5$. After washing, the residue was transferred to a tube which was evacuated. Then the sample was dried by heating the salt gradually from room temperature to 200$^\circ$ while continuously pumping through a $-80^\circ$ trap. The salt had an I/Nb ratio of 2.6. Apparently $\text{NbI}_{2.67}$ is very slightly soluble in or slowly reacts with cold water so that total time consumed in washing should not be more than 10 min. With this precaution, I/Nb ratios of 2.64 and 2.67 were obtained. This method provides a quick and easy way for
separation of NbI$_{2.67}$ from its mixtures with NbI$_4$ and gives a product of reasonable purity. High purity NbI$_{2.67}$ is probably best prepared, however, as the residue from the sublimation of tetraiodide from the mixtures.

Thermal analysis was utilized to help establish the composition of this lower iodide and to determine if another phase existed between NbI$_{2.67}$ and metal. Cooling and heating curves on samples (2.2 < I/Nb < 2.67) failed to reveal any thermal halts. A heating curve on NbI$_{2.26}$ showed no halts up to 790°. Subsequent equilibration at that temperature and cooling gave no thermal arrests. Careful examination of X-ray powder pattern for NbI$_{2.26}$ showed only lines belonging to the NbI$_{2.67}$ phase. Surprisingly, no metal lines were observed either on the sample as prepared or after equilibration at 700°. The results of equilibrations of excess metal with a lower iodide (e.g., NbI$_{2.67}$) indicate the formation of no new phase, although the I/Nb ratio of the bulk salt was reduced considerably below 2.67. The procedure followed in this analysis was to sort out unreacted bulk metal by hand and ignite the salt to Nb$_2$O$_5$. Undetected finely-divided metal accounts for the low I/Nb ratio. Efforts to devise a workable method of analysis which would allow solution of salt away from admixed metal failed. One such attempt was to digest the mixture in dil HNO$_3$, followed by treatment with hot conc HCl; however, finely-divided metal was also dissolved. X-ray pat-
terns, however, revealed only the NbI$_2$.67 phase even when the powder pattern sample was taken from salt adhering to the metal.

All the foregoing methods for the characterization of the lowest iodide phase approached the composition from mixtures of higher iodine content. This iodide was also obtained by sublimation from its mixtures with metal. Three g. of metal was placed in a quartz tube with one g. of NbI$_2$.26, the tube sealed under vacuum and heated at 600° for 24 hrs. A temperature gradient along the tube was adjusted to 100° and the mixture then heated to 750° and equilibrated 48 hrs. During this time a product sublimed to the coldest part of the tube and X-ray powder patterns and analysis confirmed this to be NbI$_2$.67. This further confirms that solid NbI$_2$.67 is the phase in equilibrium with metal. Consequently, the diiodide does not appear to exist as a solid equilibrium phase in contrast to the reported behavior of the bromide and chloride (17,36).

This lowest iodide is stable to air for several days at room temperature, being quite similar in inertness to the niobium(III) halides (5,11). This black salt is very slightly soluble in or reacts with cold water, slightly soluble in or reacts with hot water and hot conc HCl, and decomposes slowly in dil HNO$_3$. Qualitative magnetic measurements indicate that the salt is also diamagnetic.
The melting point of pure NbI$_5$ was determined to be 400°. In this determination, resublimed iodine, in amount corresponding to the approximate decomposition pressure of NbI$_5$ at 400°, was added to suppress the decomposition of pentaiodide at the melting point. As shown in Fig. 4, the apparent eutectic occurs at 400° and about NbI$_{4.82}$. A careful examination of differential heating and cooling curves on samples with $4.8 < I/Nb < 5.0$ failed to reveal any thermal halts other than that of the supposed eutectic. A sample of NbI$_{4.90}$, equilibrated at 380°, gave a halt at 400° on heating and 402° on cooling. Identical temperatures were observed on pure NbI$_5$ equilibrated at the same temperature. Heating and cooling rates on these samples were < 2°/min; faster rates tended to give lower temperatures. Powder patterns of mixtures from NbI$_{4.8}$ to NbI$_5$, either rapidly quenched or slowly cooled, did not exhibit any evidence for compound formation, phase transformation, or solid solution which could have, in part, explained the absence of a normal liquidus curve. Possibly, liquid and solidus heat effects may be too small for detection. High temperature X-ray techniques and/or other means of investigation will be necessary before a conclusive interpretation can be given for this region of the phase diagram.
B. Dissociation Pressures

Initial investigation of the niobium-iodine system started with determination of the NbI$_5$ dissociation pressure. An inflection at an unexpected low temperature ($\sim 340^\circ$) in the log $P$ vs $1/T$ plot prompted, however, an extensive examination of the phase relationship among the iodides before further work on dissociation pressures was attempted. Although this study is not complete, enough data are available on certain temperature and composition regions to be informative.

Dissociation pressures of a mixture with an I/Nb ratio of 4.55 were measured over a temperature range from 270 to 350$^\circ$ and for ratios of 4.12, 4.85, and 4.87, from 270 to 400$^\circ$. In the vicinity of 340$^\circ$ a change in slope in the log $P$ vs $1/T$ plot was observed on all samples; because the nature of this break was not understood at the time that measurements on NbI$_{4.55}$ were taken, the pressure-temperature relationship of this ratio was not followed above 350$^\circ$. Measurements on all samples extended over some weeks and only a few equilibrium determinations were possible during a single day. Moreover, observations were so arranged that some pressures that were approached from above alternated on the curve with those approached from below whenever practicable. Dissociation pressures, in mm of Hg reduced to 25$^\circ$, are given in Table 2 (see Appendix).

The same partial pressures of iodine were found over
NbI$_{4.12}$ and NbI$_{4.55}$ at any given temperature in the range 270 to 340°. As shown in Fig. 5, log $P$ vs $1/T$ plots for these mixtures superimpose on each other with small deviation. Attainment of equilibrium in this temperature region was rapid either with increasing or decreasing temperature. Above 340°, however, equilibrium was more difficult to obtain. Constancy of pressure at any particular temperature above 360° could be obtained fairly rapid with increasing temperature, but steady pressures were extremely difficult to attain with decreasing temperature. This was evidenced by a gradual decrease of pressure with time at constant temperature. Similarly, the absence of equilibrium was observed between 340 and 360° both on heating and cooling. This effect and that of slowly approaching equilibrium on falling temperature is shown in Fig. 6.

The vapor pressures obtained for the mixtures NbI$_{4.12}$ and NbI$_{4.55}$ in the temperature range of 270 to 340° were fit to the equation $\log P_{mm} = -\frac{3.836 \times 10^3}{T} + 8.071$ by least squares. Similarly, pressures for NbI$_{4.12}$ in the temperature range 350 to 400° were fit to the equation $\log P_{mm} = -\frac{2.536 \times 10^3}{T} + 5.911$. Powder patterns for these samples, quenched from both above and below 340° in ice water, revealed only lines of the NbI$_4$ and NbI$_5$ phases without any detectable shift in distances. From the phase diagram study, Part A, it may be concluded that the inflection in the log $P$
Fig. 5. Dissociation pressure data for NbI$_{4.12}$ and NbI$_{4.55}$
Fig. 6. Non-equilibrium data of NbI₄₁₂, A = 24, B = 96, and C = 138 total hours at temperature.
vs 1/T plot is associated with the α to β transformation of NbI₄. Although the equations which represent the decomposition pressure for the mixtures do not take into account possible NbI₄ and NbI₅ sublimation pressures and must be considered tentative, they are adequate for the present discussion.

Although a change in slope is observed in the log P vs 1/T graphs at approximately the same temperature as that for the preceding compositions, pressure measurements, as shown in Fig. 7, clearly indicate a different process is governing the equilibrium pressures for mixtures of NbI₄.85 and NbI₄.87. The pressure-temperature relationships below 340° differ from those of NbI₄.12 and NbI₄.55. Superposition of log P vs 1/T plots is not possible for NbI₄.85 and NbI₄.87 either below or above 340°; for the mixture NbI₄.85 exhibits the higher pressure at any given temperature. Possibly, size of the sample was a factor since the quantity of NbI₄.85 used was roughly twice that of NbI₄.87.

Dissociation pressures for NbI₄.87 and NbI₄.85 in the temperature range of 270 to 340° were fit to the equation

\[ \log P_{\text{mm}} = -\frac{3.652 \times 10^3}{T} + 7.823 \] and \[ \log P_{\text{mm}} = -\frac{2.879 \times 10^3}{T} + 6.636 \] respectively by least squares. Similarly, pressures for NbI₄.87 in the temperature range of 340 to 400° were fit to the equation \[ \log P_{\text{mm}} = -\frac{6.536 \times 10^3}{T} + 12.52 \).

X-ray powder patterns for NbI₄.85 quenched from 255 and 378° failed to reveal any evidence for a new phase, transfor-
Fig. 7. Dissociation pressure data for \( \text{NbI}_4.85 \) and \( \text{NbI}_4.87 \)
mation or solid solution. These possibilities cannot be dis-
regarded, however, since quenching to room temperature may de-
stroy the phase stable at high temperature or may readily 
separate solid solutions.

Before a conclusive interpretation can be given to the 
preliminary decomposition pressure results on this system, 
supplementary data will be needed. Determination of NbI₅ 
sublimation pressure will be helpful so that the contribution 
to the total pressure can be taken in account. Furthermore, 
high temperature X-ray techniques may prove valuable, for 
definition of dissociation pressure depends not only on the 
substance undergoing dissociation, but also on the solid 
product formed.
IV. GENERAL DISCUSSION

A. Discussion of the Niobium-Iodine System

In contrast to the reported behavior with niobium bromide and chloride, niobium diiodide apparently does not exist as a solid equilibrium phase. The lowest iodide is the heretofore unknown NbI$_2$.67 which can be sublimed from a mixture of the salt and excess metal. From lattice energy considerations, the reluctance of NbI$_2$.67 to disproportionate to a lower iodide may be partially rationalized in terms of the following process:

$$2 \text{NbX}_2(s) + \text{NbX}_4(s)(l)(g) \rightleftharpoons 3 \text{NbX}_2$.67(s)$$

(where $X = \text{Cl, Br, I}$)

or, by reduction

$$4 \text{NbX}_2(s) \rightleftharpoons \text{Nb(s)} + 3 \text{NbX}_2$.67(s).$$

As evidenced in the latter equation, the difference of the iodide from the other halides seemingly must be due to an abnormally low lattice energy of NbI$_2$ or high lattice energy of NbI$_2$.67 in that these are the only variables. Additional stabilization from probable multiple metal-metal interactions in NbI$_2$.67 may account for the unobserved formation of the diiodide. One point in favor of this view is the observed diamagnetism and the known metal-metal bonding in NbI$_4$.

As a consequence of this research, the reported preparation of NbI$_2$ by Chaigneau (9) seems dubious since the only reported positive evidence is that of analysis without any physical means of confirmation. It should be noted, however,
that in the course of this research almost any I/Nb ratio could be obtained consistently by thermal decomposition of higher iodides through appropriate adjustment of temperature and time for the decomposition process. Similarly, the alleged preparation of a pure phase NbI$_3$.2 at 585 to 600$^\circ$ by Chizhikov and Grunn'ko (10) should seemingly be viewed with caution. They suggested that a range of solid solutions was evidenced by X-ray diagrams of samples near NbI$_3$.2 in composition, but examination of their reported $d$-spacings reveals distances attributable to principally NbI$_2$.67 plus apparently NbI$_3$, NbI$_4$ and other unidentified phases. This indicates that the reported NbI$_3$.2 is not a compound but rather a mixture of lower iodides and possible unknown contamination.

Unlike the niobium trichloride with composition variable over a wide range (32,36), the triiodide is a simple stoichiometric compound which can be sublimed at moderately low temperatures (i.e., 400$^\circ$). Apparently, NbI$_3$ disproportionates irreversibly at 526$^\circ$ since equilibration over a prolonged period fails to recombine the reaction products. Whether this is due to a kinetic effect or to its metastability with respect to NbI$_4$ and NbI$_2$.67 is not known, but the high stability of NbI$_2$.67 may be significant in this respect. Interestingly, the implied stability of Nb(III) in a stoichiometric triiodide is in contradistinction to the interpretation of NbCl$_3$ in terms of Nb(II) and
Nb(IV)* and to the non-existence of niobium(III) oxide. Whether or not this is due to metal-metal bonds which could stabilize the Nb(III) state is not known, but seems worthy of further investigation.

Simultaneous solution of the two equations describing different portions of the equilibrium curve of log P vs 1/T for both mixtures NbI₄.₁₂ and NbI₄.₃₇ gives temperatures of 329 and 340° respectively for the apparent transition temperature. Because of the large hysteresis observed for NbI₄.₁₂, however, the reliability of the former temperature so obtained should be viewed with caution, since the state of the system may not be uniquely defined by a temperature and a pressure (i.e., may not be at equilibrium). Possibly the higher temperature (348°) observed on heating curves is due to superheating effects associated with a sluggish transformation. Consequently, the actual equilibrium transformation temperature may not be any of those cited, but perhaps somewhere between 329 and 348°.

The dissociation pressures found for NbI₄.₃₅ are higher than those for NbI₄.₁₂ both above and below the inflection in log P vs 1/T plots (Fig. 5,7) and no obvious explanation of the discrepancy is known. Nevertheless, certain implications

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can be drawn from the behavior exhibited by these mixtures. First, the inflection in the log P vs 1/T plots occurs at ca. 340° and is probably associated with the \( \alpha \rightarrow \beta \) transformation of NbI_4. Since phase transitions involve a positive heat effect (2,7), the decrease in heat content for the higher temperature data for NbI_4 (\( \approx 6 \) kcal/mole of iodine) implies an exothermic process in the products occurs at the inflection point. This obviously is not associated with the NbI_4 phase; therefore, it apparently must be due to an endothermic process in the NbI_5 phase that is large in comparison to the opposite heat effect of the transformation in NbI_4 since the slope of the log P vs 1/T plot decreases above ca. 340°.

In contrast to the behavior of NbI_4.12, the mixture NbI_4.85 shows a more reasonable change; that is, a higher heat of reaction above the supposed transition temperature (\( \approx 13 \) kcal/mole of iodine). As a consequence of this behavior either the heat content of NbI_4 is greater above ca. 340° or the heat content of NbI_5 is less above the transition temperature. Since energy is supplied to a system for a transformation from one structure to the other to take place the first explanation would seem adequate. However, the transformation was not thermally observed in this region, suggesting that NbI_4 may not be present as a discrete phase but rather in solid solution.
B. Polymorphic Behavior of Niobium(IV) Iodide

In general the interpretation of physical changes on minimal evidence is seldom unambiguous and the following discussion may be thus categorized. Nevertheless, comment on the polymorphism of niobium tetraiodide seems informative.

Polymorphic substances are usually divided into two groups according to whether or not the different forms are reversibly interchangeable (39). Those substances which have one or more reversible transitions below the melting point of either form are called enantistropic and niobium tetraiodide may be classified as such. Perhaps the more interesting of the two transformations among different forms of NbI₄ is that between the α and β NbI₄ at ca. 340°.

Experimentally, this transition is observed only on heating curves and equilibrations below the transformation temperature (e.g., 300°) of 10 hours or longer are required to reconvert β NbI₄ to α NbI₄. Surprisingly, even though the reverse conversion of β NbI₄ to α NbI₄ is sluggish, no evidence for the phase transformation was evident on an extensive examination of powder patterns of samples that had been annealed above and below the transition temperature. In order to understand this behavior it may be necessary to take account of the structures at the beginning and the end of this transformation.

Preliminary results of the structural determination of
\( \alpha \text{NbI}_4 \) by Dahl and Wampler (12) indicate metal-metal interaction which will readily explain the observed diamagnetism. The structure consists of infinite chains parallel to the \( a \) axis formed by \( \text{NbI}_6 \) octahedra sharing two opposite edges. The niobium atoms are displaced from the centers of the octahedra, 3.83 Å apart, toward each other in pairs such that the distance between the paired niobium atoms is 3.2 Å.

On the basis of the known structure of \( \alpha \text{NbI}_4 \), it might be possible to account for some of the characteristics of the transition at ca. 340° by an order-disorder transformation (18, 39). In the low temperature (\( \alpha \)) modification of \( \text{NbI}_4 \), the iodine atoms form a hexagonal close-packed lattice and the niobium atoms occupy one fourth of the octahedral holes in a regular manner with the requirement that the niobium atoms be grouped in pairs. Above ca. 340° \( \text{NbI}_4 \) could exist as the \( \beta \) form with the positions of the iodine atoms still in a hexagonal close-packed lattice, but with the niobium pairs now disordered with respect to separate chains. Some of the niobium atoms might have undergone slight displacements which result in irregular breaking and subsequent reforming of the metal-metal bond.

From the preceding description of the \( \beta \) form, essentially no change in the powder pattern from that of the \( \alpha \) form might be expected since statistically the number of atoms in the reflecting planes has not changed. Probably entropy con-
siderations are of major importance in this transformation, overshadowing that of internal energy since a large activation entropy might account for the sluggishness from disorder to order.

Powder patterns and the transition energy (larger than $\alpha \rightarrow \beta$ by roughly a factor of 10) between $\beta$ NbI$_4$ and $\gamma$ NbI$_4$ indicate an entirely different process is governing this transformation. Reversibility between these two forms is rapid and well-defined on both heating and cooling curves.

C. Proposals for Future Research

From the structural point of view, the lower niobium iodides should prove interesting to investigate by single crystal X-ray studies. Since the nonexistence of a stoichiometric niobium(III) chloride and niobium(III) oxide indicate that the trivalent state is not uniquely stable in the solid state, determination of the structure of NbI$_3$ might provide information needed to account for the observed stability and diamagnetism of this salt.

Generally, X-ray powder patterns are adequate to differentiate between polymorphic forms, but they fail to distinguish between $\alpha$ and $\beta$ NbI$_4$. That polymorphism is a phenomenon closely related to the stereochemistry of compounds is obvious. For this reason electrical resistivity measurements could be particularly effective for distinguishing between the two forms in that the method is sensitive to the kind and
amount of phase present. Moreover, attainment of equilibrium at the temperature of measurement is easily recognized from the data obtained, in contrast to that observed with dissociation pressure measurements, so that an accurate transition temperature would be obtained.

Because the gaseous product above a mixture of NbI$_{2.67}$ and metal probably is the active apecies involved in the production of metal by the Van Arkel-de Boer iodide decomposition process, further work on characterization and identification of the gaseous components in equilibrium with solid niobium iodides seems warranted.

Dissociation pressure studies on the NbI$_4$ - NbI$_3$ and NbI$_4$ - NbI$_{2.67}$ systems should provide information needed to give a more complete thermodynamic interpretation to the phase diagram and to the general characterization of these niobium iodides. These studies should also be effective in determining the solid disproportionation products of NbI$_4$. These determinations could be carried out in substantially the same manner as that described for the dissociation pressure of the pentaiodide-tetraiodide mixtures. At the present, little is known about the vapor pressure for any of the iodides and these are obviously relevant as a part of a study of the chemical and physical properties of these niobium iodides and to the interpretation of data of total (dissociation plus possible volatilization) pressure. As mentioned pre-
viously, more characterization of the solid phase for I/Nb ratios > 4.7 is needed. High temperature X-ray techniques should be useful in this respect.
V. SUMMARY

Lower oxidation states in the solid niobium iodides have been prepared and characterized. Thermal and differential thermal analysis, equilibrations and X-ray powder diffraction data were utilized for the construction of the phase diagram for the niobium-iodine system. The heretofore unknown NbI$_{2.67}$ has been prepared and preliminary dissociation pressures for the NbI$_5$ - NbI$_4$ system have been recorded. A summary of the iodides with some of their properties is found in Table 1.

Table 1. Niobium iodides

<table>
<thead>
<tr>
<th>$\frac{I}{Nb}$</th>
<th>Temperature of heat effect</th>
<th>Process</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>400°</td>
<td>melting</td>
<td>brassy</td>
</tr>
<tr>
<td>4.00</td>
<td>503° 417° 348°</td>
<td>incongruent melting phase transformation phase transformation</td>
<td>dark-grey, metallic-appearing</td>
</tr>
<tr>
<td>3.00</td>
<td>526°</td>
<td>disproportionation</td>
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</tr>
<tr>
<td>2.67</td>
<td>(&gt;790°)</td>
<td>(melting)</td>
<td>black</td>
</tr>
</tbody>
</table>

Three polymorphic forms of niobium tetraiodide were found. Powder patterns show distinct $\beta$ and $\alpha$ temperature forms; however, they do not distinguish between the $\beta$ and $\alpha$ temperature forms. Iodine dissociation pressures indicate that this transformation is sluggish.
In contrast to niobium trichloride, which has a wide range of variable composition, the trilodide is a simple stoichiometric compound which can be sublimed. Unlike the niobium chloride and bromide, niobium diiodide apparently does not exist as a solid equilibrium phase and the solid iodide in equilibrium with the metal is $\text{NbI}_2$. Qualitative magnetic measurements indicate that all the niobium iodides are diamagnetic. This diamagnetism of the lower iodides may be attributable to metal-metal bonding which is known to exist in the low temperature form of the tetraiodide.

The decomposition pressure results for the $\text{NbI}_5 - \text{NbI}_4$ are also discussed and some tentative interpretation of the behavior given. X-ray powder pattern data for all the iodides of niobium are reported.
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VII. ACKNOWLEDGEMENTS

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Appreciation is extended to members of Physical and Inorganic Group IX for their accommodating cooperation, their generous exchange of equipment, and their useful comments and operative criticisms.
VIII. APPENDIX
Table 2. Dissociation pressures of niobium iodide mixtures, in order taken

<p>| Nb |</p>
<table>
<thead>
<tr>
<th>Temperature</th>
<th>Dissociation pressure(mm)</th>
<th>Temperature</th>
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</thead>
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<tr>
<td>4.12</td>
<td>277.0°</td>
<td>13.3</td>
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<tr>
<td></td>
<td>306.0</td>
<td>27.7</td>
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<td></td>
<td>285.5</td>
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<td>386.2</td>
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</tr>
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<td>4.55</td>
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Table 3. X-ray powder diffraction data for niobium iodides

<table>
<thead>
<tr>
<th>NbI5</th>
<th>NbI4 (α, β)</th>
<th>NbI4 (λ)</th>
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