AN IMPROVED SUPERCONDUCTOR FOR
TRANSMISSION LINE APPLICATIONS, PHASE II

FINAL REPORT

A. I. BRAGINSKI, G. W. ROLAND, M. R. DANIEL,
A. T. SANTHANAM, AND M. A. JANOCKO

WESTINGHOUSE ELECTRIC CORPORATION
PITTSBURGH, PENNSYLVANIA 15235

JUNE, 1976

PREPARED FOR

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
OFFICE OF CONSERVATION
UNDER CONTRACT NO. E(11-1)-2522

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

AN IMPROVED SUPERCONDUCTOR FOR
TRANSMISSION LINE APPLICATIONS, PHASE II

A. I. Braginski, G. W. Roland, M. R. Daniel,
A. T. Santhanam, and M. A. Janocko

Westinghouse Research Laboratories
Pittsburgh, Pennsylvania 15235

ABSTRACT

The objective of the second phase of this program was to achieve an improvement over the state-of-the-art of the low field critical current density, J_c , and ac losses, p , of short sections of composite Nb_3Ge tape prepared by chemical vapor deposition (CVD). The following goals of Phase II were attained: (1) the enhancement of J_c by doping with Nb_5Ge_3 , nitrogen or carbon, (2) the design, construction and test of a moving tape CVD reactor capable of producing lengths of tape conductor. The goal of fabricating composite Nb_3Ge tape sections having not only high J_c but also low ac losses was not attained since the CVD system found necessary for the fabrication of such tape became available only as a result of the work described.

TABLE OF CONTENTS

	<u>Page</u>
1. INTRODUCTION	1-1
1.1 Program Objective	1-1
1.2 Original Tasks of Phase II	1-2
1.3 Modified Tasks of Phase II	1-3
1.4 Summary of Results	1-4
1.5 References	1-5
2. CHEMICAL VAPOR DEPOSITION	2-1
2.1 Scope	2-1
2.2 Deposition of Single Elements and Parameters of Co-Deposition	2-1
2.3 The CVD Gas Phase: Nb/Ge Ratio	2-7
2.4 The Nb-Ge Growth Rates and Yield	2-8
2.5 Substrate Materials and Deposition Geometry	2-15
2.6 Moving Tape Reactor	2-19
2.7 References	2-23
3. PHASES PRESENT IN Nb-Ge CVD DEPOSITS	3-1
3.1 Scope	3-1
3.2 Analytical Methods	3-1
3.3 The A15 Phase	3-3
3.3.1 Composition	3-3
3.3.2 Compositional Homogeneity	3-6
3.3.3 Cell Edge Measurements for Films on Substrates	3-6
3.3.4 Impurity Doping	3-10
3.4 A15-Phase Assemblages	3-13
3.5 Other Phases Observed	3-25
3.6 Discussion	3-25
3.7 References	3-26

TABLE OF CONTENTS (cont.)

	<u>Page</u>
4. CRITICAL TEMPERATURE	4-1
4.1 Measuring Methods	4-1
4.2 Critical Temperature in the Nb-Ge System	4-3
4.3 Effect of Gas Phase Parameters	4-8
4.3.1 Effect of Deposition Temperature	4-11
4.3.2 Effect of Hydrogen Excess	4-11
4.3.3 Effect of the Nb/Ge Ratio	4-11
4.4 Effect of N ₂ -Doping	4-14
4.5 Effect of Carbon-Doping	4-19
4.6 Discussion	4-19
4.7 References	4-20
5. CRITICAL CURRENT DENSITY	5-1
5.1 Measuring Methods	5-1
5.2 Critical Current Density and Microstructure	5-3
5.3 Effect of σ -Phase	5-4
5.4 Effect of N ₂ -Doping	5-12
5.5 Effect of Carbon-Doping	5-14
5.6 Discussion	5-17
5.7 References	5-17
6. THE AC LOSSES	6-1
6.1 Measuring Methods	6-1
6.2 Effect of Sample Configuration	6-1
6.3 Effect of Composition and Doping	6-4
6.4 Losses in Tapes on Niobium Substrates	6-13
6.5 Temperature Dependence of Losses	6-17
6.6 Discussion	6-17
6.7 References	6-17

TABLE OF CONTENTS (cont.)

	<u>Page</u>
7. EXPERIMENTS WITH THE MOVING TAPE REACTOR	7-1
7.1 Preliminary Experiments	7-1
7.2 Deposit Thickness Non-Uniformity	7-5
8. CONCLUSIONS	8-1
9. RECOMMENDATIONS	9-1
10. ACKNOWLEDGEMENTS	10-1
APPENDIX I	
APPENDIX II	
APPENDIX III	
APPENDIX IV	
APPENDIX V	
APPENDIX VI	

NOTATION

- Al5 = a cubic crystal structure of A_3B compounds that favors the occurrence of high temperature conductivity
- H = magnetic field
- H_{c2} = The second critical magnetic field, at which all bulk superconductivity disappears
- J = the current density (A/cm^2)
- J_c = the critical current density of a superconductor
- σ = the current per unit width of the tape surface, or surface current density, A/cm (rms); also - Nb_5Ge_3 phase notation
- ρ = the electric resistivity
- p = the ac surface loss in a superconductor at 60 Hz ($\mu W/cm^2$)
- T = temperature
- T_c = the temperature of the normal-to-superconducting transition
- ΔT = the width of the superconducting transition
-
- T_c^* = the transition temperature assumed for normalizing the J_c (T) dependence, extrapolated linearly from the steepest part of the J_c (T) curve
- d_x = X-ray density (g/cm^3)
- a_o = unit cell edge (lattice parameter) in $\text{\AA}$
- β = linear thermal expansion coefficient ($^{\circ}C^{-1}$)
- T_d = deposition temperature

h = superconducting deposit thickness
 h_t = deposit growth rate
 v = gas phase velocity in the deposition zone
 r = molar ratio $H_2/(NbCl_4 + GeCl_2)$
 s = molar ratio $NbCl_4/GeCl_2$ generated in the CVD system (vapor phase)
 $\textcircled{W}$ = Westinghouse Electric Corporation
BNL = Brookhaven National Laboratory
LASL = Los Alamos Scientific Laboratory

Additional notation is explained in the text.

1. INTRODUCTION

1.1 Program Objective

The overall objective of this program was to investigate and develop the highest known critical temperature (T_c) superconductor, Nb_3Ge , for application in superconducting power transmission lines.

Gavaler discovered in 1973 that Nb_3Ge can have a high critical temperature, in excess of 22 K.⁽¹⁾ In 1974 Gavaler and also Testardi achieved $T_c \approx 23$ K (onset).⁽²⁻³⁾ It was also observed in 1974 that Nb_3Ge can have high current carrying capability,⁽⁴⁾ and it was demonstrated that high- T_c Nb_3Ge can be synthesized by chemical vapor deposition (CVD), a process potentially amenable to large-scale and economical fabrication.⁽⁵⁻⁶⁾ These accomplishments prompted the U. S. Energy Research and Development Administration to institute the present program on "An Improved Superconductor for Transmission Line Applications," Contract No. E(11-1)-2522.

In the first phase of the program, requisite properties of a potential conductor based upon Nb_3Ge were defined for it to be competitive with respect to Nb_3Sn ($T_c = 17$ to 18 K). The Nb_3Sn composite tape is presently used as a conductor in the alternating current (ac) superconducting cable under development at the Brookhaven National Laboratory (BNL, Power Transmission Project, PTP). It was established that Nb_3Ge tape conductors could, if developed, represent a technically and economically attractive replacement for Nb_3Sn .⁽⁷⁾ The possible alternate advantages of Nb_3Ge included the following,

1. Significantly reduced refrigeration cost, including cryogenic envelope cost.
2. Improved fault current capability.
3. Improved mechanical properties of the cable conductor.

The above advantages were found contingent upon the availability of Nb_3Ge material having a very high critical current density, and very low ac losses at the cable operating temperature and current level, when fabricated in the form of a tape.

The second phase of the program, reported here, was, therefore, concerned with the Nb_3Ge conductor development. The objective of this phase was to achieve an improvement over the state-of-the-art of the low-field properties of short sections of Nb_3Ge tape prepared by CVD. It was anticipated that the results of the study would establish an adequate data base for:

1. A Nb_3Ge transmission line design.
2. A Nb_3Ge fabrication facility design.

1.2 Original Tasks of Phase II

The abbreviated version of the original tasks of Phase II was as follows:

1. Define the Nb_3Ge CVD parameters to obtain the pure Nb_3Ge in the form of tape sections of maximum critical current density, J_c , and minimum low field ac losses, p.
2. Investigate doping of pure Nb_3Ge with impurities to maximize low-field J_c , and define the best trade-off between T_c and J_c to upgrade Nb_3Ge properties beyond the level attained in Task 1.
3. Design, fabricate, and test short composite tape sections up to 30 cm (1 ft.) in length. Deliver five such sections to ERDA for testing by Brookhaven National Laboratory (BNL).
4. Provide the background information for the conceptual design of the conductor fabrication facility.

Tasks 3 and 4 were redefined in the course of the work, when it was found that the CVD laboratory facility used in the investigation was unsuitable for fabricating tapes having uniform J_c and p over any practical length of tape.

Furthermore, the revision of Task 3 was necessitated by the fact that in 1975 BNL found it necessary to adopt a double-helix transmission cable design in order to eliminate axial magnetic fields.⁽⁸⁾ In a double-helix cable the magnetic field is present on both sides of the tape.⁽⁹⁾ Consequently, the superconductor deposition on all normal substrate tape surfaces became necessary to exclude the flux from the interior of the conductor and thence to avoid the related high ac losses. The existing laboratory CVD facility allowed controllable deposition only on one side of the tape, and was, therefore, unsuitable for fabricating a composite conductor having the required coating geometry.

Additionally, more emphasis than originally anticipated had to be placed on the doping of Nb_3Ge (Task 2) after it was found in Task 1 that the pure Nb_3Ge grown by CVD has low J_c , and therefore high ac losses due to an insufficient concentration of flux pinning centers.

The modification of the program Tasks was approved by U. S. ERDA following a mid-term review meeting of Phase II held on February 25, 1976.

1.3 Modified Tasks of Phase II

The abbreviated version of the revised Tasks 2 and 3 was as follows:

Task 2: Investigate doping of pure Nb_3Ge with: a) the σ -phase Nb_5Ge_3 , b) gas phase impurities to maximize the low field J_c .

Task 3: Perform experiments providing a base for designing a running tape CVD reactor capable of producing uniform, long Nb_3Ge tape coated on all surfaces. Design and test the reactor, to be built at Westinghouse's expense.

Fabrication of composite tape sections was deleted from the Work Statement of Phase II since it was deemed unfeasible prior to producing tapes coated on all surfaces.

1.4 Summary of Results

Doping with σ -phase produced the highest J_c results at the lowest deposition temperature of $T_d = 750^\circ\text{C}$ where the grain size of the deposit is the smallest.⁽¹⁰⁾ That indicated that flux pinning on grain boundaries of the Al5 phase can make a secondary but nonetheless beneficial contribution to J_c . Experiments with gas phase impurity doping were performed only at $T_d = 900^\circ\text{C}$. Doping with nitrogen and ethane produced a high J_c level, comparable to that attained with σ -phase at $T_d = 900^\circ\text{C}$, without significant reduction of T_c . The reproducibility of the effect was, however, not as good as in the case of σ -phase doping. In contrast, doping with CO_2 resulted in degradation of T_c and J_c , presumably due to an unidentified compound formation. Doping with oxygen, attempted to a very limited extent only, did not produce any interesting results and is not reported further. Table 1.1 compares the properties of best specimens prepared using various dopants.

The ac losses of short tapes, coated with Nb_3Ge on one side only, remained high, well above the target, even for high- J_c samples. High losses originated at the boundary diffusion layer between Nb_3Ge and the Hastelloy B substrate, and were further augmented by the hysteretic contribution of the substrate itself.

A moving tape CVD reactor was designed, constructed and tested by depositing pure (undoped) Nb-Ge layers. Tape specimens up to 2 m long could be prepared, and values of J_c were obtained exceeding those previously observed for the undoped material. Uniform coating on all tape substrate surfaces was, however, not achieved. To improve the coating uniformity resistive heating of the substrate tape by electric current was implemented. It could not be tested, however, prior to the termination date of the program.

Table 1.1 - Best Properties of Nb₃Ge Short Tape
Sections for Various Dopants Used

Introduced Dopant		None	—	N ₂	C ₂ H ₆	CO ₂	O ₂	Comments
Species Formed		—	Nb ₅ Ge ₃	NbN	NbC	NbC, ?	NbO, ?	
Range of doping gas delivery rates	cm ³ /min	—	—	0.1 to 1000	0.1 to 100	0.1 to 100	0.1 to 10	
Range of dopant concentration in the deposit (analyzed)	%	—	5 to 90 by volume	0.02 to 1.67 by weight	0.06 to 1.0 by weight	0.09 to 0.33 by weight	not analyzed	
Dopant concentration in best sample	%	—	5 (± 3 ?) 10 ± 5	0.2	0.3	n/m*	—	
Critical temperature (midpoint)	T _c , K	21.1 21.7	18.7 21.4	20.7	19.2	16.7	~ 13	T _d = 750°C 900°C 950°C
Critical current density, at 4.2 K, H _l = 5 kG	J _c , A cm ⁻²	4 × 10 ⁵ 0.7 × 10 ⁵	3.0 × 10 ⁶ 2.4 × 10 ⁶	1.8 × 10 ⁶	2.3 × 10 ⁶	3 × 10 ⁵	n/m	750°C 900°C 950°C
Low field loss at 4.2 K, 60 Hz, 1000 A/cm (rms)	P, μWcm ⁻²	130	35 60	40	n/m	n/m	n/m	sample + substrate (one-side coated)

* n/m = not measured.

In conclusion, Phase II demonstrated successful alternative methods of obtaining high- J_c tapes of Nb_3Ge , and resulted in a facility permitting the fabrication of long tape specimens. More work is needed to obtain uniform coating on all tape surfaces, and, consequently, to achieve low tape losses comparable to those obtained on tubular specimens. (11)

1.5 References

1. J. R. Gavaler, Superconductivity in Nb-Ge Films Above 22 K, Appl. Phys. Lett. 23, 8, 480 (1973).
2. J. R. Gavaler, M. A. Janocko, and C. K. Jones, Preparation and Properties of High- T_c Nb-Ge Films, J. Appl. Phys. 45, 3009 (1974).
3. L. R. Testardi, J. H. Wernick, and W. A. Royer: Superconductivity with Onset Above 23 K in Nb-Ge Sputtered Films, Solid State Comm. 15, 1 (1974).
4. S. Foner, E. J. McNiff, Jr., J. R. Gavaler, and M. A. Janocko, Upper Critical Fields of Nb_3Ge Thin Film Superconductors, Physics Letters 47A, 6, 485 (1974).
5. A. I. Braginski and G. W. Roland, Chemical Vapor Deposition of Superconducting Nb_3Ge Having High Transition Temperatures, Appl. Phys. Lett. 25, 12, 762 (1974).
6. L. R. Newkirk, F. A. Valencia, A. L. Giorgi, E. G. Szklarz, and T. C. Wallace, Bulk Superconductivity Above 20 K in Nb_3Ge , IEEE Trans. MAG-11, 2, 221 (1975).
7. A. I. Braginski, S. F. Mauser, G. W. Roland, et al., An Improved Superconductor for Transmission Line Applications, Phase I, Final Report, U. S. ERDA No. C00-2522-1 (1975).
8. G. Morgan and E. B. Forsyth, Considerations of Voltage Drop and Losses in the Design of Helically-Wound Superconducting AC Power Transmission Cables, Adv. Cryo. Eng. Vol. 22 (in press).

9. M. Garber, J. Bussiere, and G. Morgan, Design of Double Helix Conductors for Superconducting AC Power Transmission, IEEE Trans. MAG-12 (Proc. 1976 MMM-Intermag Conf. in press).
10. Appendix IV, this report.
11. J. D. Thompson, M. P. Maley, L. R. Newkirk, and F. A. Valencia, Measurement of Low Hysteretic Losses in CVD Prepared Nb_3Ge , Submitted to Physics Letters A (LASL manuscript LA-UR 76-555).

2. CHEMICAL VAPOR DEPOSITION

2.1 Scope

The purpose of this section is to summarize the additional information on the fabrication process which may be helpful in discussing the results of Phase II but was not reported in earlier reports and publications.^(1,2) Furthermore, the results leading to a new CVD reactor design are presented and the reactor described.

2.2 Deposition of Single Elements and Parameters of Co-Deposition

Work on deposition of elemental Nb and Ge was performed prior to Phase II under a different program,^{*} and was already reported.⁽¹⁾ It is, however, useful to present data which served as a basis for selecting the parameters used in the present program for Nb and Ge co-deposition by reducing a generated mixture of NbCl_4 and GeCl_2 vapors with hydrogen. The single element data are limited to low values of $r \leq 15$, where r is the molar ratio of hydrogen to chloride, NbCl_4 or GeCl_2 , in the gas phase delivered to the reaction tube. As a result of the discovery of the tetragonal T2 phase (Section 3), much higher r values, 80-330, were used in Phase II to prevent the T2 occurrence. Nevertheless, the single element data provided useful qualitative guidelines for the interpretation of co-deposition results. Measured were: (1) the total reaction yield or efficiency, Y , defined as the ratio of the element mass deposited to the element mass delivered in form of the chloride, and (2) the longitudinal profile of growth rate in the deposition tube. The experiments have been performed using

^{*} Contract No. AFOSR-F44620-74-C-0042.

quartz substrate tubes of ~ 2.5 cm ID and various length. Helium was used as inert carrier gas. The total gas phase velocity, v , was considered as one of the parameters of the process.

Figure 2-1 shows $Y(r)$ for niobium at three temperatures. Yield increases with T_d and r (and eventually saturates at high r values). Analogous results were obtained for Ge.

Figure 2-2 compares $Y(r)$ for Nb and Ge at $T_d = 800^\circ\text{C}$. The efficiency of germanium chloride reduction was found to be higher than in the case of NbCl_4 in the whole temperature range investigated (750 – 950°C). Hence, a preferential deposition of germanium, and the resulting preferential depletion of gas phase, could be expected in case of co-deposition.

Figure 2-3 shows Ge growth rate profiles as a function of r . With increasing r the reaction rate increased, the gas phase depleted more, and consequently the profiles show a pronounced peak even before the temperature reaches the plateau ($T_d = 800^\circ\text{C}$) on the inlet side of the tube. Analogous results were obtained for Nb. The use of low r to obtain flat film thickness profiles thus appeared desirable.

Figure 2-4 shows Ge growth rate profiles as function of total gas velocity at $r = 10$. Higher gas velocities at constant GeCl_2 delivery were obtained by increasing the delivery rate of carrier gas. Hence, changes in v were associated with changes in vapor phase dilution by the inert carrier. Increasing v resulted in flattened rate profiles. This was interpreted as the result of finite residence time required for the reaction, rather than the effect of dilution. The effect of dilution was separately studied by setting v and r constant at $T_d = 800^\circ\text{C}$, and varying the delivery rate from 0.02 to 0.3 mole/hour. The yields were found to be almost independent of the delivery within the above limits. The results for Nb were again analogous. Hence, the $Y(r, T_d, v)$ data provided directly usable information for scaling and predicting growth rates.

Fig. 2-1 - Molar Ratio: $H_2/NbCl_4 = r$

Yield vs r for Nb; effect of T_d

Fig. 2-2 - Yield vs r for single elements

Fig. 2-3 - Growth rate profiles, Ge; $r = \text{param.}$

Fig. 2-4 — Growth rate profiles: Ge, v = param.

The results shown above formed a base for assuming standard conditions used in early co-deposition experiments,⁽¹⁾ i.e., at the inception of Phase II. Assumed were: $T_d \simeq 900^\circ\text{C}$, $r = 10$, $v = 500$ cm/sec. The chloride delivery level was 0.15 mole/hour for thick deposits and 0.03 mole/hour for thin layers. In these conditions it was indeed possible to obtain relatively flat growth rate profiles so that deposition of Nb_3Ge tapes, up to 25-30 cm long appeared possible.⁽¹⁾ However, once much higher r values were implemented (to eliminate the T2 phase) with other deposition parameters unchanged the rate profiles became much steeper (Section 2.4). The fulfillment of the objective of the original Task 3 (Section 1.2) was no longer possible. From that point on the program centered on studying the x -profiles of the tape properties.* No attempts were made to flatten the profiles by increasing v_x significantly above 500 cm/sec.

The gas delivery rates were already pretty high: ~ 20 l/min for the $\text{H}_2 + \text{He}$ mixture. Also, v could not be increased significantly without a transition from laminar to turbulent flow regime. Consequently, in the whole Phase II the gas velocity, and the chloride delivery rates were maintained on the previous level. Varied were: T_d , r and s .^{**}

2.3 The CVD Gas Phase: Nb/Ge Ratio

An earlier publication⁽¹⁾ and report⁽²⁾ described the CVD reactor and the manner in which the gas phase Nb/Ge molar ratio, s , was controlled by the Cl_2 gas flows through the Nb and Ge chlorination beds. It was evident, however, that the s value for the gas phase at the deposition zone was somewhat different because of the formation of deposits in the reactor mixing zone. During this phase the deposits in the reactor mixers were analyzed and some idea of the magnitude of the correction required for s was obtained.

* x is the position coordinate along the tape.

** $s = \text{NbCl}_4/\text{GeCl}_2$.

Two types of deposits occurred in the mixing zone: 1) a black granular material and 2) a metallic coating. Chemical analyses of the black deposit gave an average value of 42.2 wt.% Nb, 9.4 wt.% Ge, 48.4 wt.% Cl. This composition recalculates to $(\text{Nb,Ge})\text{Cl}_{2.3}$, consistent with the existence of a black niobium chloride phase having NbCl_{3-x} composition. It's quite probable, however, that a mixture of chloride phases was present. The metallic phase was chloride-deficient and very variable in composition. In all cases, the black chloride-rich material was predominant, e.g. for a typical series of runs (total running time 120 minutes) at deposition temperature, $T_d = 900^\circ\text{C}$, the total accumulated black deposit in the mixing zone was 15.4 grams. The metallic deposit amounted to less than a gram.

Material lost in the mixing zone has two effects: 1) the total amount of Nb and Ge delivered to the deposition zone is reduced, and 2) the value of s at the deposition zone is changed. For the series of runs described above, the amount of Nb and Ge delivered was reduced by 26% and 36% respectively. Because of the larger reduction in Ge, the s value correspondingly increased 14%. For economic reasons the loss of material is a more important problem than a change in s value. Therefore, in a commercial process, a system using NbCl_5 as the source of Nb at the deposition zone offers advantages since gas mixing can be done at low temperature where mixing-zone deposits do not form.⁽³⁾ Because the correction in s is small, only the initial s values as set by chlorine flows to the chlorination chambers are used in reporting experimental details.

2.4 The Nb-Ge Growth Rates and Yield

The deposited tapes have been cut into ~5 cm sections, and the growth rate, h_t (in $\mu\text{m}/\text{hour}$) determined from each section deposit weight, assuming a standard substrate weight. This way the growth or deposition rate profiles $h_t(x)$, where x is the position coordinate in the deposition zone, could be obtained. The value $x = 0$ was assigned to a point where the gas temperature reached a constant level, T_d . For $x > 0$, $T = T_d$ while for $x < 0$, $T < T_d$.

Table 2.1 presents $h_t(x)$ data obtained at $T_d = 900^\circ\text{C}$, in the constant temperature deposition zone, for various r and s values where s is the molar ratio Nb/Ge in the generated chloride mixture (uncorrected for losses in the mixing zone). Table 2.2 gives $h_t(x)$ data for various T_d and extreme s values at a constant $r = 200$.

Both tables show that the growth rates decrease along the deposition zone, i.e., with increasing x . This is a result of the gas phase depletion, and generation of HCl in the chloride reduction reaction with hydrogen.⁽¹⁾ At high deposition temperatures, and higher r values, the reduction efficiency of both elements is high (Section 2.2) and the depletion more pronounced. Hence, $h_t(x)$ decreases more steeply with increasing x . However, in the whole range of T_d , from 750°C to 1000°C , the rates are comparable, $40\text{--}80\text{ }\mu\text{m/hour}$ at $x = 0$, if r is sufficiently high, i.e., in the range shown. For low $r \approx 10$, rates are prohibitively low at 750°C due to low reduction efficiency (Section 2.2). Since low r values have been originally used for Nb-Ge deposition,⁽¹⁾ temperatures below $T_d = 800\text{--}850^\circ\text{C}$ were considered impractical. The need for high r to prevent the formation of the T2 phase (Section 3) automatically extended the temperature range down to 750°C . However, the presence of Nb chloride lines ($\text{NbCl}_{2.66}$) was observed in x-ray diffraction patterns of deposits grown at 750°C thus indicating that the reduction was not complete.

Figures 2.5 and 2.6 show the $h_t(x)$ profiles over the whole deposition zone, including the inlet zone ($x < 0$) where $T < T_d$. In addition to illustrating the stronger gas phase depletion effect at higher T_d and/or r , the graphs show that deposition occurs at a high or peak rate in the inlet zone ($x < 0$). For low s , set such that the tetragonal Nb_5Ge_3 σ phase deposits at $x = 0$, the h_t peaks at $x \leq 0$ are much higher than in the case of Al5 and shifted to lower x (lower temperature). This suggests that the free energy of formation of the tetragonal phase is lower than that of Al5, and also that the gas phase is preferentially depleted in Ge already at $x = 0$. A larger fraction

Table 2.1. Growth Rate Profiles $h_t(x)$ in $\mu\text{m}/\text{hour}$ for Various r and s Values, $T_d = 900^\circ\text{C}$.

Run No.	r	s	$x = 0 \text{ cm}$	$x = 10 \text{ cm}$	$x = 20 \text{ cm}$	$x = 30 \text{ cm}$	$x = 40 \text{ cm}$
211	80	2.5	72	53	37	31	23
206		3.1	75	52	35	26	17
207		3.6	67	49	28	26	19
208		4.2	75	56	42	36	21
209		5.0	65	50	26	25	21
212		8.3	66	51	27	24	19
195	200	2.5	76	42	23	13	9
184		3.1	53	33	18	19	14
181		3.6	74	44	30	23	13
202		4.2	61	45	33	23	19
182		6.3	63	38	27	25	14
183		8.3	62	42	27	22	18
196	330	2.5	68	24	28	19	5
193		3.1	108	45	17	11	7
192		3.6	51	39	24	17	8
188		4.2	41	21	11	11	2
189		5.0	49	35	23	17	7
191		8.3	36	33	18	9	11

Table 2.2. Growth Rate Profiles $h_t(x)$ in $\mu\text{m}/\text{hour}$
for Various T_d and s Values, $r = 200$.

Run No.	T_d K	s	$x = 0$ cm	$x = 10$ cm	$x = 20$ cm	$x = 30$ cm	$x = 40$ cm
275	750	3.1	64	46	43	34	29
273		6.3	44	42	29	36	23
231	800	3.1	76	45	29	24	21
227		6.3	63	52	30	29	21
375	850	3.6	37	45	27	22	24
372		6.3	65	45	25	23	16
184	900	3.1	53	33	18	19	14
182		6.3	63	38	27	25	14
259	950	2.5	63	35	12	4	3
253		6.3	68	39	28	8	3
265	1000	3.1	67	47	20	5	~0
261		6.3	59	42	15	11	7

Fig. 2-5 - Growth rate profiles, $h_t(x)$, for σ and A15 phases at two r values, $T_d = 900^\circ\text{C}$. The constant temperature zone starts at $x=0$; the arrow indicates the direction of gas flow.

Fig. 2-6 — Growth rate profiles, $h_t(x)$, for σ and A15 phases and two extreme deposition temperatures, $r = 200$. The constant temperature zone starts at $x = 0$; the arrow indicates the direction of gas flow.

Table 2.3. Yield of Solid Deposit on Substrate in the Constant Temperature Zone, Y_{eff} , for Various Values of T_d , r , and s

Run No.	T_d °C	m	s	Y_{eff} %
275	750	200	3.1	15.9
273			6.3	13.6
231	800	200	3.1	12.8
227			6.3	15.3
375	850	200	3.6	10.4
372			6.3	12.8
211	900	80	2.5	14.9
212			8.3	15.4
195		200	2.5	10.4
183			8.3	14.1
196		330	2.5	9.0
191			8.3	8.3
259	950	200	2.5	7.2
253			6.3	10.0
265	1000	200	3.1	9.6
261			6.3	10.1

of the deposit is thus lost in the inlet zone. In consequence, for given T_d and r the rates at $x > 0$ are similar for both, σ and Al5 deposits.

Table 2.3 gives effective yield data for the investigated range of T_d , r and s . The effective yield, Y_{eff} , is defined as the ratio of the mass of solid deposited on the 1.27 cm wide tape substrate in the constant temperature zone ($x = 0-40$ cm) to the mass of metal converted into chlorides. The values of Y_{eff} are uniformly low, 7-15%, due to: 1) losses in the mixing zone (Section 2.3), 2) deposition in the inlet zone ($x < 0$), 3) deposition on the walls of the reactor tube in the deposition zone. The effective yield decreases slightly with increasing T_d and r , due to stronger depletion in the inlet zone (2) which is also responsible for the fact that in most cases $Y_{eff}(\text{Al5}) > Y_{eff}(\sigma)$. The total yield of the reduction reaction at high r is very high, approaching 100%, when taking into account the mixing zone loss (1).

The level of h_t and Y_{eff} appears acceptable for a fabrication process, although higher values of h_t , of the order of 100-200 $\mu\text{m}/\text{hour}$ would be preferable from the economical point of view. However, if (2) and (3) could be prevented, then at comparable h_t and Y_{eff} a much flatter $h_t(x)$ profile could be obtained due to reduced depletion of the gas phase. This possibility is discussed in Section 2.6.

2.5 Substrate Materials and Deposition Geometry

During the course of the work performed in Phase II, the Nb-Ge films have been deposited on various substrate materials. The typical substrate material was a Ni-base stainless steel, Hastelloy B which was in the form of a tape 1.27 cm wide and 50 μm thick. Additional substrate materials were Cu, Nb, polycrystalline alumina, single-crystal sapphire, Type 303 stainless steel, and Cu-clad Nitronic stainless steel. No adhesion problems were encountered in the case of Cu or Cu-clad materials, polycrystalline alumina, or sapphire. Deposits on Nb required that the Nb be carefully cleaned by etching (for oxide removal) with a

solution composed of 50 ml HNO_3 , 50 ml HF , 10 ml H_2O_2 for the deposit to adhere. Unfortunately, this was established by the end of the program (see Section 6). Deposits on Type 303 stainless steel were easily spalled away from the substrate due to strain caused by thermal expansion mismatch.

For most of the studies, the substrate material was held on a flat quartz sample holder designed to be positioned along the deposition zone of the CVD reactor. In this geometry, therefore, deposition occurred only on one side of the substrate, that surface exposed to the gas phase in the CVD reactor tube. However, a substrate completely coated by Nb_3Ge , on both sides and around the edges, is necessary to exclude magnetic flux from the interior of the sample, and achieve meaningful measurement of surface current losses in the very low field range ≤ 500 A/cm rms, where the contribution of the substrate and of the diffusion layer can be significant (Section 6). Attempts to deposit such samples at 900°C by suspending the substrate Hastelloy tape in the center of the reactor deposition tube can be successful (Fig. 2-7) but much more typically resulted in tapes with fractured (Fig. 2-8) or completely broken away tape edges. It is seen in Fig. 2-8 that the integrity problems at the tape edges are caused by dendritic-type growth, apparently due to breakdown of a smoothly growing interface at the tape corners (as seen in cross-section). Attempts were made to round these corners and prevent such breakdown in regular growth. Three approaches were tried:

- acid solution
- standard polishing techniques
- coarse mechanical abrasion.

The first two were notably unsuccessful. Either corner removal was too slow to be practical, or so rapid as to catastrophically destroy the tape. The third technique, mechanical abrasion, was developed however to yield tapes of lengths 3-5 feet with smoothly rounded edges, but again an adhering crack-free deposit was not obtained.

Fig. 2-7. Nb_3Ge layer grown around a Hastelloy substrate. $T_d = 900^\circ\text{C}$. X500.

Fig. 2-8. Nb_3Ge layer grown around a Hastelloy substrate. $T_d = 900^\circ\text{C}$. X200.

Can the CVD process be used to deposit Nb_3Ge completely around a metallic tape? Two lines of evidence suggest that the method can be successful. The first is the observation that in the very limited number of suspended-tape depositions done at a deposition temperature of $T_d = 820^\circ\text{C}$ the coating was integral around the tape (Fig. 2-9). These experiments were, however, performed in the new moving-tape reactor in which other parameters were changed as well. In particular, the diameter of the deposition zone was increased since such an increase also might aid coating uniformly around the tape. The CVD Nb_3Sn deposited on Hastelloy by the RCA process (heated tape) as used by Canada Superconductor and Cryogenics Co., Ltd. (CSCC) show excellent integrity around the tape. The condition of lowered deposition temperature and/or a heated substrate geometry should be successful in solving this problem. Both are implemented in the new $\text{\textcircled{W}}$ moving tape reactor (see below).

Fig. 2-9. Nb_3Ge layer grown around a Hastelloy substrate. $T_d = 820^\circ\text{C}$. X500.

2.6 Moving-Tape CVD Reactor

In Sections 1.2 and 2.2, it was shown that, because of reactor design and the nature of the CVD gas-phase reaction, it was not possible to achieve uniform Nb-Ge deposit properties in the stationary substrate reactor. This was especially true after increasing r from 10 to 80-330. It was also shown in Section 2.5 that the reactor was unsuitable for tape coating on all surfaces. Hence, the modified Task 3 (Section 1.3) called for the design, construction and test of a new system which would obviate the above difficulties.

After preliminary experiments simulating the geometry of the deposition zone, a moving tape reactor was designed and constructed. Although the delivery of NbCl_5 was found to be desirable (Section 2.3), the previous NbCl_4 generator was retained due to the lack of time for experiments with low-temperature niobium chlorination. Use was made of furnaces, controllers, etc. employed in the previous, stationary system. All the new, additional parts were supplied and/or fabricated at Westinghouse expense.

The new, T-shaped reactor is again horizontal, due to laboratory space restrictions. All the tubing is made of vitreous silica. A schematic diagram is shown in Fig. 2-10 and the general view of the system is shown in Fig. 2-11. A special T-section furnace is employed to allow the vapor mixture injection from the side (T-leg) while the substrate tape runs through the straight tube (T-arms). Vapor locks and cooling chambers at each side of this straight section permit the use of external drive mechanisms. Adjustable stainless steel tracks inside the deposition zone were initially provided to allow control of the deposition zone length and position. After deposition experiments described in Section 7 these stainless steel tracks were replaced by quartz tubes to avoid deposit contamination by steel components. Both symmetrical and asymmetrical (one side) tape coating should be possible owing to the use of exchangeable tracks. Tape widths between 3 and 13 mm (1/8 to 1/2 in.) can be accommodated.

Figure 2-10 — Running tape CVD reactor for Nb_3Ge conductor fabrication.

Figure 2-11 -- General view of the running tape CVD reactor for Nb₃Ge conductor fabrication. Numbers refer to parts identified in Figure 2-10.

Figure 2-12 -- Carbon brush fixture used to energize the tape.

The motorized drive mechanism employing reels, 30 cm in diameter, is fitted with a gear mechanism ensuring the tape speed control over two orders of magnitude, from ~30 cm/hour (1 ft) up. In experiments of Section 7, it was found that the drive operates satisfactorily at speeds ≥ 60 cm/hour. All the drive system components are mounted on carriages positioned on a track bench to permit easy reversal of the tape motion.

The electric current heating of the tape was implemented to reduce the gas phase depletion due to coating of reactor tube walls (Section 2.4), and thus to extend the length of the useful deposition zone. The tape was energized through carbon brush fixtures shown in Fig. 2-12, and attached to the vapor locks at the cold ends of the reactor. The whole drive mechanism was electrically insulated from the track bench. Temperature calibration was performed for Hastelloy tape substrates 6 mm wide and 25 μ m thick. Tape temperatures up to $T_d = 850^\circ\text{C}$ were attained for deposition zone temperatures $\geq 550^\circ\text{C}$.

As already stated, the experiments performed in the new reactor are described in Section 7.

2.7 References

1. G. W. Roland and A. I. Braginski, Chemical Vapor Deposition Of Nb_3Ge , Adv. Cryo. Eng., vol. 22 (in press).
2. A. Braginski et al., An Improved Superconductor for Transmission Line Applications, Phase 1, U.S. ERDA Report C00-2522-1 (1975).
3. L. R. Newkirk, Los Alamos Scientific Laboratories, personal communication (1976).

3. PHASES PRESENT IN Nb-Ge CVD DEPOSITS

3.1 Scope

This section of the report first briefly describes the analytical tools used for phase characterization, and then proceeds to a discussion of the results of our characterization studies. It goes without saying that the bulk of our phase characterization work was done on the superconducting Al5 structure phase of nominal composition Nb_3Ge . To more fully understand the chemistry and crystal chemistry of Nb_3Ge , it was also necessary to characterize the other phases that occurred in Al5-containing phase assemblages and to study changes in phase assemblages as a function of various CVD parameters. Finally, conclusions based on these phase studies are drawn relative to changes in the CVD process for improvement in superconducting properties.

3.2 Analytical Methods

X-ray powder diffraction methods were used extensively to identify phases present and measure unit cell sizes. Generally, we used the Debye-Scherrer film method (camera size 114.6 mm) with powdered samples obtained by dissolving the metallic Hastelloy substrates in 1:1 HNO_3 :water solution. The Nb-Ge phases are inert to this solution for short periods of time (< 1 hour). A Norelco x-ray diffractometer was used to obtain x-ray powder patterns of Nb-Ge films as deposited on substrates. In this way we were able to observe textural effects on x-ray line intensity and strain effects caused by the film-substrate mismatch in thermal expansion, effects that are obscured by grinding powders for Debye-Scherrer film. $\text{CuK}\alpha$ radiation, Ni-filtered, was used throughout.

A standard reflected-light metallographic microscope was used to examine polished sections of Nb-Ge films grown on various substrates. Phase identification in the thin films was difficult under the microscope because all the Nb-Ge phases have similar optical properties in reflected light. Usually the various phases were intimately intergrown so that techniques such as anodization were not very useful in enhancing compositional differences. We were, however, often able to see obvious gross inhomogeneities, such as layering of two different phases. Extensive use of microscope measurements was made to establish film thicknesses.

Polished film cross-sections were measured quantitatively using a MAC Model 400 electron probe micro-analyzer. The films were first examined for homogeneity by making x-ray intensity traces across the films. In this mode of operation (line trace) the specimen was traversed under the electron beam, starting in the substrate and travelling through the film while monitoring the x-ray intensity for Nb, Ge, and Ni simultaneously. The second mode of investigation was to perform point counts in the films with a stationary beam, measuring background radiation, duplicating these measurements on pure standards, and reducing this data with the "Colby Original Magic Computer Program." The computer program made corrections for absorption, fluorescence, etc., and gave a quantitative chemical analysis as output.

Surface topography of Nb-Ge films was studied by scanning electron microscope (SEM). This could be done with the films on their substrate or after removal of the substrate by etching. In the latter case, we could also examine fractured film cross-sections to observe grain morphology. Either a MARK II A or MAC SX II microscope was used. The MARK II A was equipped with accessories for energy-dispersive x-ray spectroscopy (EDAX) for surface analyses of regions between $1 \times 1 \text{ mm}^2$ and $0.1 \text{ }\mu\text{m}$ in diameter with a penetration depth between several hundred angstroms to several micrometers.

Thin foils were prepared from Nb-Ge films by a combination of electropolishing and ion milling and examined by transmission electron

microscopy (TEM). The thickness of the Hastelloy substrate was just sufficient to provide mechanical support to the brittle Nb-Ge films during handling and subsequent thinning. The instrument used was a Phillips EM-300 microscope operating at 100 kV. This method proved superior to the SEM technique for observing grain size, grain boundaries, and fine precipitates in the films.

Spectrographic techniques were used for impurity analysis of Nb-Ge films. A spark source mass spectrometer (SSMS) was used to obtain bulk impurity analyses. Samples were mounted in the source region of an AEI-702 mass spectrometer and were spark cleaned before analysis to remove any contamination from handling. Auger electron spectroscopy (AES) was used to examine impurity content as a function of depth in the films. This technique analyzes the first 3 to 5 atomic layers of an exposed surface for all elements except H and He. The sensitivity for heavier elements is comparable to that of the electron microprobe, but AES is more sensitive to the light elements. Typical detection limits are of the order of 0.1 at.% (1000 ppm) and fairly constant across the periodic table. The technique was most valuable in combination with layer removal methods (sputtering) where the extreme depth resolution of AES ($\sim 10 \text{ \AA}$) is limited only by the sputtering damage considerations and sputtering rates.

The impurity level in samples intentionally doped with N_2 and C was measured by inert gas fusion (for N_2) and by combustion analysis combined with chromatography (for C). A LECO TC-30 Automatic Nitrogen Analyzer was used for N_2 (He inert gas) and for C the analytical instrument was a LECO Model 400 Automatic Carbon Analyzer. Standard wet chemical analysis was used for Nb and Ge content in bulk chloride-rich deposits in the CVD reactor.

3.3 The Al5 Phase

3.3.1 Composition

The measured cell edge, a_0 , of the Al5 phase in the CVD deposits typically varied from 5.14 $\text{\AA}$ to 5.18 $\text{\AA}$ indicative of a substantial solid solution range. Data in the literature were combined with cell edge

measurements of microprobe-analyzed samples to define the cell edge versus composition curve in Fig. 3-1. The analyzed samples had very sharp x-ray diffraction lines and were therefore assumed to be homogeneous.

From Fig. 3-1, the composition of the CVD A15 phase ranged from about 14 at.% Ge to essentially stoichiometric Nb_3Ge (25 at.% Ge). It is well verified that at high temperature the solid solution limits of the A15 phase do not reach the ideal 3:1 ratio; at $\sim 1600^\circ\text{C}$, for example, the homogeneity limits are reported⁽¹⁾ as $\text{NbGe}_{0.15 \pm 0.01}$ ($\text{Nb}_{6.6}\text{Ge}$) and $\text{NbGe}_{0.22 \pm 0.01}$ ($\text{Nb}_{4.5}\text{Ge}$). There are no data on the solubility limits as a function of temperature below 1600°C , although the position of the Ge-rich boundary assumes considerable importance since it is generally believed that the highest T_c for any A15 compound will occur in the ordered stoichiometric phase.

There are three possible explanations for the occurrence of stoichiometric, or nearly stoichiometric, Nb_3Ge in CVD deposits:

- 1) a stoichiometric Nb_3Ge phase is thermodynamically stable at $T < 1000^\circ$,
- 2) CVD Nb_3Ge (25% Ge) is a metastable phase,
- 3) impurity stabilization results in deposition of essentially stoichiometric Nb_3Ge .

We have not systematically tried to determine which alternative is correct. Many recent studies have, however, focussed on impurity stabilization as the mechanism by which an ordered stoichiometric A15 phase can be prepared under impure deposition conditions but is absent in the pure system. A CVD system is inherently "dirty" because it is a reactive system. Minor amounts of elements such as Cu, Fe, Ni can come from chlorine attack of control valves, and Si plus O_2 contaminants can come from attacked quartz walls of the reactor. In addition, the solid deposit can be contaminated by gas phase components such as chlorine or hydrogen. We examined several of our films using the EDAX attachment to the SEM and were unable to detect any metallic elements other than Nb and Ge (except at the Hastelloy-film interface where a diffusion layer is present, as discussed below). The detection limit of the EDAX unit is ~ 1 wt.%. A spark source mass spectroscopy analysis of

Fig.3-1 - The cell edge of the A15 Nb-Ge phase as a function of Ge content.

a pure Al5-phase film showed $C1 < 0.0120$, $Si = 0.0052$, $Al < 0.0015$ at.%. Inert gas fusion analyses for oxygen in Nb_3Ge powders showed oxygen contents from 0.67 wt.% (6.7 at.%) to 1.28 wt.% (12.5 at.%) with an average of 12 samples of 0.85 wt.% (8.6 at.%). This oxygen is, however, probably a result of the acid treatment used to remove films from Hastelloy, because Auger analyses of films on Hastelloy always showed less than 0.1 at.% O_2 (the detection limit).

In a few of our samples deposited under very Nb-rich conditions, we obtained Al5 material for which the cell edge was >5.20 (one sample had $a_0 = 5.225$ Å). From Fig. 3-1, this would correspond to almost a pure Nb Al5 phase (others too have reported this, see, for example, Ref. 1). The occurrence of such a structure for Nb would be particularly interesting in light of the occurrence of an Al5 structure for tungsten that is believed to be oxygen stabilized. We did not, however, pursue these interesting crystal chemical aspects of low T_c Nb-rich deposits.

3.3.2 Compositional Homogeneity

Although many of our CVD films are very uniform in composition throughout their thickness (Fig. 3-2), others are notably nonuniform. This was evidenced by broad x-ray diffraction lines, broad or multiple superconducting transitions, and by electron microprobe traces across the films. Some films were even layered (Fig. 3-3). The reasons for these nonuniformities in composition are not clear; most likely they arise because of imperfect gas-phase mixing or aerodynamic flow patterns in the deposition tube.

3.3.3 Cell-Edge Measurements for Films on Substrates

We previously reported⁽²⁾ the thermal expansion coefficient for Nb_3Ge ($\beta = 7.7 \times 10^{-6}/^{\circ}C$) and noted that thermal mismatch with Hastelloy B ($\beta = 13.0 \times 10^{-6}/^{\circ}C$) is sufficient to cause tape deformation when Nb_3Ge is deposited on one side only. During this study we investigated further the strain effects by x-ray cell-size measurements for

Curve 680821-A

Fig. 3-2 — Electron microprobe traces of uniform single phase Nb_3Ge deposit. Analyzed composition: 81 at % Nb, 19 at. % Ge.

Fig. 3-3 — Electron microprobe trace of a layered Nb - Ge deposit

Table 3.1
Cell-Size Measurements for Nb₃Ge on
Substrates and for Nb₃Ge Powder

	<u>Sample Description</u>	<u>a₀, Å</u>
201-6	Al5 + σ on 50 μ m thick Hastelloy tape	5.1582 $\pm$ 0.0002
201-6	Al5 + σ powder obtained by dissolving Hastelloy B	5.1450 $\pm$ 0.0005
383-Block	Al5 + σ on solid Hastelloy B block	5.1693 $\pm$ 0.0002
222-7	Al5 + σ on 25 μ m thick Nb tape	5.1439 $\pm$ 0.0002

Al5 material on various substrates and for Al5 powder obtained after substrate removal. The data are reported in Table 3.1. The a_0 for the Nb₃Ge powder obtained from Tape 201-6 are typical of the cell-size values obtained for all samples containing the σ phase. We had anticipated lower values for a_0 in σ -phase containing samples on Hastelloy B because of the thermal expansion mismatch. In fact, the values are much higher and if the Al5 is deposited on a solid Hastelloy B block that does not deform during cooling, $\Delta a_0 = 0.025$ Å. We suspect that the increase in a_0 is caused by a tetragonal distortion, i.e., a_0 shrinks in the two directions planar with the tape interface and is expanded in the third ("c axis") direction. If this is so, because of preferred orientation effects in our highly textured Al5 films, the major contribution to line intensity would come from planes having expanded d values. For Al5 material on Nb tape, the a_0 obtained by diffractometer is very nearly the same as the typical powder value; this is in accord with the fact that β for Nb ($7.8 \times 10^{-6}/^\circ\text{C}$) is essentially the same as for Nb₃Ge.

A tetragonal expansion for Al5 Nb₃Ge on metallic substrates could introduce a significant anisotropy to measured superconducting properties. This area deserves considerable attention but insufficient time was available for us to pursue it further.

3.3.4 Impurity Doping

The purpose of doping the Al5 phase was to introduce additional flux pinning centers, and thus to enhance the critical current density. The doping gases were selected as potentially effective dopants following the earlier study of impurity-doped Nb₃Sn.⁽³⁾ In case of nitrogen it could be expected that particles of niobium nitrate, NbN, will be introduced into the Al5 (or Al5 + σ) matrix. The NbN is superconducting up to 14K, and additional pinning could occur, for example, on particle grain boundaries. All deposition experiments were performed at $T_d = 900^\circ\text{C}$.

3.3.4.1 Effect of Nitrogen-Doping

The nitrogen gas was introduced to the deposition zone with the carrier gas, at a rate between 0.1 and 1000 cc/min. Measurable amounts of N₂ present, above the reference (blank) sample level of 0.02 wt.%, were found for delivery rates between 70 and 1000 cc/min. Figure 3-4 shows the correlation between the flow rate and the nitrogen content in solid as determined by the inert gas fusion analysis of samples collected at the position coordinates $x = 0$ and $x = 20$ cm. The nitrogen concentration increases nearly proportionally to the delivery rate so that some degree of control should be available. The maximum N₂-content recorded: 1.67 wt.% at the maximum delivery of 1000 cc/min (for $x = 40$ cm) is equivalent to 17.3 mol.% of N₂.

The longitudinal distribution of the dopant along the deposition zone was determined for several sample series. Figure 3-5 shows that the N₂ content increases with x . This trend indicates that a rather long residence time (compared to that needed for chloride reduction) is required to incorporate N₂ into the solid.

3.3.4.2 Effect of Carbon-Doping

Two gaseous species have been used in carbon-doping experiments: CO₂ and C₂H₆. As in case of nitrogen these gases were selected because of their effectiveness in Nb₃Sn.⁽³⁾ Of course, CO₂ may represent both

Fig. 3 -4 - Nitrogen content in the deposit vs the N_2 delivery rate.
Only points above the reference level were used to draw the curves.
The nitrogen analyses are precise to $\pm 5\%$ of the amount present

Fig. 3-5 — Nitrogen distribution along the deposition zone. The nitrogen analyses are precise to $\pm 5\%$ of the amount present

carbon- and oxygen-doping, whereas C_2H_6 (which cracks easily) should introduce only carbon as a dopant. Each gas was introduced to the deposition zone with the carrier gas at a rate between 0.1 and 100 cm^3/min .

The results of CO_2 -doping were discouraging since significant degradation of the critical temperature was observed as shown in Section 4. The x-ray pattern of an unidentified compound have been observed in samples containing above 0.15 wt.% carbon. No effective control of carbon content was obtained: for CO_2 delivery rates from 0.1 to 100 cm^3/cm the analyzed concentration varied erratically between ~ 0.09 to 0.33 wt.% (4 to 10 mole % C), as shown in Table 4.4, and did not scale with the CO_2 delivery. The blank, reference sample (#206-5) contained ~ 0.04 wt.%. Hence, the CO_2 alternative was not pursued in more detail.

The results of C_2H_6 -doping were more encouraging, although also in this case a satisfactory control of carbon content was not achieved. This is illustrated in Table 4.5, which summarizes analytical data vs. C_2H_6 -delivery and sample position (x-coordinate). As in the case of nitrogen the concentration of carbon along the deposition zone tends to increase with x, at least up to $x = 20-30$ cm, although the results are more erratic.

The x-ray analysis of samples prepared at high C_2H_6 delivery rates indicated the presence of niobium carbide, NbC.

3.4 Al5-Phase Assemblages

Although we were able at will to synthesize a pure Al5 phase, more typically our CVD films contained one or more solid Nb-Ge phases in a phase assemblage including Nb_3Ge . In fact, a most useful feature of the CVD method as we have used it is the ease with which the Nb-Ge ratio (and therefore the phase assemblage) in the deposited films can be varied by changing deposition conditions. By changing the $NbCl_4/GeCl_2$ delivery ratios, for example, the phase fields in the Nb-Ge system can be surveyed as with any other tool for phase diagram determination but

with the added advantage of rapid reaction kinetics prevailing in the gas phase (although the phase assemblage may not reflect complete equilibrium because of gas-flow complexities). Similarly, other depositional parameters have an influence in determining phase assemblage.

The most common second phases occurring with Nb_3Ge in our experiments have a tetragonal structure. One of these, the σ phase of nominal composition Nb_5Ge_3 is well known, but the second has not previously been reported for the Nb-Ge system. We indexed the powder diffraction data (Table 3.2) and found that the unreported tetragonal phase is probably isostructural with the low-temperature tetragonal modification of Nb_5Si_3 ⁽⁴⁾ and $\text{TaGe}_{0.5}$ ⁽⁵⁾ and with the high-temperature form of $\text{TaSi}_{0.6}$ ⁽⁶⁾. We refer to it with the notation T2 of Parthe et al.⁽⁴⁾ The T2 phase is compared to the σ phase in Table 3.3.

Deposition parameters determine which tetragonal phase is deposited in a given run. For example, the phase assemblages as a function of s (Nb/Ge ratio) observed in a typical series of CVD runs are reported in Table 3.4. The expected progression from Nb to $\sigma \text{Nb}_5\text{Ge}_3$ is seen as s is decreased, with the A15 phase and T2 deposited at intermediate s values. The sequence of phase fields, i.e., the occurrence of T2 at s values intermediate between the values for deposition of A15 and $\sigma \text{Nb}_5\text{Ge}_3$, suggested that the composition of T2 is more Nb-rich than that of the σ phase. Microprobe analyses confirmed this, giving a Ge content of 34.8 at.% for the σ tetragonal phase and 33.4 at.% Ge for the T2 tetragonal phase prepared at 900°C. Both compositions lie within the range reported for the σ phase at higher temperature.

The occurrence of the two tetragonal Nb-Ge phases as a function of the CVD parameters T_d and $r = \text{H}_2/(\text{NbCl}_4 + \text{GeCl}_2)$ is shown in Fig. 3-6. The T2 phase is favored by low temperature and/or low H_2 content in the gas phase. The strong dependence of phase vs. H_2 content suggested to us that the presence of T2 might represent an incomplete H_2 reduction of the Nb and Ge chlorides in the gas phase. Indeed, spark source mass spectroscopy (SSMS) analyses showed high contents of Cl_2 in T2-containing

Table 3.2

X-RAY DIFFRACTION DATA FOR Nb-Ge PHASE
HAVING THE LOW-TEMPERATURE Nb₅Si₃ (T2) STRUCTURE

Indexed for a tetragonal unit cell with $a = 6.63\text{\AA}$, $c = 11.96\text{\AA}$.

hkl	$d_{\text{calc}} (\text{\AA})$	$d_{\text{obs}} (\text{\AA})$	I^*
211	2.878	2.883	vw
114	2.521	2.520	m
213	2.379	2.381	vs
220	2.344	2.345	w
204	2.220	2.221	s
310	2.097	2.098	s
006	1.993	1.993	s
314	1.717	1.714	w
400	1.657	1.665	w
402	1.597	1.598	w
330	1.563	1.569	w
008	1.495	1.498	m
420	1.483	1.486	m
404	1.450	1.450	s
334	1.385	1.390	m
406	1.274	1.278	m
336	1.230	1.234	m
318	1.217	1.220	m
0010	1.196	1.197	m
523	1.176	1.182	m

Additional reflections with lower d values.

* Intensity. vw = very weak, w = weak, m = medium, s = strong,
vs = very strong.

TABLE 3.3
TETRAGONAL Nb-Ge PHASES

	<u>σ Phase</u>	<u>T2 Phase</u>
Composition, at % Ge:	32.4-37.5 at T ~ 1500°C (Nb ₅ Ge ₃)	33.4 at T ~ 900°C
Cell Size, Å		
a	10.15	6.63
c	5.15	11.96
Crystal Structure:	Mo ₅ Si ₃ -type	like low-temperature Nb ₅ Si ₃

Table 3.4

Nb-Ge Phases Present as a Function of Gas Phase Nb/Ge Ratio, s^{*}
 (Constant molar ratio H₂/chlorides = 10)

<u>Nb/Ge Ratio in Gas Phase, s</u>	
12.5	Nb
10.0	Nb
7.0	A15-Nb ₃ Ge
5.6	A15-Nb ₃ Ge
4.5	A15-Nb ₃ Ge
4.2	A15-Nb ₃ Ge + T2 Tetragonal Phase
3.8	A15-Nb ₃ Ge + T2 Tetragonal Phase
2.9	A15-Nb ₃ Ge + T2 Tetragonal Phase
2.6	Nb ₅ Ge ₃ + T2 Tetragonal Phase

* Position in the isothermal deposition zone (measured downstream), x = 15-17 cm.

Fig.3-6-Tetragonal phase occurrence vs. deposition temperature, T_d , and hydrogen to chloride ratio, r . $\circ$ - T2 tetragonal phase present. $\bullet$ - σ - tetragonal phase present.

samples, e.g., a sample of T2 prepared at 900°C in conditions $r = 10$ contained 20.0 at.% of Cl_2 as compared to a content of 0.19 at.% in a σ phase sample prepared at 900°C but with $r \approx 300$. A marked, but less striking, difference was observed also for samples prepared at 800°C; <0.2 at.% Cl_2 in σ phase prepared at $r = 200$ vs. 1.6 at.% Cl_2 in T2 prepared at $r = 80$. Some of the chloride content of the chloride-rich samples is undoubtedly due to included unreduced niobium or germanium chlorides; nevertheless, T2 samples always contained at least twice the amount of Cl_2 as Al5 samples prepared under the same T_d and r conditions (but different Nb/Ge gas ratio) or σ samples prepared at the same T_d but higher r . It is thus quite possible that the T2 phase is impurity (chlorine) stabilized.

The phase assemblage(s) observed in a particular CVD run depended not only on the set CVD parameters, but also on the sample position, x , in the reactor deposition zone. As discussed earlier, the ratio Nb/Ge in the solid deposit increased with x , i.e., along the deposition zone, as was reflected by changes in $a_o(x)$ and $T_c(x)$. We did not understand why the cell size and T_c of the Al5 phase occurring with the T2 phase was not constant as would be expected for an invariant Al5 composition in a two-phase binary phase assemblage. This now appears to be resolved by our finding that the T2 phase is not a strictly binary phase, since in a ternary system the Al5 composition in the two-phase assemblage T2 + Al5 can vary in response to changing Nb/Ge ratio. If the σ phase is a strict binary phase, then we would expect the Al5 cell edge to be invariant in Al5 + σ phase assemblages. This is confirmed in our runs at high r value where T2 does not form. Two graphs of $a_o(x)$ are shown in Fig. 3-7 and Fig. 3-8 along with x-ray determined phase assemblages. Note that a_o is unchanging in the Al5 + σ phase assemblage but that as the Nb/Ge ratio increases with x and pure Al5 phase is deposited, then the cell size increases. This is as would be predicted from the binary system for increasing Nb concentration. As well as at $T_d = 900^\circ\text{C}$, the increasing Nb/Ge ratio in the deposit as x increased was noted at $T_d = 800^\circ\text{C}$, 950°C , and 1000°C .

Fig. 3-7 — Unit cell size of the A15 phase vs x for run # 201

Fig. 3 -8 - Unit cell size of the A15 phase vs x for run # 208

The superconducting properties of two-phase Al₅ + σ tapes depended on the amount of σ phase present (a function of x). This is most likely due to microstructure changes; we devoted some considerable effort to identifying the grain size and amount of σ phase present. The amount of σ phase present was determined from x-ray line intensity by comparison with a standard set of films obtained from prepared mechanical mixes of the two phases. The accuracy is considered to be ± 5 vol % σ phase. Optical microscope, SEM, etching, and anodizing techniques were all tried unsuccessfully to image the σ phase. We did, however, identify σ phase by TEM using our recently developed techniques⁽⁸⁾ for preparation of thin foils from CVD Nb-Ge films. The identification of σ phase in a known two-phase film involved the following steps:

- (1) Determine the d-spacings for the allowed reflections for the Al₅Nb₃Ge and the σ (Nb₅Ge₃) phases.
- (2) Measure d-spacings from electron diffraction pattern for the specimen.
- (3) Identify the reflections belonging to the σ -phase in the diffraction pattern.
- (4) Image the σ -phase reflections by dark field microscopy technique and identify the σ -phase particles in the bright field micrographs.

A typical electron diffraction pattern for the CVD Nb-Ge film (specimen #201-4) is presented in Fig. 3-9a. Table 3.5 summarizes the d-values of the reflections in this pattern. Also shown in this table are the calculated d-values for allowed reflections for the Al₅Nb₃Ge phase and the σ -phase. For the Al₅ phase, the lattice parameter, a_o , was assumed to be 5.145 Å. It can be seen that there are only six reflections that belong to the σ -phase alone (last column in Table 3.5). The measured d-values (first column in Table 3.5) show that only two reflections belong to the σ -phase alone. Even among these two reflections, only the (110) σ -phase reflection is sufficiently far removed from other Al₅ reflections to permit imaging of the σ -phase separately. The (110) σ -phase reflection was therefore chosen for imaging the σ -phase in dark

Table 3.5: Summary of Observed and Calculated d-Spacings
for CVD Nb-Ge Film (Specimen #201-4)

d_{hkl} (Å) (Observed)	Calculated $Nb_3Ge^\dagger$ (A15 Phase)	d-Spacings (Å) Nb_5Ge_3 (σ -Phase)
7.19		7.18 (110)
5.18	5.145 (100)	5.07 (200)
		4.59 (101)
3.64	3.64 (110)	
2.58	2.57 (200)	2.58 (002)
		2.47 (321)
		2.42 (112)
2.32	2.30 (210)	2.30 (202)
		2.27 (420)
2.24		2.23 (411)
2.10	2.10 (211)	2.09 (222)
1.84	1.82 (220)	1.81 (402,440)
1.63	1.63 (310)	
	1.48 (222)	
1.43	1.43 (320)	
1.38	1.38 (321)	
1.31	1.29 (400)	
1.23	1.21 (411,330)	
1.13	1.15 (420)	

[†]The lattice parameter, a_o , was assumed to be 5.145 Å.

(a)

(b)

(c)

Fig. 3-9. Selected Area Electron Diffraction Pattern (SAD) and TEM micrograph of two phase ($\text{Al}_5 + \sigma$) Nb-Ge film (Sample 201-4, $T_d \sim 900^\circ\text{C}$). a) SAD Pattern, b) Bright Field, c) Dark Field. The dark field micrograph was obtained by placing an objective aperture over the σ -phase reflection as shown in (a). The small bright grains are σ -phase.

field. The specimen under consideration had a bimodal distribution of grains (see Fig. 3-9b) and the smaller grains were identified as σ -phase particles. These are seen as the small bright spots in Fig. 3-9c. The σ -particles had an average size of 600 Å with a mean interparticle spacing of 1600 Å.

3.5 Other Phases Observed

As well as the phases already discussed, we have observed other Nb-Ge phases but not studied them in systematic fashion. Several runs exceptionally rich in Ge have yielded the hexagonal Nb_3Ge_2 phase, both pure and with Nb_5Ge_3 (in accord with the Ge-rich nature of this phase with respect to Nb_5Ge_3). In runs at 750°C (and occasionally also at 900°C) hexagonal Nb_3Ge_2 is replaced by another phase for which we have not indexed the diffraction data. Possibly, it is a low temperature modification of either Nb_3Ge_2 or NbGe_2 . One run surprisingly yielded material for which we indexed the x-ray pattern according to that reported for the Cu_3Au structure modification of Nb_3Si by Galasso and Pyle.⁽⁹⁾ We did not analyze this material for Si.

The diffraction patterns of film material obtained by dissolving the Hastelloy substrates also often contain lines that can be ascribed to Ni_3Nb with occasional samples giving lines for NiNb as well. These lines originate from a diffusion layer at the film-substrate interface as previously seen for Nb_3Sn .⁽¹⁰⁾ Our phase identifications are not entirely conclusive, but this is to be expected in view of the weak intensity of the lines and the unknown effect that Fe and Mo incorporated in Hastelloy would have on the diffraction patterns. Auger profiles for Ni across the diffusion boundary show the diffusion layer to be about 1-1/2 μm thick at 900°C and approximately the same at 1000°C.

3.6 Discussion

The above discussion on the Al₅ Nb_3Ge and associated phases as-deposited by CVD leads to an important conclusion regarding the CVD

process itself, a conclusion which derives from the observed variation in Nb/Ge ratio in the deposits as a function of x . There are advantages and disadvantages to the variation in composition as a function of x . The advantage lies in the availability of Al5 samples having different composition and second phase content in any particular Al5-containing run. This allowed us to determine superconducting properties as a function of composition in any given run and so define the optimum deposition parameters for optimum superconducting material. The disadvantage is that because the properties depend on x , there is only a small range of x (a few inches) over which optimum material is deposited in any run. Therefore, for long lengths of tape to be prepared, we must consider a moving tape reactor already discussed in Section 2.

3.7 References

1. L. J. Vieland and A. W. Wicklund, High T_c Nb_3Ga and Nb_3Ge by CVD, Phys. Lett. 49A, 5, 407 (1974).
2. A. I. Braginski, G. W. Roland, and Michael R. Daniel, Preparation of Nb_3Ge by Chemical Vapor Deposition, Applied Polymer Symposium No. 29, 93 (1976) (Appendix I, this report).
3. R. E. Enstrom, J. J. Hanak, J. R. Appert, and K. Strater, Effect of Impurity Gas Additions on the Superconducting Critical Current of Vapor-Deposited Nb_3Sn , J. Elec. Soc. 119, 6, 743 (1972).
4. E. Parthe, B. Lux, and H. Nowotny, Der Aufbau der Silizide M_5Si_3 , Monatsh. Chem. 86, 859 (1955).
5. H. Nowotny, A. W. Searcy, and J. E. Orr, Structure of Some Germanides of Formula M_5Ge_3 , J. Phys. Chem. 60, 677 (1956).
6. L. Brewer, A. W. Searcy, D. H. Templeton, and C. H. Dauben, High Melting Silicides, J. Am. Ceram. Soc. 33, 291 (1950).
7. G. W. Roland and A. I. Braginski, Chemical Vapor Deposition of Nb_3Ge , Adv. Cryo. Eng., Vol. 22 (1976), in press.

8. A. T. Santhanam and P. M. Yuzawich, Revealing the Microstructure of Nb_3Ge Superconducting Films by Transmission Microscopy, submitted for publication in Jour. Materials Science.
9. F. Galasso and J. Pyle, Nb_3Si , A Superconductor with the Ordered Cu_3Au Structure, Acta. Cryst. 16, 228 (1963).
10. R. E. Enstrom and R. Appert, Preparation and High-Field Superconducting Properties of Vapor-Deposited Nb_3Sn Alloys, J. Appl. Phys. 45, 1, 421 (1974).

4. CRITICAL TEMPERATURE

4.1 Measuring Methods

The routine measurements of the critical temperature have been performed resistively using the standard four-point method. Samples in the form of narrow strips, ~ 1.27 cm long and ~ 0.3 cm wide, have been extracted from the 1.27 cm wide tape by scissor-cutting perpendicular to the tape axis. In case of narrower tape substrates the longer axis of the sample was parallel to the tape axis. To expedite the characterization of a large number of samples fabricated in this program, a special measuring probe was designed and constructed by Westinghouse, making it possible to measure up to 20 samples in one run. Figure 4-1 is a photograph of this probe. The probe is assembled into a stainless steel tube whose wall makes thermal contact with the probe end through finger stock. Probe temperature is controlled by exchange gas and heaters. The temperature is measured with an accuracy of ± 0.2 K using calibrated Ge-thermometers mounted in the copper block body of the probe, directly under the samples. Plots of resistance vs temperature transitions are recorded. The critical temperature is defined as the 50% resistive midpoint, T_c . The onset of superconductivity is defined as T_c -onset, the onset of normality as T_c -tail. The width of the transition from onset to tail is labeled ΔT .

Inductive (susceptibility) measurements of T_c were performed on selected, powdered samples, ~ 20 mg in weight, obtained by dissolving the Hastelloy B substrate in HNO_3 , and grinding the deposit to a grain size of 40 to 60 μm . The measuring setup consists of a mutual inductance bridge operating at 17 Hz with the probe inductively coupled to a differential coil forming one arm of the bridge. The variable temperature cryostat operates with pumped hydrogen and the helium exchange gas. A

Fig. 4-1 Multiple Sample T_c Probe.

The resistive superconducting transition temperatures of up to twenty samples can be measured in one loading and cool-down. Ten samples are mounted on each side of the probe.

calibrated germanium thermometer is placed in the immediate vicinity of the sample and the measurement accuracy is again ± 0.2 K. Comparison of resistive and inductive T_c measurements resulted in a generally good agreement, as shown in Figure 4-2. The inductive transition was usually broader, indicating a possible nonuniformity of the sample, but the agreement of mid-point T_c 's was within 0.5 K (Figure 4-2). Since the inductive measurement necessitated destruction of a relatively large tape sample, 1 x 1 cm, approximately, it was used only occasionally for the verification of results.

In case of especially interesting samples, the temperature measurements were performed with an accuracy of ± 0.05 K. This was achieved either by using a gas bulk thermometer built by one of the authors,* or by extrapolating the upper critical field vs temperature dependence $H_{c2}(T)$ determined in pumped hydrogen. This last type of measurement has been performed at the National Magnet Laboratory. The results of routine T_c characterization were within 0.5 K of those obtained by one of the above two methods.

Finally, a measure of T_c could be obtained from critical current density vs temperature measurements described in Section 5.1. In this case the maximum slope dJ_c/dT was linearly extrapolated to $J_c = 0$. The T_c^* such obtained was typically 10 to 20% below the resistive mid-point.

4.2 Critical Temperature in the Nb-Ge System

The critical temperature, T_c , of A15 compounds, A_3B , depends upon the composition, i.e., the deviation from the ideal ratio $A/B = 3$, and, for any given composition, upon the degree of long-range order. Establishing a nonambiguous correlation between the Nb-Ge composition and T_c was found difficult in this study while the correlation with the degree of long-range order has not been attempted. The results given below indicate, however, the general trends observed, and are useful in interpreting the effect of deposition parameters (Section 4.3).

* M. A. Janocko

Fig. 4-2 -Transition curves of Nb_3Ge sample 23-8.

It is known that for a given composition of the Al5 phase the critical temperature tends to increase with the long-range order parameter.⁽¹⁾ Disorder inherent to the synthesis process, or introduced, e.g., by irradiation, reduces T_c , whereby the cell edge, a_o , increases. Appropriate low-temperature annealing permits recovery, and may also improve the long-range order, thus enhancing T_c . In case of Nb_3Ge , extensive irradiation and recovery studies have been performed by Sweedler, et al.,⁽²⁾ and also by Poate, et al.⁽³⁾ The T_c enhancement by low-temperature annealing was demonstrated by Blaugher.⁽⁴⁾ He used the sample 253-5 of this study and achieved a T_c increase of up to 1.5 K above the initial, as-deposited, value. Unfortunately, such low-temperature process takes up to several months, and is thus ill-suited for practical applications. Annealing was not included, therefore, in this program. All T_c values given below are those of as-deposited samples. The highest onset of superconductivity measured in such samples was 22.6 ± 0.05 K with $\Delta T = 1$ to 2 K.

The highest T_c 's have been observed in single-phase Al5 samples having a cell edge $a_o = 5.14$ to 5.17 Å. The closest to stoichiometry (i.e., richest in Ge) composition coexisting with σ phase had typically $a_o = 5.140$ to 5.145 Å (Section 3). However, from Fig. 3-1 one would infer the Ge-concentration in higher- a_o -samples to be comprised between ~ 23.5 and 16 atomic %. Such high- T_c samples were thus decidedly Ge-deficient. The deviation from stoichiometry implies disorder resulting from the creation of antistructural defects, unless long-range ordering of some other defects occurs. Excluding the latter alternative, the long-range order should have improved when approaching the 3:1 stoichiometry (25 to % Ge), other conditions being equal. It thus appeared unlikely that samples further away from stoichiometry would have high T_c 's. Unfortunately, insufficient accuracy of analytical techniques other than the X-ray diffraction, and also the observed compositional nonuniformity (Section 3) prevented a precise determination of the sample composition independent of a_o data. When the observations were first made, it was thought, therefore, that phase inhomogeneity should be blamed for the

confusion. (5) The high a_o would be characteristic of the major, lower- T_c phase, while the minor, high- T_c phase would manifest its presence due to filamentary superconductivity. Good agreement between resistive and inductive T_c measurements (Figure 4-2) could, perhaps, be explained by a very fine dispersion of the high- T_c phase, such that even in powdered samples the low- T_c phase would be shielded. The critical current density, $J_c(T)$, curves obtained by magnetization measurements tended to support this interpretation. (5) The amount of the highest- T_c phase estimated from the shape of the $J_c(T)$ dependence was, however, surprisingly low, of the order of 2 vol. %. Continued study of J_c characteristics (Section 5) has also shown that the $J_c(T)$ curve shape could equally well be due to the low density of flux pinning centers. The basic question: "is high T_c a characteristic of the bulk of the nonstoichiometric sample?" could only be answered decisively by low temperature specific heat, $c(T)$ measurements. The c anomaly due to superconducting transition is a characteristic of the bulk. The $c(T)$ measurements on a nonstoichiometric sample (23-8) have been performed by G. Stewart at Stanford University. Unfortunately, his results remained ambiguous, and further specific heat measurements of Nb-Ge samples are in progress at Stanford. At this time, it appears probable, however, that the very high T_c of nonstoichiometric samples with $a_o = 5.15$ to $5.17 \text{ \AA}$ is, indeed, a bulk property. As shown in Section 5, enhanced flux pinning due to introduced impurities resulted in relatively high J_c of such samples. This would be unlikely with only a few percent of high- T_c phase present.

For larger Ge-deficiencies, T_c was falling off rather abruptly. For $a_o = 5.18$ to $5.19 \text{ \AA}$, T_c decreased below 10 K and approached the values typical for the metallurgically prepared, i.e., arc- or levitation-melted, high temperature phase. This low- T_c phase had a very narrow, well defined transition, $\Delta T \approx 0.1 \text{ K}$.

In the presence of excess Ge over that incorporated at $a_o \approx 5.14 \text{ \AA}$, the σ phase coexisted with Al5 as discussed in Section 3. With increasing fraction of σ phase, T_c was gradually decreasing and the

Fig. 4-3 —The critical temperature vs composition in the Nb-Ge system.

transition broadened due, presumably, to increasing internal strains. However, up to 90 Vol. % of σ phase T_c was still above 10 K.

Assuming the validity of data shown in Figure 3-1, a schematic diagram of T_c and the transition width, ΔT , vs Ge-concentration was constructed as shown in Figure 4-3. It should be stressed that it is only a semi-quantitative graph useful in interpreting the results given in the following Section (4.3).

4.3 Effect of Gas Phase Parameters

In the stationary substrate deposition runs the average composition of the Nb-Ge layer varied along the deposition zone such that the molar ratio Nb/Ge (in the solid) monotonically increased from the inlet to the outlet end of the zone (Section 3). In consequence, variations of T_c along the tape substrate have been observed. The $T_c(x)$ profile data, where x is the position coordinate in the constant temperature zone, are given in Tables 4.1 and 4.2. Table 4.1 presents $T_c(x)$ data obtained at the deposition temperature $T_d = 900^\circ\text{C}$ for various values of the ratio $s = \text{Nb/Ge}$, and for several values of $r = \text{H}_2/(\text{NbCl}_4 + \text{GeCl}_2)$ in the gas phase. The data are restricted to those obtained at r sufficiently high to prevent the occurrence of T_2 phase. Table 4.2 gives $T_c(x)$ at a constant r equal 200, and a variable s at several deposition temperatures. The value $r = 200$ was sufficient to prevent the occurrence of T_2 -phase in the whole temperature range (Figure 3-6). The phases occurring at a fixed position $x = 0$ are also listed in both tables.* The average compositions of representative layers have been determined by using the $a_o(x)$ profiles rather than the uncertain quantitative analysis. In Figure 4-6 such profiles are correlated with $T_c(x)$. Data of Table 4.1 show that at $T_d = 900^\circ\text{C}$ the high critical temperature varied little for a rather wide range of r and s , and that the reproducibility of T_c results, in consecutive runs (see runs 200 to 209, for example), performed in the same or similar conditions was very good. The apparent uniformity of $T_c(x)$ led, in fact, to the initial belief that relatively long tape sections

* At $T_d = 750^\circ\text{C}$ $x = 10$ cm.

Table 4.1 - Critical Temperature Profiles, $T_c(x)$, for Various r and s Values, $T_d = 900^\circ\text{C}$

Run No.	r	s	$x = 0 \text{ cm}$	$x = 10 \text{ cm}$	$x = 20 \text{ cm}$	$x = 30 \text{ cm}$	$x = 40 \text{ cm}$	Phases ⁺⁺
211	80	2.5	21.0, 19.5, 19.2	21.4, 20.7, 20.4	21.8, 20.3, 17.9	21.9, 21.0, 20.6	21.9, 19.2, 17.9	$\sigma_m + A15$
206	80	3.1	21.6, 21.3, 20.6	21.9, 21.3, 20.8	21.4, 20.7, 20.5	21.2, 20.5, 20.2	21.0, 20.1, 19.7	$A15_m + \sigma$
207	80	3.6	21.4, 20.7, 20.2	21.4, 20.7, 20.5	21.4, 20.7, 20.4	21.9, 21.1, 20.6	21.9, 20.9, 20.2	$A15_m + \sigma$
208	80	4.2	22.4, 21.4, 20.8	21.9, 21.2, 20.8	21.9, 21.0, 20.2	22.4, 21.2, 20.2	21.9, 20.6, 19.8	$A15_m + \sigma$
209	80	5.0	22.5, 21.9, 21.6	22.4, 21.6, 21.3	22.2, 21.4, 21.1	21.9, 21.1, 20.6	21.9, 21.0, 20.5	$A15 + \sigma_t$
210	80	6.3	21.4, 20.0, 19.5	22.1, 21.6, 21.3	22.1, 21.6, 21.3	21.4, 19.3, 16.1	15.8, 14.0, 12.2	$A15$
200	200	3.6	21.4, 19.5, 18.2	22.4, 21.0, 17.9	22.0, 20.7, 19.8	21.5, 20.6, 20.0	20.2, 18.9, 18.4	$A15_m + \sigma$
205	200	3.6	21.9, 20.5, 20.0	22.0, 20.9, 19.8	21.9, 18.7, 17.9	21.9, 20.8, 20.4	21.6, 21.0, 20.6	$A15_m + \sigma$
201	200	3.8	21.0, 20.2, 19.6	21.6, 20.6, 20.2	22.0, 21.1, 20.8	22.3, 21.6, 20.7	21.4, 20.8, 20.3	$A15_m + \sigma$
204	200	3.8	21.4, 20.2, 19.6	21.3, 20.1, 19.6	20.6, 20.0, 19.0	21.4, 20.5, 20.0	21.4, 20.5, 20.0	$A15_m + \sigma$
300	200	4.0	21.4, 20.7, 20.0	21.4, 19.9, 19.8	21.6, 20.5, 19.6	21.6, 20.4, 19.8	21.9, 21.0, 20.5	$A15_m + \sigma$
299	200	4.2	21.4, 20.4, 19.5	21.9, 20.4, 19.8	21.4, 19.8, 19.3	21.5, 20.4, 19.8	21.6, 20.7, 19.8	$A15_m + \sigma$
202	200	4.2	21.4, 20.8, 20.6	22.4, 21.3, 20.6	22.3, 21.2, 19.8	21.8, 20.7, 19.7	21.2, 20.7, 20.4	$A15_m + \sigma$
203	200	4.2	20.2, 19.3, 18.8	20.6, 19.2, 17.9	21.2, 20.0, 19.3	21.5, 20.4, 20.0	21.5, 20.8, 20.2	$A15_m + \sigma$
298	200	4.6	20.6, 19.5, 18.7	20.6, 19.6, 19.2	21.6, 20.6, 20.2	21.6, 20.6, 20.2	21.6, 21.0, 20.6	$A15_m + \sigma$
297	200	4.8	21.4, 20.3, 19.7	21.6, 20.2, 17.9	22.1, 21.2, 20.2	22.4, 21.2, 20.7	Sample Damaged	$A15_m + \sigma$
294	200	5.0	22.1, 21.0, 20.7	22.4, 21.1, 20.6	22.4, 21.1, 20.7	22.2, 21.2, 20.4	21.6, 20.3, 19.2	$A15_m + \sigma$
295	200	5.4	21.4, 20.2, 18.8	21.9, 20.1, 19.6	21.2, 21.0, 20.6	21.6, 21.0, 20.7	21.7, 20.8, 20.6	$A15_m + \sigma$
293	200	5.6	21.4, 20.7, 20.2	21.9, 20.6, 17.7	19.5, 16.4, 13.0	8.9, 7.6, 6.2	6.6, 6.2, 5.9	$A15 + \sigma_t$
193	330	3.1	20.4, 19.4, 18.5	21.0, 20.3, 19.5	20.6, 19.6, 19.0	19.2, 18.5, 18.2	17.2, 16.5, 16.2	$A15 + \sigma_t$
192	330	3.6	18.8, 18.1, 17.2	18.2, 16.4, 14.0	8.2, 16.4, 14.0	8.9, 8.3, 7.5	6.4, --, --	$A15 + \sigma_t$
188	330	4.2	18.5, 15.3, 13.8	18.7, 17.4, 14.3	17.7, 15.1, 8.1	7.2, 6.8, 6.4	--, --, --	$A15 + \sigma_t$
190	330	6.2	22.1, 20.7, 17.7	21.0, 19.8, 9.6	9.6, 8.0, 6.6	6.7, 6.6, 6.5	--, --, --	$A15$

⁺Each set of three values corresponds to onset, midpoint, and tail.

⁺⁺_m - major phase, _t - traces.

Table 4.2 - Critical Temperature Profiles for Various T_d and s , $r = 200$

Run No.	T_d °C	s	$x = 0$ cm	$x = 10$ cm	$x = 20$ cm	$x = 30$ cm	$x = 40$ cm	Phases ⁺
275	750	3.1	← No Superconductivity Above 4.2°K →				18.5, 16.5, 13.6	σ
279	750	4.2	16.3, 14.3, 9.2	17.9, 15.7, 15.1	18.2, 16.7, 14.3	19.2, 18.2, 17.4	18.5, 16.7, 15.1	$A15 + \sigma$
273	750	6.3	16.6, 16.3, 15.9	17.0, 16.8, 16.6	17.2, 16.8, 16.6	17.5, 17.0, 16.7	20.1, 19.2, 18.7	$A15_m + \sigma$ ($x = 10$ cm)
232	800	2.8	← No Superconductivity Above 4.2°K →				17.7, 14.8, 11.1	σ
231	800	3.1	As Above	17.9, 16.1, 14.6	20.0, 19.3, 18.8	20.4, 19.6, 19.3	20.3, 19.6, 19.8	$\sigma + A15$
230	800	3.6	14.3, 10.5, 7.5	20.2, 19.2, 18.3	20.2, 19.5, 18.8	19.8, 19.0, 17.5	20.3, 19.5, 19.0	$A15 + \sigma$
229	800	4.2	18.5, 15.1, 12.2	20.6, 19.6, 19.0	20.2, 19.2, 18.8	20.6, 19.5, 18.5	19.2, 18.4, 17.9	$A15 (m) + \sigma$
227	800	6.3	19.0, 18.2, 17.9	20.0, 19.3, 18.5	19.8, 19.2, 18.7	Not Measured (n/m)	20.0, 17.9, 15.7	$A15$ ($x = 0$ cm)
375	850	3.6	← No Superconductivity Above 4.2°K →					$\sigma + D8_8$
374	850	4.2	19.4, 18.7, 18.2	19.6, 18.9, 18.4	20.0, 18.5, 16.0	n/m	n/m	$\sigma_m + A15$
373	850	5.0	19.4, 18.7, 19.6	19.6, 19.0, 18.5	20.2, 19.4, 18.4	20.4, 19.3, 18.2	20.4, 19.2, 18.7	$A15 + \sigma$
372	850	---	20.8, 20.2, 18.9	20.8, 19.7, 19.3	21.4, 20.5, 20.0	21.9, 21.0, 20.6	21.9, 21.0, 20.7	$A15_m + \sigma$ ($x = 0$ cm)
---	900	---	See Table					
259	950	2.5	← No Superconductivity Above 4.2°K →					$\sigma + D8_8$
256	950	3.6	20.6, 19.2, 18.2	18.8, 17.2, 15.1	19.5, 16.9, 15.8	21.3, 20.1, 19.5	n/m	$A15 + \sigma$
254	950	5.0	21.0, 19.8, 19.4	21.4, 20.4, 19.2	18.5, 18.1, 17.7	6.7, 6.6, 6.0	6.7, 6.5, 6.0	$A15_m + \sigma$
253	950	6.3	22.2, 21.2, 20.6	22.4, 21.5, 21.0	18.8, 17.4, 16.9	7.5, 7.1, 7.0	7.5, 7.4, 7.0	$A15$ ($x = 0$ cm)
267	1000	2.5	← No Superconductivity Above 4.2°K →					σ
265	1000	3.1	21.4, 19.5, 18.8	21.4, 18.7, 17.6	n/m	8.0, 7.6, 6.6	n/m	$A15 + \sigma$
263	1000	4.2	22.4, 21.0, 19.7	21.6, 20.3, 19.8	19.8, 18.7, 18.3	6.9, 6.7, 6.6	n/m	$A15_m + \sigma$
262	1000	5.0	22.6, 19.3, 16.1	21.9, 19.1, 16.1	7.0, 6.5, 6.4	7.2, 6.9, 6.0	n/m	$A15$ ($x = 0$ cm)

⁺ m - major phase

having uniform critical current density and loss profiles can be fabricated in a stationary substrate arrangement.

The discussion of Section 4.2, the $a_o(x)$ profile examples of Figure 4-6, and additional X-ray results allow one to summarize and interpret the $T_c(x)$ data as follows.

4.3.1 Effect of Deposition Temperature

In the temperature range between $T_d = 750$ and 1000°C , rather high critical temperatures $T_c \geq 19$ K (mid-point) could be achieved as shown in Figure 4-4. The relatively lowest T_c 's at 750°C were attributed to the deposit contamination by unreduced NbCl_3 ($\text{NbCl}_{2.66}$) identified by the X-ray phase analysis. Between 900 and 1000°C , the T_c mid-points in excess of 21 K and onsets in excess of 22 K were common. At 1000°C , with onsets still high, the transition widths broadened thus indicating an increased phase inhomogeneity. Figure 4-5a shows $T_c(x)$ obtained for $T_d = 900, 950$, and 1000°C at $r = 200$ and $s = 5$. The increasingly abrupt fall of T_c at higher x for 950 and 1000°C is caused by a more pronounced variation of the Nb/Ge ratio in the solid vs. x . The single element data of Section 2 suggest that preferential Ge-depletion of the gas phase with increasing temperature is responsible for the above effect.

4.3.2 Effect of Hydrogen Excess

The effect of hydrogen excess on $T_c(x)$ profiles was similar to that of deposition temperature. Figure 4-5b shows such profiles for $r = 80, 200$, and 330 , $T_d = 900^\circ\text{C}$, $s \approx 6$, while Tables 4.1 and 4.2 give analogous data for a variety of other conditions. Again, preferential Ge-depletion caused by a higher GeCl_2 reactivity was responsible for stronger compositional variation with increasing hydrogen excess.

4.3.3 Effect of the Nb/Ge Ratio

At a sufficiently low initial s the pure σ phase was deposited and there was no superconductivity above 4.2 K (Table 4.2, runs 375, 259, and 267). However, in any given run the ratio Nb/Ge increased with x .

Fig. 4-4 — Highest achieved critical temperature, T_c , vs the deposition temperature, T_d . The bars indicate the width of the superconductive transition.

Fig. 4-5 - Critical temperature (midpoint) profiles, $T_c(x)$.
 Plots a) and b) illustrate the effect of depositional parameters upon the composition profile Nb/Ge vs x . (Plot c shows the effect of initial gas phase composition.)

Hence, at higher x some Al5 could form, and high temperature superconductivity could occasionally be observed, as shown in Table 4.2, runs 275, 231, and 232.

Higher initial s values allowed the two phases to coexist over a wider x range while the fraction of σ phase decreased, and that of Al5 increased with x up to a single phase Al5 region. If such single phase region was reached, as signaled by a knee on the $a_o(x)$ curve, then a local, shallow maximum of $T_c(x)$ could be observed. In general, however, for not too high deposition temperatures ($T_d \leq 900^\circ\text{C}$) the $T_c(x)$ profiles were relatively flat as shown by most data of both tables and Figure 4-6. Finally, at sufficiently high initial s values the Al5 phase was the only phase present in the whole x range. Then at least at higher temperatures ($T_d > 750^\circ\text{C}$) the usual Ge-depletion could result in a low- T_c , high a_o Al5 phase depositing at higher x . The effect of increasing s from 5 to 6 at $T_d = 900^\circ\text{C}$, $r = 200$ is shown in Figure 4-5c. The values of s belonging to the above "low," "higher," and "high" categories have been defined by the other deposition parameters as shown by the tabulated data. In view of the uncertainty of effective s values discussed in Section 2, the values have only a relative significance. At $T_d = 900^\circ\text{C}$, $r = 200$ where most data have been collected, a typical s range for obtaining flat $T_c(x)$ profiles was $3.6 \leq s \leq 5$.

4.4 Effect of N₂-Doping

Background information on the nitrogen-doping is given in Section 3. All the deposition experiments were performed at $T_d = 900^\circ\text{C}$ with a constant $s = 3.8$ to obtain typical composition profiles such that the nearly stoichiometric Al5 composition would form near $x = 20$ cm. Accordingly the two-phase (Al5 + σ) range would extend from $x = 0$ up to $x \approx 20$, and at higher x Ge-deficient Al5 phase would form, as discussed in Section 3. This objective was achieved, as shown in Figure 5-6, Section 5.

Table 4.3 summarizes the critical temperature profile data, $T_c(x)$, for samples doped using various N₂ flow rates between 10 and

Fig.4-6—The cell edge, a_0 , and critical temperature, T_c , profiles along the deposition zone; x is the sample position coordinate, a — run 372, b — run 201.

Table 4.3 - Critical Temperatures for N₂-doped Samples (degrees K)*
and Nitrogen Concentrations (wt. %)[†]

Run No.	N ₂ -rate cm ³ /min	x = 0 cm	x = 10 cm	x = 20 cm	x = 30 cm	x = 40 cm
312	10	<u>21.9, 21.2, 20.8</u> 0.010	21.9, 21.2, 20.3	21.4, 20.2, 19.5	21.4, 20.0, 18.8	20.6, 19.8, 18.8
311	30	<u>21.0, 20.1, 19.7</u> 0.022	n/m	21.0, 19.6, 19.2	n/m	21.4, 20.6, 20.2
359	70	<u> </u> 0.015		<u> </u> 0.047		
310	100	<u>21.9, 20.9, 20.5</u> 0.039	21.4, 20.9, 20.6	<u>21.3, 20.7, 20.5</u> 0.21	21.3, 20.7, 20.2	<u>21.0, 20.3, 19.8</u> 0.14
322	200	<u>20.8, 19.7, 19.4</u> 0.13	<u>20.8, 19.9, 19.5</u> 0.22	<u>20.6, 19.8, 19.5</u> 0.39	<u>20.6, 20.0, 19.8</u> 0.44	<u>21.4, 20.4, 19.8</u> 0.59
321	500	<u>20.8, 19.8, 19.2</u> 0.10	19.5, 18.8, 17.9	<u>20.6, 18.8, 17.3</u> 0.56	21.0, 19.7, 18.5	21.0, 19.5, 17.6
323	1000	<u>20.6, 19.5, 18.2</u> 0.35	<u>20.6, 19.5, 19.0</u> 0.63	<u>21.0, 20.2, 19.2</u> 0.92	<u>21.4, 20.6, 19.8</u> 1.20	<u>21.6, 20.6, 19.2</u> 1.67

* Onset, mid-point, and tail.

[†] In denominator (where available).

Table 4.4 - Critical Temperatures of CO₂-Doped Samples (degrees K)*
and Carbon Concentrations (wt. %)[†]

Run No.	CO ₂ -rate cm ³ /min	x = 0 cm	x = 10 cm	x = 20 cm	x = 30 cm	x = 40 cm
318	0.1	<u>21.0, 19.9, 19.4</u> 0.14	21.0, 19.9, 19.5	20.4, 19.5, 18.8	20.2, 19.3, 18.7	19.6, 18.5, 17.2
306	0.3	19.8, 19.0, 18.4	19.8, 19.0, 18.2	19.2, 18.1, 17.3	20.2, 18.7, 17.7	19.8, 19.3, 19.0
305	0.7	<u>19.8, 18.8, 18.2</u> 0.17	19.2, 18.6, 17.9	18.5, 17.7, 17.4	17.2, 16.7, 15.8	17.2, 15.8, 14.0
304	1.0	19.3, 18.3, 17.6	19.2, 18.1, 16.9	18.2, 17.2, 15.5	16.7, 16.1, 15.6	16.1, 15.2, 13.8
317	3.0	<u>20.9, 20.3, 20.0</u> 0.13	21.6, 20.4, 19.5	21.9, 20.7, 18.8	n/m	<u>21.9, 20.6, 20.1</u> 0.16
303	5.0	<u>18.8, 16.8, 15.1</u> 0.19	18.8, 17.3, 16.1	n/m	18.5, 17.4, 15.3	16.7, 15.4, 14.3
302	10	<u>21.0, 19.2, 17.1</u> 0.089	19.5, 17.5, 16.5	16.9, 15.1, 13.4	13.5, 13.0, 11.4	n/m
307	30	<u>17.9, 16.9, 14.9</u> 0.14	18.2, 16.5, 14.6	16.5, 15.1, 14.0	13.3, 12.0, 9.6	n/m
308	70	18.2, 17.2, 14.8	17.9, 17.2, 15.6	16.5, 15.3, 13.0	14.3, 13.1, 12.3	n/m
309	100	<u>17.9, 14.8, 10.3</u> 0.33	16.3, 15.2, 13.3	13.0, 12.4, 11.2	12.0, 10.9, 9.6	n/m

* Onset, mid-point, and tail.

[†] In denominator (where available).

Table 4.5 - Critical Temperatures of C₂H₆-Doped Samples (degrees K)^{*}
and Carbon Concentrations (wt. %)[†]

Run No.	C ₂ H ₆ -rate cm ³ /min	x = 0 cm	x = 10 cm	x = 20 cm	x = 30 cm	x = 40 cm
338	0.1	20.6, 19.5, 18.7	20.6, 19.5, 18.8	<u>20.6, 18.7, 18.2</u> 0.13	<u>19.8, 18.7, 18.2</u> 0.19	n/m
334	0.3	<u>21.0, 20.1, 19.5</u> 0.17	21.2, 20.2, 19.5	21.4, 19.8, 18.5	22.1, 21.2, 20.4	21.5, 20.8, 20.5
335	0.7	<u>20.2, 18.3, 16.3</u> 0.08 - 0.13	<u>19.2, 18.2, 17.4</u> 0.16	<u>20.2, 19.2, 18.7</u> ~ 0.30	<u>18.4, (low)</u> ~ 0.26	<u>n/m</u> ~ 0.23
336	1.0	<u>20.9, 20.1, 19.7</u> 0.16	<u>21.2, 20.3, 19.8</u> 0.061	<u>21.6, 20.5, 19.5</u> 0.12	21.0, 19.8, 18.9	<u>20.7, 19.7, 19.5</u> 0.12
337	3.0	<u>20.4, 19.4, 19.0</u> 0.064	20.7, 19.6, 19.2	<u>21.0, 18.8, 17.9</u> 0.14	21.4, 20.3, 19.8	19.5, 16.1, 13.4
333	5.0	<u>20.6, 19.8, 19.5</u> 0.24	20.6, 19.8, 19.3	<u>20.4, 19.7, 19.3</u> 0.17	<u>20.6, 19.8, 19.3</u> 0.13	20.6, 18.8, 18.3
332	10	<u>n/m</u> < 0.07	<u>n/m</u> 0.10	<u>19.2, 17.5, 16.7</u> 0.18	<u>0.44 - 0.51</u>	<u>19.6, 18.2, 17.6</u> 0.41
329	100	<u>n/m</u> 1.0	n/m	21.1, 20.5, 16.1	n/m	20.2, 17.6, 16.3

* Onset, mid-point, and tail.

† In denominator (where available).

1000 cm³/min. The analyzed nitrogen content is also indicated where available. It is clear that the presence of N₂ (or NbN, if it forms) has no substantial effect on the critical temperature, especially in absence of σ -phase, i.e., in the range of $x = 20$ to 40 cm. From this point of view the use of nitrogen-doping to enhance flux pinning raises no objections.

4.5 Effects of Carbon-Doping

Background information on the carbon-doping is given in Section 3. As in the case of nitrogen all the deposition experiments were performed at $T_d = 900^\circ\text{C}$ with a constant $s = 3.8$.

A summary of the critical temperature profile data, $T_c(x)$, is given in Table 4.4 for CO₂-doping and in Table 4.5 for C₂H₆-doping. The analyzed carbon contents are also indicated where available.

Table 4.4 shows a remarkable degradation of T_c which, although with fluctuations (probably due to an erratic incorporation of dopant), follows the trend of increasing CO₂ delivery rate.

Table 4.5 shows that C₂H₆-doping also results in degradation of T_c but less pronounced than in the case of CO₂. The reduction of T_c is not scaling clearly with the C₂H₆ delivery rate or carbon content. Hence, the C₂H₆-doping has been pursued in more detail in spite of the visibly erratic carbon incorporation.

4.6 Discussion

It was established prior to this program that CVD produces material with critical temperature onsets approaching 23K. Consequently, not much emphasis has been placed on achieving highest possible T_c . A realistic midpoint value of 21.0-21.5K is at present representative of "good" samples containing some σ phase (Tables 4.1, 4.2), and addition of gas impurities generally reduces that value to a lesser or greater extent (Tables 4.3-4.5). The width of the transition, ΔT , exceeds somewhat

that of sputtered samples, and remains a cause of concern. The problem manifests itself most dramatically in the discrepancy between T_c and T_c^* (Section 4.1 and Appendix V). It is the T_c^* value which is most relevant for high-temperature, high transport current application in transmission lines. The value of T_c^* is presently on the level of 17-19K at best, only a couple of degrees above that measured for Nb_3Sn . Increase of T_c^* up to, at least, 20K is desired. Unfortunately, no progress in this direction was accomplished in Phase II. It is believed that the broad transition reflects primarily an inhomogeneity of the Al5 phase composition, although local internal stresses associated e.g. with second phase particles might contribute as well. Some improvement in the Al5 phase homogeneity should be achieved through the implementation of the moving tape reactor (Section 2). It is not clear, however, whether this measure will be sufficient.

Can T_c of Nb_3Ge be increased further, i.e., above 23K? The preliminary low temperature annealing results by Blaugher⁽⁴⁾ need further verification but suggest that T_c onsets up to 25K might be possible. Significant reduction of stresses, and the resulting tetragonal deformation caused by thermal expansion mismatch with the Hastelloy substrate (Section 3) could also raise T_c by $\sim 0.5K$, as indicated by measurement of samples deposited on sapphire substrates. For practical conductor application, however, the deposit should be under considerable compressive stress, and Hastelloy B is still considered as a viable tape substrate.

Overall, a marginal increase of T_c onsets is, from practical point of view, of lesser importance than a reduction of the transition width and the difference between T_c and T_c^* .

4.7 References

1. R. D. Blaugher, R. E. Hein, J. E. Cox, and R. M. Waterstrat, Atomic Ordering and Superconductivity in Al5 Compounds, J. Low Temp. Phys. 1, 6, 539 (1969).

2. A. R. Sweedler, D. E. Cox, S. Moehleck, R. H. Jones, L. R. Newkirk, and F. A. Valencia, Superconductivity and Phase Stability of Nb_3Ge , J. Low Temp. Phys. 24, 5/6 (1976).
3. J. M. Poate, L. R. Testardi, A. R. Storm, and W. M. Augustyniak, ^4He -Induced Damage in Superconducting Nb-Ge Films, Phys. Rev. Lett. 35, 19, 1290 (1975).
4. R. D. Blaugher (Westinghouse Research Laboratories), private communication.
5. Appendix I, this report.

5. CRITICAL CURRENT DENSITY

5.1 Measuring Methods

The method of determining the critical current density, J_c , which has been the most used in this study is based on the magnetization measurement.

Magnetization has been measured using a Foner-type vibrating sample magnetometer (P.A.R. model 155). This type of measurement has been the most convenient to perform since very small, disc-shaped samples, 3 mm in diameter, could be used. The effect of sample composition variation with x (the position coordinate) was, therefore, minimized and nonambiguous characterization made possible. Experimental results and calculations discussed in Appendix 2 demonstrated that the method can be used for the J_c determination with the magnetic field, $H_{\perp}$, perpendicular to the disc sample face at field intensities from a few kilogauss up. Results given in Appendix 3 indicated that the sample damage, occurring when extracting discs from the tape, was causing a rather small J_c error, of no more than -15%. An additional convenience of the magnetization measurement has been the wide temperature range: from 4.2 K up to T_c , resulting from the use of a helium exchange gas cryostat. The accuracy of the temperature measurement was ± 0.3 K.

The most serious reservation against the magnetization method is that it would not permit direct determination of self-field $J_c(0)$, most relevant to the transmission line application. Indeed, once tapes are fabricated with their composition and properties truly uniform, test specimens of adequate length should be used to measure $J_c(0)$ by dc and ac transport methods. For the purpose of this study, however, the magnetization measurement proved invaluable. The $J_c(H_{\perp})$ characteristics were routinely measured between 5 and 65 kilogauss, and the value at 5 kG

was used as the representative low-field critical current density. The comparison with results of independent self-field transport measurements performed at LASL was made on LASL samples and one (w) tape ~20 cm long. The results are shown in Table 5.1.

Table 5.1
Comparison of Critical Current Densities from
Magnetization with the Self-Field Values
Measured at LASL (1)

Sample	Temperature T, K	Thickness h, μm	J_c (5 kG) A/cm^2	J_c (0) A/cm^2	$\frac{J_c(0)}{J_c(5)}$
47 - (w)	4.2	1.5	0.4×10^6	1.55×10^6	3.9
154M-12-LASL	4.2	19.5	0.85×10^6	$5 \times 10^6^*$	5.9
154M-12-LASL	13.8	19.5	2.15×10^5	1.1×10^6	5.1
274-B6-LASL	13.8	13.5	1.4×10^5	1.2×10^6	8.6

* Value scaled from the 13.8K point using the $J_c(T)$ dependence.

Depending upon the steepness of the $J_c(H_{\perp})$ curve in the low-field range, the self-field J_c at 4.2K is 3 to $\frac{1}{6}$ times that of the value at $H_{\perp} = 5$ kG. At 14K the ratio is 5 to 9. Samples having $J_c(5) = 2$ to $3 \times 10^6 \text{ A cm}^{-2}$ at 4.2K thus have $J_c(0)$ at least in the range of 6×10^6 to $1 \times 10^7 \text{ A cm}^{-2}$. At 14K samples with $J_c(5) = 0.2$ to $0.5 \times 10^6 \text{ A cm}^{-2}$ should have $J_c(0) = 1$ to $4 \times 10^6 \text{ A cm}^{-2}$.

An independent estimate of self-field J_c has been obtained also from 60 Hz ac loss measurements on samples having a sufficient flux pinning level to make low-field J_c nearly independent of the field intensity, $H_{||}$, parallel to the film plane. In such a case the Bean model of critical state (which assumes field-independent J_c)⁽²⁾ is approximately valid and gives:

$$J_c \text{ (A cm}^{-2}\text{)} = \frac{0.5}{12\pi^2} \frac{f \text{ (Hz)} \times H_p^3 \text{ (G}^3\text{)}}{p \text{ (}\mu\text{W cm}^{-2}\text{)}} \quad (5-1)$$

To estimate J_c we used Eq. (5-1) inserting $f = 60$ Hz, a peak magnetic field $H_p = 1777$ G (surface current density $\sigma = 1000$ A/cm,rms) and the corresponding loss per unit area, p , for samples obeying the relation $p \sim H_p^3$ up to at least 1000 A/cm.

5.2 Critical Current Density and Microstructure

Critical current density, $J_c(H, T)$, is an extrinsic characteristic of type II superconductors. It depends not only upon the intrinsic superconducting properties such as T_c , and the upper critical field, H_{c2} (T) but also upon the metallurgical microstructure of the material. The microstructure should provide a suitable spatial distribution of effective flux pinning centers. Grain boundaries, dislocations, nonsuperconducting impurities or voids, and other typical microstructural discontinuities or defects can be most effective as pinning centers if their size is of the order of magnitude of the coherence length which for Nb_3Ge is approximately $\xi_0 \approx 30 \text{ \AA}$. The defect spacing (dispersion) should, at any given temperature and field intensity, match the unit cell spacing of the fluxoid lattice. In single-phase Al5 compounds such as Nb_3Sn , grain sizes of the order of 1000 $\text{\AA}$ and below appear to be compatible with the lattice spacing since strong flux pinning is then observed. The Lorentz-force $F = J \times H$ which acts on the fluxoids is trying to break the pins and move the lattice. The stronger is the pinning, the higher

is the critical value of J at which the breakage occurs by one or another mechanism. Once this happens the fluxoid lattice flow takes place, and a voltage is generated across the superconductor. Resulting dissipation turns the material normal. An up-to-date review of the flux pinning problem is given in the recent book by Ullmeier.⁽³⁾

In this program the characterization of the microstructure has been performed mostly by scanning electron microscopy (SEM) of CVD film fractures and surfaces. Only towards the end of the program the development of a suitable sample thinning technique made possible the transmission electron microscopy (TEM) a few Nb-Ge deposits.⁽⁴⁾ Both methods produced grain size estimates which are in semi-quantitative agreement. The TEM and electron diffraction also permitted detection of the dispersed σ -phase (Nb_5Ge) and of impurities such as unreduced chlorides. The method used is described in Section 3 and the results of the σ -phase observation are discussed below.

5.3 Effect of σ -Phase

As already mentioned in Section 1, at the inception of this program (Phase II) the single-phase A15 material of a composition closest possible to stoichiometry, Nb_3Ge , was expected to support J_c 's higher than those of most early samples which typically contained the second phase, Nb_5Ge_3 (σ or T2) or were Ge-deficient. This belief was based on the observation that the microstructure of all CVD deposits was similar, independent of their composition whereas highest intrinsic properties, T_c and H_{c2} , would be characteristic of nearly stoichiometric, single-phase samples.

Systematic J_c measurements correlated with the results of X-ray phase analysis produced, however, a different picture. The second-phase-containing deposits had, as a rule, higher J_c 's than the pure A15 samples. This can be seen in Table I, Appendix 4. The table shows also that in the deposition temperature range $T_d = 750$ to 1000°C the variation in grain size, although significant could not offset the effect of the

σ -phase presence. In the whole temperature range the grain structure was relatively coarse, from a couple of thousands angstroms up to a few microns. It is thus conceivable that the mean spacing between grain boundaries was too large to offer an acceptable match with the fluxoid lattice. Typically, the pure Al5 deposits exhibited J_c 's less than $1 \times 10^6 \text{ A cm}^{-2}$, of the order of 10^5 A cm^{-2} to 10^4 A cm^{-2} at 5 kG, 4.2 K. The J_c 's in excess of $1 \times 10^6 \text{ A/cm}^2$ have been observed only for σ -containing samples, and were tentatively attributed to flux pinning on nonsuperconducting Nb_5Ge_3 particles dispersed in the Al5 matrix.

A closer correlation of J_c with the presence of σ -phase was possible by comparing the $J_c(x)$ and $a_o(x)$ profiles obtained for an appropriate range of $s = 3.8$ to 4.2 at $T_d = 900^\circ\text{C}$. Examples of such profiles are shown in Figure 5-1 (and Figure 1, Appendix 1). As discussed in Section 3, Nb_5Ge_3 (σ) is present in the x range where a_o is constant, and at least an upper limit to the σ -phase concentration can be estimated from the Debye-Scherrer patterns using powder standards. With increasing x , the ratio Nb/Ge increases in the deposit and the concentration of σ -phase decreases accordingly until it reaches zero. At this point a_o starts to rise. The Al5 composition closest to stoichiometry occurs at the knee of $a_o(x)$, marked $x = x_b$ in Figure 5-1. With increasing $a_o(x)$ the Al5 phase becomes increasingly Ge-deficient, and possibly nonuniform.

In Figure 5-1 $J_c(x)$ decreases with increasing x , i.e., with decreasing σ content. At $x = 0$, the upper limit to the σ -concentration is $10 \pm 5 \text{ vol. \%}$, a level apparently appropriate for obtaining high J_c 's, (see below). A local peak of J_c is usually observed at, or near $x = x_b$. This peak can be attributed to the trade-off between the decreasing level of pinning on the σ -phase, and improved properties of the Al5 matrix due to gradual reduction of internal strains, inhomogeneities, etc. when $x \rightarrow x_b$. For samples with low level of pinning at $x \approx 0$ the peak dominates the $J_c(x)$ curve, as it was expected before recognizing the role of σ -phase. Once $a_o > 5.15 \text{ \AA}$, J_c decreases again, probably due to the non-uniformity of the Ge-deficient Al5 phase. This result is in contrast to

Fig. 5-1 — Profiles of the critical current density, and cell edge, a_0 vs. the position coordinate, x , for 3 series of samples deposited at $T_d = 900^\circ\text{C}$.

the high T_c level maintained up to $\sim 5.17 \text{ \AA}$ (Section 4), and represents an argument against the contention that high T_c is an intrinsic property of Ge-deficient Nb_3Ge .

The $a_o(x)$ and $J_c(x)$ profiles for films deposited at T_d other than 900°C were investigated to much lesser extent. At 750°C the determination of a_o was usually impossible due to line broadening and presence of unreduced chlorides. At 1000°C the X-ray patterns were dominated by lines attributed to the diffusion layer. However, as discussed in Section 3, evidence was found that between 800 and 1000°C the $a_o(x)$ profiles (for appropriate s) qualitatively resembled those of Figure 5-1 with $x_b = 20$ to 30 cm . The compositional variation was less pronounced at lower, and more steep at higher T_d 's reflecting the temperature dependence of chloride chemical activity, and the resulting differential depletion. Correspondingly, the $J_c(x)$ profiles were also similar as shown in Figure 5-2 for $T_d = 750$ and 950°C . The generally very low J_c 's for 950°C (and 1000°C) were attributed to nickel diffusion from the substrate (Section 3).

Could s be set such that σ -phase would be present at a low level over the whole length of the deposit to achieve a relatively uniform J_c profile? Yes, at least at temperatures below 900°C . Figure 5-3 shows remarkably flat $a_o(x)$ and $J_c(x)$ profiles at 850°C which illustrates this possibility.

What is the optimum concentration of σ -phase to achieve high J_c ? No definite answer to this question could be found. Figure 5-4 shows the maximum achieved J_c vs σ -phase concentration (upper limit) which implies that the optimum resides at $\sim 5 \text{ vol. \%}$. However, the effectiveness of pinning depends upon the σ -particle size and spacing. Both can vary for any given concentration, depending upon the process parameters. The TEM analysis of sample 201-4 ($x \approx 0$, in Figure 5-1) indicated a mean σ -particle size of $600 \text{ \AA}$ with an average spacing of $1600 \text{ \AA}$. The particles are both, intragranular and located at grain boundaries of the Al_5 matrix. Figure 5-5 shows the pertinent photomicrograph and

Fig. 5-2 — Profiles of critical current density, J_c , vs position coordinate, x , for $T_d = 750^{\circ}C$ and $950^{\circ}C$. Samples containing σ -phase at $x \approx 0$.

Fig. 5-3 — Profiles of cell edge, a_0 , and critical current density, J_c , at $T_d = 850^\circ\text{C}$. Series 372 - low σ concentration.

Fig.5-4—Maximum achieved critical current density vs the upper limit σ phase concentration. Samples from runs 279, 206, 201.

a

b

Fig. 5-5 TEM micrograph of (a) single phase Al5 (Sample 244-5, $T_d \approx 950^\circ\text{C}$) and (b) Al5 + σ (Sample 201-4, $T_d \approx 900^\circ\text{C}$).

compares it with the single Al5-phase microstructure. The concentration of σ -phase in 201-4, as determined using a microscopic feature counter and area integrator (Zeiss Classimat) was found to be 9 to 11 vol. %, in remarkable agreement with the X-ray estimate of 10 ± 5 vol. %. Unfortunately this is the only available σ -phase analysis at this time so that the effect of varying the process parameters upon the σ -phase dispersion remains unknown. All that can be said is that at the level of several volume percent the presence of σ -phase particles is associated with enhanced pinning of the fluxoid lattice, and that the size of these non-superconducting particles is comparable to the grain size of sputtered single-phase Nb_3Ge deposits having high J_c 's.

All the above results were obtained at 4.2 K. However, temperature dependences of J_c have been determined for (1) σ -phase containing samples, (2) the Al5 near stoichiometry, and (3) those Ge-deficient. For (1) and (2) $J_c(T)$ are similar, and are discussed in Appendix 5. A comparison of (2) and (3) is given in Appendix 1.

5.4 Effect of N_2 -Doping

Background information on N_2 -doping is given in Section 3 whereas critical temperature data are presented in Section 4.

Figure 5-6 shows the correlation of nitrogen content, $a_o(x)$ and $J_o(x)$ profiles. Highest J_c 's are observed near $x = x_b$, i.e., for the composition free of σ -phase and closest to stoichiometry. The pinning effect of σ -particles does not appear to be additive. The critical current densities of Ge-deficient samples are higher than in the absence of doping. This last result suggests that the very low J_c 's found in Ge-deficient, undoped samples could, at least in part, be attributed to low levels of flux pinning rather than to the Al5 phase nonuniformity (see also Section 6.3).

Nonambiguous correlation of J_c with the N_2 -concentration is difficult since it requires untangling of the combined effects of σ -phase, nitrogen and Al5 composition. The amount of analytical data collected

Fig. 5-6 — Profiles of the critical current density, J_c , cell edge a_0 , and nitrogen concentration vs the position coordinate, x . Series 310.

is limited (Table 4.3), and the sensitivity of the x-ray powder method of σ -phase determination is low, 2-3 vol %, so that meaningful amounts of σ -phase may remain undetected. Limiting the attention to presumably σ -free samples at $x = 20$ to 30 cm one obtains a tentative dependence of J_c upon the nitrogen content shown in Fig. 5-7. The highest $J_c \approx 1.8 \times 10^6 \text{ A cm}^{-2}$ at 5 kG, 4.2K was obtained at a concentration of $N_2 \approx 0.2 \text{ wt.}\%$ (samples 310-9). This J_c value is close to the highest recorded for σ -containing samples deposited at the same temperature, $T_d = 900^\circ\text{C}$. The TEM photograph of the sample, shown in Fig. 5-8, is different from those shown in Fig. 5-5. The structure is characterized by numerous faults, and strings of small precipitates which are present along the grain boundaries as well as within the grains. Since x-ray diffraction indicated the presence of niobium nitrate in samples with highest content of nitrogen, the precipitates are thought to be NbN particles. Whether flux pinning occurs directly on NbN remains to be established.

5.5 Effect of Carbon-Doping

The CO_2 -doped samples exhibited generally low critical current densities, below $6 \times 10^5 \text{ A cm}^{-2}$ at 5 kG, 4.2K. The highest value could be attributed to the presence of σ -phase. At $x \approx 20 \text{ cm}$, J_c was typically 0.4 to $2 \times 10^5 \text{ A cm}^{-2}$. The observed $J_c(x)$ profiles were similar to those of nitrogen-doped samples.

High critical current densities were observed in C_2H_6 -doped samples incorporating 0.2-0.5 wt.% of carbon. However, only few such samples have been successfully prepared, since they were very brittle and easily spalled from the substrate. Values of J_c between 1.0 and $2.3 \times 10^6 \text{ A cm}^{-2}$ at 5 kG, 4.2K were measured in the above carbon concentration range. This is again the level of J_c comparable to that of σ -doped samples. The number of prepared samples was insufficient to establish a tentative correlation of J_c with the carbon content. The highest J_c value was obtained at 0.3 wt.% ($\sim 8.0 \text{ mole } \%$). Preparation

Fig. 5-7 — Critical current density and critical temperature vs the nitrogen content

Fig. 5-8. TEM micrograph of sample 310-9 doped with 0.2 wt% N_2 .

of TEM samples was difficult due to the brittleness of the material, and no microphotographs were available at the time of this writing. As already stated in Section 3, the presence of niobium carbide was indicated by x-ray diffraction. The erratic carbon incorporation, and the observed brittleness make C_2H_6 -doping less attractive than N_2 -doping.

5.6 Discussion

The results of the J_c investigation demonstrate clearly that the material grown by CVD in the temperature range between 750 and 1000°C can exhibit high J_c at low (and high) fields only if additional flux pinning centers are provided by means of doping. The incorporation of a few vol % of σ -phase, or of impurities such as niobium nitrate or niobium carbide, results in J_c values comparable to those of Nb_3Sn at 4.2K, and considerably higher than for Nb_3Sn at 14K. These values should not be regarded as ultimate since the uniformity of Nb_3Ge deposits needs further improvement, and more effective distributions of flux pinning centers could probably be obtained as a result of continuing investigation.

5.7 References

1. L. R. Newkirk (LASL), private communication.
2. C. P. Bean, Magnetization of High Field Superconductors, Rev. Mod. Phys. 36, 1, 31 (1964).
3. Ullmeier, Irreversible Properties of Type II Superconductors, Springer-Verlag, Berlin-New York (1975).
4. A. T. Santhanam and P. M. Yuzawich, Revealing the Microstructure of Nb_3Ge Superconducting Films by Transmission Microscopy, submitted for publication in J. Mat. Sci.

6. THE AC LOSSES

6.1 Measuring Methods

The ac loss measuring methods were reviewed in the Final Report, Phase I of this program.⁽¹⁾ In Phase II use has been made mostly of the short sample (≤ 5 cm) test method^(1,2) to minimize the effect of the compositional nonuniformity of tapes. Tape lengths of ~ 30 cm would be required for the shorted-turn superconducting transformer measurement.^(1,3) Measurements have been performed at 4.2K, 60 Hz, in the field range up to $H_{||} = 2$ kG peak equivalent to the rms surface current density of $\sigma \sim 1125$ A/cm. The ac field was generated by a superconducting solenoid. Model IH-744 low power factor wattmeter, constructed by BNL, was used to measure losses. The results were always expressed as loss per unit surface, p , in $\mu\text{W}/\text{cm}^2$. The temperature dependences $p(T)$ up to the vicinity of T_c were determined by magnetometer.⁽¹⁾

6.2 Effect of Sample Configuration

The standard sample configuration used is shown in Fig. 6-1a: a 1.27 cm (0.5 inch) wide, 2.5 to 5 cm long tape with the Nb-Ge superconductor deposited on one side of a metallic substrate, typically Hastelloy B, of ~ 50 μm thickness. In such configuration the ac loss measured in externally applied field, $H_{||}$, parallel to the major or minor axis of the tape represents a sum of superconductor and substrate losses. In sufficiently low fields the loss components are (Fig. 6-1):

1. Hysteretic surface current losses in the superconducting film surface, $p_1 \sim H_{||}^3$.
2. Hysteretic surface current losses in the superconductor interface with the substrate, $p_2 \sim H_{||}^3$.

3. Eddy current losses in the substrate, $p_3 \sim H_{||}^2$.

4. Hysteretic losses in the substrate, if ferromagnetic (case of Hastelloy B) $p_4 \sim H_{||}$, or superconducting (case of niobium) $p_4 \sim H_{||}^3$.

It was shown by Bussire and Suenaga that after a suitable surface treatment the losses in Nb_3Sn can be extremely low in fields below the surface barrier field, ΔH , having a magnitude of several hundred A/cm.⁽⁴⁾ For $\sigma = 500$ A/cm, rms losses $\sim 1 \mu W/cm^2$ have been observed, an order of magnitude below the pre-treatment value. At higher fields, however, well above ΔH , the losses were not affected by the treatment. Analogous results were recently obtained for Nb_3Ge by Thompson *et al.*⁽⁵⁾ In both cases tubes with a superconducting layer on the outer surface have been employed (the Kim tube configuration) so that the magnetic flux was excluded from inside of the sample, its interface with the substrate, and the substrate itself. Hence, only the outer surface losses have been measured.

The tape configuration closest to that of the Kim tube consists of a substrate coated on all surfaces, i.e., around-the-edge, as shown in Fig. 6-1b. The low-loss Nb_3Sn tapes fabricated by liquid or bronze diffusion on both sides of the substrate approach this geometry even without an around-the-edge coating, at least below $\sim 8.5K$, since the supercurrent, I , (Fig. 6-1) can circulate through the superconducting edge of the niobium substrate.

For the double-helix SPTL cable the flux exclusion from the substrate, and the superconductor/substrate interface, is a necessity since the magnetic field is present on both sides of the tape.⁽⁶⁾ The short sample measurement thus represents an appropriate test of the tape suitability for double-helix cable application. However, for determining the surface current losses in one-side coated tapes the shorted turn transformer (or hairpin) configuration should be used since the field is confined there to one side of the sample. At the inception of Phase II the predominant use of the shorted-turn transformer measurement was

LOSS COMPONENTS:

1. Superconductor - surface
2. Superconductor/substrate interface - diffusion boundary
3. Substrate - eddy current
4. Substrate - hysteretic

Fig. 6-1 - Sample geometry and loss components

indeed planned. Once the longitudinal nonuniformity of $J_c(x)$ was observed, the use of ~30 cm long tape samples became unacceptable, and the short sample test remained as the only practical one. Earlier observed severe discrepancy between the short sample and transformer results⁽¹⁾ was now easily explained by the longitudinal nonuniformity.

Attempts to fabricate around-the-edge coated tapes 3 and 6 mm wide have been unsuccessful, as discussed in Section 2. Hence, total losses $p = p_1 + p_2 + p_3 + p_4$ have been measured.

The routine measurements of the total loss were more relevant at higher field amplitudes where $(p_3 + p_4)$ contribution should be relatively small since its exponent in the $p \sim H^n$ relation is low, $1 < n < 2$, for a nonsuperconducting substrate.

Attempts were made to estimate indirectly what loss components are dominant, and what is the order of magnitude of surface current losses at low fields. Deposition on niobium substrates has also been employed for that purpose. The results are discussed in Section 6.4, after reviewing in Section 6.3 the effect of composition and doping. For convenience the field intensity $H_{||}$ is everywhere expressed by the surface current density σ , although this is not physically correct in case of partial flux penetration, or in case of nonsuperconducting substrate material measurement.

6.3 Effect of Composition and Doping

Figure 6-2 shows three $p(\sigma)$ curves representing the three characteristic groups of samples:

a) The two-phase (Al5 + σ) deposits which exhibit high J_c not very dependent upon the field intensity conform approximately to the Bean model of critical state, and $p \sim \sigma^3$ ($n \sim 3$). For such samples losses are inversely proportional to, and scale well with, J_c as shown in Fig. 6-3. The behavior of flux-pinned, high J_c material is nearly identical for σ -, and N_2 -doped samples. This is illustrated in Fig. 6-4.

Fig. 6-2 — Three types of loss, p , vs surface current density, σ , dependences. Critical current densities were determined from magnetization @ $H_1 = 5 \text{ kG}$

Fig. 6-3 -Correlation between the 60 Hz ac loss and the dc critical current density for A15 + σ samples

Fig. 6-4 - Loss curves of high - J_c samples with various dopants

b) The single phase Al5 deposits close to stoichiometry which have lower J_c 's significantly decreasing with increasing σ conform to analytical loss models assuming a J_c variation with the field intensity. As a result of the J_c decrease one expects and observes $n > 3$.^{*} At relatively low σ , between 500 and 1000 A/cm, the slope of the $p(\sigma)$ curve decreases and $n \rightarrow 1$ indicating a premature flux penetration due to insufficient pinning. In the flux penetration range the losses do not scale with J_c .

c) The single phase Al5 deposits which are Ge-deficient ($a_o > 5.15 \text{ \AA}$), and have low J_c even more field dependent than (b), do not conform to analytical loss models. The exponent n is much less than 3, although higher than one. A plausible explanation of such behavior is that the flux pinning is so ineffective that a partial flux penetration starts at a very low field level, just above $H_{c1} \approx 100 \text{ A/cm, rms}$. An alternative hypothesis would invoke the Al5 phase inhomogeneity such that with increasing field intensity a decreasing fraction of surface remains superconducting and contributes to losses.

A profile $n(x)$, correlated with the $a_o(x)$ curve in Fig. 6-5, summarizes the effect of compositional variation along the deposition zone where all three types of sample loss behavior are represented. Figures 6-2 and 6-5 explain convincingly the discrepancy between loss data obtained in Phase I for $\approx 30 \text{ cm}$ long tapes and a 3-5 cm section cut from one end of the tape.

* In the so-called " α -model" $J_c = \frac{\alpha}{H}$. As a consequence, the calculated $n \approx 4$. In general, if $J_c = \frac{\alpha}{H^m}$, then $n = 3 + m$.

Fig. 6-5 — Profiles of the field power exponent, n , and cell edge, a_0 , vs the position coordinate; series 201.

The results shown and discussed above were all obtained for films deposited on Hastelloy B. Since the character of the $p(\sigma)$ curves is clearly determined by the superconductor, the substrate contribution ($p_3 + p_4$) should not be qualitatively important. Figure 6-6 shows the $p(\sigma)$ curves for a bare Hastelloy B substrate determined electronically and from magnetization measurements in perpendicular field. The magnetometer measures only hysteretic losses, p_4 , and, accordingly, $n \approx 1$. However, the electronic measurement gave an average n close to $n \approx 1.5$, suggesting that the eddy current loss component, p_3 , is not negligible, in spite of the relatively high resistivity of the alloy, $\rho_{25} \approx 100 \mu\Omega\text{cm}$. Eddy current losses calculated for this ρ_{25} value (50 μm thickness, $\mu/\mu_0 = 1$) are an order of magnitude lower. It is possible, therefore, that the eddy component comes from the pickup coil. The sum $p_3 + p_4$ is low, but sufficient to obscure the presence of a surface barrier in the low field range. At $\sigma = 500 \text{ A/cm}$, 4.2K, losses measured on various Hastelloy pieces were 5-10 $\mu\text{W/cm}^2$, thus representing the level specified by BNL for the total composite superconductor tape ($p \leq 10 \mu\text{W/cm}^2$). As expected, the substrate contribution can be neglected in higher fields of the order of 1000 A/cm, where it represents 5-10% of the total. Hence, at higher fields the measured $p(\sigma)$ curves such as those of Fig. 6-2 reflect the behavior of the superconductor, i.e., $p \approx p_1 + p_2$. A significant correction would be required only in case (c), which is of no practical significance.

For flux-pinned samples having high J_c 's, the losses ($p_1 + p_2$) at 4.2K lie in the range of 35-100 $\mu\text{W/cm}^2$, about an order of magnitude above the specified limit of 10 $\mu\text{W/cm}^2$. The lowest loss value was determined for sample 279-12 which was deposited at 750°C, and where Ni-diffusion from Hastelloy B to form the potentially lossy (p_2) boundary layer was less pronounced than at higher deposition temperatures.

A first attempt to separate p_1 and p_2 was made by polishing the top surface of a high- J_c sample (204-5). After the polishing the surface was etched following the LASL recipe⁽⁷⁾ used successfully in

Fig. 6-6 — The 60 Hz losses in Hastelloy B from magnetization and ac measurement.

Ref. 5. If $p_1 \approx p_2$, then a loss reduction of $\leq 50\%$ could be expected in low fields, below ΔH . No reduction in losses was, however, observed within the accuracy of the measurement. Sample annealing at 800°C for 15 min. also didn't produce any loss reduction.

Although it is possible that the surface treatment was simply ineffective in enhancing the surface barrier, in contrast to the data of Refs. 4 and 5, the absence of any loss reduction may also be interpreted as indicating $p_1 \ll p_2$. In this case further changes in p_1 would have a negligible effect on the sum, $p_1 + p_2$.

It is worth noting that the J_c and $p(\sigma)$ of sample 204-5 are of the same magnitude as for the Nb_3Ge material deposited at LASL and measured in the flat sample configuration of Fig. 6-1a.⁽⁸⁾ Analogous LASL material when deposited in Kim tube configuration has shown lower losses, and responded to the surface treatment.

6.4 Losses in Tapes on Niobium Substrates

A natural way to determine surface losses p_1 at 4.2K without the p_2 and substrate components, would be to deposit the superconductor on both sides of the niobium substrate. Even if coating around the edge isn't achieved, the resulting sandwich configuration should be equivalent to that of the Nb_3Sn tape where the supercurrent closes through Nb, as discussed in Section 6.2.

In Runs 367, 368, and 370 deposition on ~ 6 mm wide Nb-1% Zr tape was performed at $T = 900^\circ\text{C}$, $s \approx 3.8$, and losses were measured. The results are shown in Fig. 6-7 which compares losses in samples of the 3 types discussed in Section 6.3, i.e., Al5 + σ (a), Al5 (b), and Ge-deficient Al5 (c). In each case p was calculated assuming that losses occur on external surfaces only. Curve (a) shows straight line behavior, $n \approx 3$, but the level of losses is more than twice that of samples on Hastelloy B. Shape of curves (b) and (c) strongly implies superposition of Nb-Ge losses (with the characteristic flux penetration knee) and

Fig. 6-7 - Loss curves for three types of Nb-Ge sandwich deposits on Nb-substrate tape.

losses in the niobium substrate. Above the knee total losses (b) and (c) are identical. Results of Fig. 6-7 suggest that the supercurrent does not close through niobium, and the measured losses represent the sum $p = p_1 + p_2 + p_4$ where $p_4 \sim H^n$ with $n \geq 3$.

That this is the case was demonstrated by mechanically removing the Nb-Ge from one side of the tape (samples 367-5,6). The losses after removal equaled to 0.6-0.7 of those in sandwich configuration calculated per unit of external surface. It can be easily shown that this result defines uniquely the case of separate supercurrents in the two external layers of the sandwich and in the substrate. Evidently, a normal layer at the Nb-Ge/Nb interface prevented the circulation of the supercurrent across Nb. Since the Nb-Zr tape was not etched prior to deposition, it is probable that NbO was the culprit. Change in the loss ratio* vs. σ indicated that the contribution of Nb to the total loss became dominant at higher fields.

Splitting similar sandwich tapes (#370-6,7) longitudinally did not produce any loss change at higher fields. Since eddy current losses in the sandwich substrate are proportional to square of the tape width,⁽⁶⁾ the eddy current contribution to Nb-losses must be small.

It is clear from the above that the experiments with Nb-substrates failed to separate p_1 from p_2 . In the absence of other evidence the surface treatment experiment of Section 6.3 represents, therefore, the only available indication that $p_1 \ll p_2$. Unambiguous determination of p_1 will become possible when either coating-around-the-edge succeeds, or longer uniform tapes become available.

* Ratio of losses before and after removal of one layer.

6.5 Temperature Dependence of Losses

Since it was assumed that the measured losses are dominated by loss components p_2 to p_4 which are not representative of the Nb_3Ge surface, no special effort was made to measure $p(T)$. In a few cases the temperature dependence of losses was deduced from magnetometer measurements. For an undoped Al5 sample the $p(t)$ curve was flat up to $t = 0.3$ and then gradually decreased with temperature (sample 201-9). For Al5 + σ $p(t)$ increased up to $t = 0.7$ and then decreased abruptly (sample 201-5).

6.6 Discussion

The results presented demonstrate clearly that the goal of Nb_3Ge tape ac loss reduction was not achieved due to the coating geometry, and longitudinal uniformity constraints. The ac losses of the Nb_3Ge material itself could not be even measured nonambiguously due to the presence of additional loss components. In retrospect, the approach of the LASL group to characterize the material using tubular specimens⁽⁵⁾ was more rewarding than the head-on attack on the practical tape conductor adopted in this study. The LASL result proved invaluable in demonstrating that Nb_3Ge material losses can be extremely low when measured in appropriate form. On this basis one can predict with assurance that the around-the-edge coated Nb_3Ge tapes will eventually have very low ac losses.

6.7 References

1. A. I. Braginski et al., An Improved Superconductor for Transmission Line Applications, Phase I, Final Report, ERDA No. C00-2522-1 (1975).
2. O. Horigami, J. F. Bussière, and Y. Tanaka, AC Losses of V_3Ga Tapes, Cryogenics 15, 660 (1975).
3. E. B. Forsyth and G. M. Morgan, A Transformer for Measuring 60 Hz Loss, Cryogenics 14, 316 (1974).

4. J. F. Bussière and M. Suenaga, Reduction of AC Losses of Nb_3Sn by Surface Treatment, J. Appl. Phys. 42, 707 (1976).
5. J. D. Thompson, M. P. Maley, L. R. Newkirk, and F. A. Valencia, Measurements of Low Hysteretic Losses in CVD Prepared Nb_3Ge , LASL preprint LA-UR 76-555.
6. M. Garber, J. Bussière, and G. Morgan, Design of Double Helix Conductors for Superconducting AC Power Transmission, IEEE Trans. MAG-12 (1976) -- in press (Proc. 1976 Joint MMM-Intermag Conference).
7. L. R. Newkirk (LASL) -- private communication.
8. Y. B. Kim and K. S. Kim, Reduction of AC Losses in High Temperature Superconductors, Final Report EPRI TD-136, Project 7845 (April 1976).

7. EXPERIMENTS WITH THE MOVING TAPE REACTOR

7.1 Preliminary Experiments

The assembled reactor system, described in Section 2, was debugged by gradually eliminating numerous gas leaks. A satisfactory solution for tightening moving tape parts (vapor locks, Figure 2-10) was eventually found by filling the split-flow locks shown in Figure 7-1 with sponge rubber seals. The tape moves freely through the parts with only 2 l/min. of helium per lock needed to prevent any detectable in-leak of air.

Desired temperature profiles were established by trial-and-error.

Depositions on stationary Hastelloy B tape 1.27 cm wide were performed at $T_d \approx 850$ and 820°C in conditions $s = 3.8$ to 5 , $r = 200$ and geometry (one-side coating) used in the previous reactor. The results were standard with regard to rate, phases deposited and cell edge value (for $\text{Al}_5 + \sigma$, $a_o = 5.144 \text{ \AA}$, run 381).

On this basis the conclusion was reached that the previous synthesis conditions are restored, and the reactor is ready for moving tape experiments (without tape heating by current).

In preparation for the experiments the inner diameter of the deposition zone liner quartz tube was increased from ~ 22 to ~ 35 mm to improve chances for coating around-the-edge, as discussed in Section 2. The stainless steel tracks (Figure 7-2) were then installed such that the "window" between the tracks, where deposition would take place, was 15 cm long. In runs #391 and 393 the 6 mm wide tape was driven with an average speed of 0.6 m/hour over a period of three hours to coat ~ 1.8 m (6 ft.) of substrate on both sides and, hopefully, around the edge. The deposition temperature was $T_d = 820^\circ\text{C}$ and the ratio s set to obtain pure Al_5

Fig. 7-1 Section and general view of the split-flow vapor lock.

Fig. 7-2 Photograph of a 321 stainless steel track after a series of deposition runs.

phase. Since a_o provides a convenient measure of the deposit composition in absence of σ -phase, deposition of pure Al5 constituted a good tape uniformity test.

The tape coated in both runs was considerably warped and discolored, at the start, and became gradually better looking with increasing deposition time. The X-ray photograph indicated very diffuse Al5 back reflection lines with enormously high cell edge, gradually decreasing with coating time, i.e., with the coated tape length, l :

$$a_o \approx 5.31 \text{ \AA} \quad \text{at } l = 75 \text{ cm}$$

and
$$a_o \approx 5.24 \text{ \AA} \quad \text{at } l = 165 \text{ cm}$$

These a_o values exceed those found in the binary Nb-Ge system, and must reflect, therefore, the presence of a considerable amount of some impurity(s). Suspicion arose that the stainless steel track which has shown considerable signs of chemical attack could be the source of impurities (as the track was gradually coated with Nb-Ge the gas phase contamination would decrease in time). The track preceding the deposition zone (i.e., the window) was thus replaced with a purged silica tube.

In a stationary tape short run (#394), the single-phase Al5 deposit had $a_o \approx 5.148 \text{ \AA}$. Hence, the stainless steel track was the major source of contamination.

The composition was then readjusted, by varying s , in a semi-stationary run #395. During deposition the tape was stationary, but after completion of the coating at a given s the tape was moved out of deposition zone, prior to any readjustment of s . A new s value was then set, and after 10 min. of gas phase equilibration a new segment of tape was again exposed to the coating atmosphere. A single-phase Al5 tape section #395-50 with $a_o \approx 5.150 \text{ \AA}$ had $J_c \approx 0.7 \times 10^6 \text{ A cm}^{-2}$ at 4.2 K, 5 kG. This is a record high J_c for that Al5 composition indicating that the deposit uniformity along the normal to the tape plane was better than in typical

stationary experiments where composition necessarily varied during start and shut-off procedures thus resulting in layered deposits.

Since the results of the above run were satisfactory with regard to the properties of Al₅ phase, the final two moving tape experiments were performed (#396 and 397). In run #396 a very short deposition zone of 5 cm was set. The resulting thickness of the Nb-Ge deposit varied between 0 and 1 μ m and was therefore difficult to characterize (in particular, no X-ray results could be obtained). The J_c level could only be estimated, due to thickness nonuniformity and was comparable to that of run #395.

In the final run #397 the deposition zone was expanded to 15 cm to obtain a thicker deposit. The X-ray results showed the presence of two Al₅ phases thus indicating that the compositional variation along the 15 cm deposition zone was excessive. No additional characterization of the #397 tape was therefore performed.

The data on the deposits thickness uniformity are given in the next section.

7.2 Deposit Thickness Nonuniformity

Two types of tape nonuniformity are of interest:

1. The phase uniformity or micro-nonuniformity (homogeneity) and
2. The uniformity of coating and composition, i.e., the macro-nonuniformity.

The deposit micro-nonuniformity over an arbitrarily small area or volume can result from local fluctuations (ripples) of gas phase composition in space and time, even at a constant delivery rate and average gas phase composition. It can be further accentuated by the solid phase instability, dispersion of a second phase, etc. This micro-nonuniformity of Nb₃Ge deposits can at present be evoked as a speculative

concept useful in explaining some of the observed Al5 phase characteristics such as x-ray line broadening, wide superconductive transition and the discrepancy between T_c and T_c^* , high T_c of Ge-deficient deposits, etc. In the present work the micro-nonuniformity could not be characterized nonambiguously because of the superposition of macro-nonuniformity effects.

The macro-nonuniformity of deposits results from (1) space- and time-variations in the vapor components delivery, which cause changes in average gas composition, (2) flow geometry (aerodynamic) effects, and (3) from differential gas phase depletion which produces compositional profiles discussed in previous sections. The measurement of the deposit thickness along the tape which was moved through the deposition zone can provide information about (1) and (2) while x-ray diffraction results reflect the effect of (3) as shown in Section 7.1.

Table 7.1 shows thickness measurement results for tapes #391 and #397 prepared with a 15 cm "window" before and after the elimination of stainless steel tracks. The tapes were cut in 15 cm intervals, micrographic sections prepared, and thickness measured optically. For tape #391 the measurements were made in the center of each side coating (top and bottom side, since the tape was positioned and translated in horizontal plane). For tape #397 measurements were made also at the edges.

The results can be summarized as follows:

- (1) The average deposit thickness on top side (center) is about twice the thickness of the bottom layer.
- (2) Thickness at the edges is twice or more that at the center.
- (3) Thickness on both sides varies $\pm$ 30-50% along the length of the tape.

While (1) and (2) are geometry-related effects, (3) can be caused both by geometry (tape warping), and by delivery rate fluctuations in time.

Table 7.1

Thickness Uniformity of Moving Tape, h, in μm

Run No. 391			Run No. 397						
Position ℓ cm	Side 1 (top) Center	Side 2 (bottom) Center	Position ℓ cm	Side 1 (top)			Side 2 (bottom)		
				Edge 1	Center	Edge 2	Edge 1	Center	Edge 2
15.0	3.4	2.0	15.0	7.2	3.2	9.5	4.3	1.5	6.6
30.0	3.9	2.4	30.0	6.8	3.9	7.0	6.6	2.4	5.0
45.0	5.6	2.4	45.0	10.6	4.3	8.8	8.7	2.8	5.9
60.0	4.9	2.4	60.0	12.0	4.9	8.8	10.5	3.5	5.8
90.0	4.4	2.7	75.0	12.8	4.6	10.6	11.0	3.5	7.1
120	4.1	2.0	90.0	15.0	5.5	11.7	12.1	4.3	7.6
135	3.4	1.0	105	12.3	4.9	10.6	9.5	2.2	7.9
150	4.4	1.0							
Average	4.3	2.0	Average		4.5			2.9	
Stand.Dev.	0.74	0.65	Stand.Dev.		0.70			0.95	
Tolerance	-20% +30%	-30% +50%	Tolerance		-30% +10%			+50%	

The data of Table 7.1 should be considered as negative, and indicating the need for tape heating by current. Once geometry effects are minimized, it will be possible to assess the effect of delivery fluctuations. This work is to be conducted in the next phase of the program.

Coating around the edge was achieved in several tape sections, as indicated in Section 2.5.

8. CONCLUSIONS

1. The following goals of the modified tasks of Phase II have been achieved:
 - (1) the enhancement of the critical current density of Nb_3Ge by doping with Nb_5Ge_3 , nitrogen or carbon,
 - (2) the design, construction and successful test of a moving tape reactor capable of producing lengths of tape conductor.
2. The understanding of the Nb-Ge phase relations and of Nb_3Ge current carrying properties has been improved thus laying ground for the fabrication of long tape conductors having high critical currents and low ac losses. Progress was made, therefore, towards the stated objective of the program.
3. The original specific goal of fabricating composite Nb_3Ge tape conductor sections having high critical current and low ac losses was not attained since the suitable CVD system needed for fabrication became available only at the termination and as a result of Phase II. Further work is, therefore, necessary.

9. RECOMMENDATIONS

1. Continue the development of Nb_3Ge composite tape conductor for ac transmission line application to a point where a short coaxial cable test of the conductor will become possible.
2. Concentrate on achieving low ac losses in the tape geometry, and on improving the tape uniformity prior to fabricating long Nb_3Ge tape conductors for the coaxial test.
3. Approach the goal of loss reduction and uniformity improvement by studying deposition of Nb_3Ge in a moving tape CVD reactor with a provision for electric current heating of the substrate.

10. ACKNOWLEDGEMENTS

The authors acknowledge the help and advice offered by members of the staff of the Brookhaven National Laboratory, and particularly, by E. B. Forsyth, D. Gurinsky, M. Garber, and J. Bussire. Friendly information exchange and cooperation offered by L. R. Newkirk and his colleagues at Los Alamos Scientific Laboratory was invaluable for the progress of this work.

Sincere thanks are due to M. T. Miller, P. A. Piotrowski, H. C. Pohl, R. P. Storrick, and P. M. Yuzawich who offered technical help and expertise. A. L. Foley contributed significantly to the design of the moving tape reactor, C. Cook and R. Darby fabricated tape substrates, R. W. Palmquist performed the microprobe analysis, C. W. Hughes the SEM, K. W. Guardipee the vacuum fusion analysis, J. Hrizo the SSMS and J. J. Schreurs the Auger spectroscopy. Careful typing of this report was performed by Marilyn B. Warren and Cathie Kowalczuk.

APPENDICES

- I. "Preparation of Nb_3Ge by Chemical Vapor Deposition," by A. I. Braginski, G. W. Roland, and Michael R. Daniel, J. Appl. Polymer Science, 22 (1975).
- II. "Critical Current Determination from the Magnetization of Type II Superconducting Disc Samples," by Michael R. Daniel and M. Ashkin, published in Cryogenics (1976).
- III. "Observations of Damage to Nb_3Ge Tape during Sample Preparation," by Michael R. Daniel, Westinghouse internal memo 76-9C31-SULIN-M4 (1976).
- IV. "Critical Current Density and Flux Pinning in Nb_3Ge ," by A. I. Braginski, Michael R. Daniel, and G. W. Roland, to be published in the Proceedings of the 1976 MMM Conference.
- V. "The Temperature Dependence of J_c in Superconducting Nb_3Ge ," by Michael R. Daniel, et al., submitted to the Journal of Appl. Phys. (1976).
- VI. "Progress Toward a Practical Nb-Ge Conductor," by A. I. Braginski, et al., to be published in the Proceedings of the 1976 Applied Superconductivity Conference.

APPENDIX I

PREPARATION OF Nb₃Ge BY CHEMICAL VAPOR DEPOSITION

A. I. BRAGINSKI, G. W. ROLAND, and MICHAEL R. DANIEL

*Westinghouse Research Laboratories,
Pittsburgh, Pennsylvania 15235*

SYNOPSIS

Superconducting Nb₃Ge tape fabrication by chemical vapor deposition (CVD) and the relevant material properties have been investigated. The known phases in the Nb-Ge system are reviewed and a new tetragonal phase coexisting with the A-15 superconducting phase is reported. High superconducting transition temperatures, T_c , observed in Ge-deficient samples are tentatively explained by the A-15 phase inhomogeneity. Critical current densities of high- T_c samples measured in low and high magnetic fields confirm the technological potential of CVD-grown Nb₃Ge.

INTRODUCTION

Chemical vapor deposition (CVD) methods for the synthesis of A-15 superconducting compounds were originally developed by Hanak et al. [1] a decade ago. In a recent resurgence of interest, such techniques have been successfully adapted in several laboratories [2-8] to the synthesis of Nb₃Ge having the A-15 cubic structure and high superconducting transition temperatures ($T_c > 20K$) and, indeed, CVD technology is currently among the methods being evaluated for its potential to evolve Nb₃Ge from a laboratory curiosity into a technologically useful superconducting material. Other techniques, such as quenching from a melt or diffusion, have so far failed to yield high T_c although they have been successfully used for other A-15 materials such as Nb₃Sn.

The intent of the present work is to report on the material properties of our CVD Nb-Ge films and to discuss the influence of depositional parameters on the obtained deposits. Such data are critical to defining growth parameters yielding high T_c Nb₃Ge films in a routine fashion. More importantly, however, they can lead to enhanced understanding of the crystal chemistry and phase chemistry of the Nb-Ge system in general. This information is particularly important at low temperatures, i.e., below 1000°C, where any commercially practical synthesis of Nb₃Ge is likely to be carried out, either by CVD or some other technique.

PREPARATIVE TECHNIQUES

The CVD technique as we use it was recently described [7] so that only a brief description is repeated here. Our system was designed to fabricate

superconducting tape sections on metallic substrates 30-50 cm long. The process involves direct chlorination of Nb and Ge to NbCl_4 and GeCl_2 with subsequent reduction of the chloride gas mixture by hydrogen to form metallic deposits. Chlorination, gas mixing, and reduction proceed in a resistively heated quartz glass reactor operating at atmospheric pressure. The block diagram of the system is shown in Figure 1. The two critical stages of the reactor are the deposition zone, specifically designed to provide a $\pm 5^\circ\text{C}$ uniform temperature zone over 30-50 cm, and the gas-mixing zone, which must be held low enough in temperature to prevent hydrogen reduction yet high enough to prevent chloride condensation. The reduced Nb-Ge phases deposit on the walls of the quartz tube in the deposition zone and on the desired substrate material. An inert component in the gas phase, He or Ar, allows us to modify the deposition profile by controlling gas velocity and thus gas residence time in the deposition zone during H_2 reduction.

One typical set of deposition conditions is as follows: deposition temperature, $T_d = 900^\circ\text{C}$, He carrier flow rate = 20 liters/min, total chloride delivery rate = 0.15 moles/hr, molar ratio $\text{NbCl}_4/\text{GeCl}_2$, $s = 6$, molar ratio $\text{H}_2/\text{chlorides} = 10$, deposition time = 30 min. Such conditions yield Nb_3Ge growth rates of 20-40 $\mu\text{m/hr}$.

Nb-Ge DEPOSIT PROPERTIES

Sample Description

Hastelloy B (Ulbrich Stainless Steel Co., Wallingford, Connecticut 06493) tape, 1.27 cm wide and 50 μm thick, is the typical, high strength substrate

FIG. 1. Block diagram of the Nb₃Ge tape fabrication system using CVD.

FIG. 2. A SEM photograph of a fractured A-15 deposit (with the Hastelloy substrate removed; 14 μm thick film of Nb_3Ge), $\times 5300$.

used. The substrate is coated on one side over the length of ~ 50 cm. The deposit thickness varies along the reactor tube and is in the range of $h = 1$ to 100 μm depending upon the deposition time and/or chloride delivery rate. The adhesion to the Hastelloy substrate is excellent due to the formation of a diffusion layer at the deposit-substrate interface. Figure 2 shows a scanning electron microscope (SEM) photograph of a fractured A-15 deposit with the substrate removed and the diffusion layer visible. The columnar grain growth observed is typical for films thicker than $h = 2\text{--}3$ μm and is partly responsible for the pronounced surface roughness of thicker films. The column diameter is in the range of $0.3\text{--}1$ μm . The columnar texture is probably of (100) type, as determined by other investigators [4].

Phases Present

A most useful feature of the CVD method is the ease with which the Nb-Ge ratio in the deposited films can be varied by changing the $\text{NbCl}_4/\text{GeCl}_2$ delivery ratio, s . Thus, the phase fields in the Nb-Ge system can be surveyed as with any other tool for phase diagram determination but with the added advantage of rapid reaction kinetics prevailing in gas-phase reactions. Two disadvantages must be kept in mind, however. First, the system is inherently "dirty," i.e., gas phase contamination with N_2 and O_2 is likely at leaky glass joints, minor amounts of elements such as Cu, Fe, Ni may be picked up from control valves and Si plus O_2 contaminants can come from attacked quartz walls of the reactor. In addition, the solid deposit can be contaminated by gas phase components such as chlorine or hydrogen. Second, the deposited phase

assemblage is unlikely to reflect complete equilibrium because of gas-flow complexities, for example.

The phases present at liquidus temperatures in the Nb-Ge system have been well characterized by several workers [9]. Along with Nb (containing Ge in solution) and the cubic Nb₃Ge A-15 phase, there occurs a tetragonal phase isostructural with Mo₅Si₃ and having a composition range of about 32.4 to 37.5 at.% Ge at high temperatures (> 1400°C), a hexagonal phase isostructural with Mn₅Si₃ (D8₈ type) having the composition range about 38.3 to 41.9 at.% Ge, and a hexagonal NbGe₂ phase having the CrSi₂ structure (C40 type). Usually these phases are referred to, respectively, as Nb₅Ge₃ (or σ phase), Nb₃Ge₂, and NbGe₂. It is well verified that the solid solution limits of the A-15 phase do not include the ideal 3:1 atomic ratio at high temperature. At $\sim 1600^\circ\text{C}$, for example, the homogeneity limits are reported to be NbGe_{0.15} ± 0.01 to NbGe_{0.22} ± 0.01 [10]. The position of the Ge-rich boundary at lower temperatures assumes considerable importance since it is generally believed that the highest T_c for any A-15 compound will occur in the ordered stoichiometric phase. No systematic data on the position of this boundary as a function of temperature are available below 1600°C.

The phase assemblages, as a function of *s*, observed in a typical series of CVD runs are reported in Table I. These were deposited on a Hastelloy substrate and identified by x-ray powder diffraction after removal of the substrate by dissolving it in 20% HNO₃ solution. The expected

TABLE I
Nb-Ge Phases Present as a Function of Gas Phase Nb/Ge Ratio, *s*^a
(Constant molar ratio H₂/chlorides = 10)

Nb/Ge Ratio in Gas Phase, <i>s</i>	
12.5	Nb
10.0	Nb
7.0	A15-Nb ₃ Ge
5.6	A15-Nb ₃ Ge
4.5	A15-Nb ₃ Ge
4.2	A15-Nb ₃ Ge + T2 Tetragonal Phase
3.8	A15-Nb ₃ Ge + T2 Tetragonal Phase
2.9	A15-Nb ₃ Ge + T2 Tetragonal Phase
2.6	Nb ₅ Ge ₃ + T2 Tetragonal Phase

^aPosition in the isothermal deposition zone (measured downstream), $z = 15\text{--}17$ cm.

TABLE II

X-Ray Diffraction Data for Nb-Ge Phase Having the
Low-Temperature Nb₅Si₃ (T2) Structure^a

<u>hkl</u>	<u>d_{calc}</u> (Å)	<u>d_{obs}</u> (Å)	<u>I</u> ^b
211	2.878	2.883	vw
114	2.521	2.520	m
213	2.379	2.381	vs
220	2.344	2.345	w
204	2.220	2.221	s
310	2.097	2.098	s
006	1.993	1.993	s
314	1.717	1.714	w
400	1.657	1.665	w
402	1.597	1.598	w
330	1.563	1.569	w
008	1.495	1.498	m
420	1.483	1.486	m
404	1.450	1.450	s
334	1.385	1.390	m
406	1.274	1.278	m
336	1.230	1.234	m
318	1.217	1.220	m
0010	1.196	1.197	m
523	1.176	1.182	m

^aIndexed for a tetragonal unit cell with $a = 6.63$ Å, $c = 11.96$ Å. Additional reflections with lower d values.

^bIntensity: vw = very weak, w = weak, m = medium, s = strong, vs = very strong.

progression from Nb to Nb₅Ge₃ is seen as s is decreased. We observe, however, the presence of an additional phase not previously reported for this system. The powder diffraction data (Table II) have been indexed for a tetragonal cell with $a = 6.63$ Å, $c = 11.96$ Å, and it is probable that this phase is isostructural with the low-temperature tetragonal modification of Nb₅Si₃ [11] and TaGe_{0.5} [12] and with the higher temperature form of TaSi_{0.6} [13]. We use the shorthand notation, T2, of Parthe et al. [11] to refer to it. The occurrence of T2 in the Nb-Ge system would strengthen the correlation between the occurrence of Nb-Ge and Nb-Si phases [14]. The only other finding of such a phase in the Nb-Ge system occurred in the single-crystal growth experiments by Horyń and Dryś [15]. They believed the phase to be Nb₅Si₃ due to contamination of Si from quartz containers and indeed Si may be the stabilizing factor for the tetragonal phase we observe. An analysis using the EDAX attachment to a scanning electron microscope, however, showed Si

to be below the limit of detection ($\sim 3\%$). More sensitive analytical techniques are presently being applied to the problem. The sequence of phase fields as a function of s (Table I), particularly the occurrence of the $T2 + Nb_5Ge_3$ assemblage, suggested to us that the composition of T2 is more niobium rich than that of Nb_5Ge_3 . Microprobe analyses confirmed this, giving a Ge content of 34.8 at.% for T1 and 33.4 at.% Ge for the pure tetragonal T2 phase prepared at $900^\circ C$. Both these compositions lie within the range reported for the Mo_5Si_3 -type phase at higher temperatures.

As well as the phases in Table I, we have observed other Nb-Ge phases but not studied them in systematic fashion. Several runs exceptionally rich in Ge have yielded Nb_3Ge_2 , both pure and with Nb_5Ge_3 (in accord with the Ge-rich nature of this phase with respect to Nb_5Ge_3). In runs at $750^\circ C$ (and occasionally also at $900^\circ C$) the hexagonal phase is replaced by another phase for which we have not indexed the diffraction data. Possibly, it is a low temperature modification of either Nb_3Ge_2 or $NbGe_2$. One run surprisingly yielded material for which we indexed the x-ray pattern according to that reported for the Cu_3Au structure modification of Nb_3Si by Galasso and Pyle [16]. We did not analyze this material for Si. One thing seems clear—the Nb-Ge phase diagram is significantly more complicated at low temperatures than at the liquidus.

The diffraction patterns of film material obtained by dissolving the Hastelloy substrates also often contain lines that can be ascribed to Ni_3Nb with occasional samples giving lines for $NiNb$ as well. These lines originate from the diffusion layer at the film-substrate interface shown in Figure 2 and previously seen for Nb_3Sn [17]. The identifications are not entirely conclusive, but this is to be expected in view of the weak intensity of the lines and the unknown effect that Fe and Mo incorporated in Hastelloy would have on the diffraction patterns.

A-15 Solid Solution Range

The measured edge cell size, a_0 , of the A-15 compound in our deposits varies from 5.14 to 5.18 Å. Three samples of material giving extremely sharp x-ray diffraction patterns were selected for microprobe analysis and these data, combined with the a_0 data for quench/anneal runs found in the literature, yielded the curve for A-15 unit cell size versus the composition shown in Figure 3. Our findings are consistent with those of other workers in that Nb_3Ge prepared below $1000^\circ C$ can contain several percent more Ge than is possible at higher temperatures. One would expect that in the pure Nb-Ge system the a_0 of Nb_3Ge occurring with the T2 phase would be invariantly fixed at the smallest a_0 possible at a given temperature. This is not what we see, however, for a_0 values ranging from 5.14 to 5.17 Å have been measured for A-15 with T2, although in all cases the A-15 diffraction lines on such films are very diffuse, probably indicating inhomogeneous compositions.

FIG. 3. Correlation between the composition of the A-15 phase and the unit cell edge, a_0 .

Thermal Expansion of Nb_3Ge

The thermal expansion coefficient, β , of Nb_3Ge must be known in order to properly match the CVD films to substrate materials.

The thermal expansion of an Nb_3Ge sample removed from the Hastelloy substrate was determined by W. E. Kramer of our laboratories over the temperature range 25-760°C by measuring the length of the unit cell edge at various temperatures in a Unicam high temperature x-ray camera. The sample was sealed in a 0.02 mm diameter quartz capillary tube to prevent oxidation during heating. $M_0\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$) was used to prevent unwanted Fe fluorescence from fogging the film (the Fe being due to the Nb_3Ge -Hastelloy substrate diffusion layer). Line positions were measured and the data adjusted using the standard Nelson-Riley extrapolation to $\sin \theta = 1$ ($\theta = 90^\circ$). From the cell size versus T data we calculate that the thermal expansion coefficient for Nb_3Ge over the measured temperature range is $7.7 \times 10^{-6}/^\circ\text{C}$. The room temperature cell size indicates that this value applies to an Nb_3Ge compound containing about 21.5 at.% Ge, but we do not believe that β will change substantially for other compositions of the Nb_3Ge solid solution.

The value of β for Nb_3Ge is compared with that of Nb_3Sn and several candidate substrate materials in Table III. The value for Nb_3Ge is about the same as that for Nb_3Sn and considerably less than for stainless steel, Hastelloy, and Cu. This is verified by our observation that CVD tapes of A-15 on all these three metallic substrates are invariably curled because of the thermal expansion mismatch when examined at room temperature. Deposits on Nb, for which the expansions are fairly closely matched, show no evidence of thermal mismatch. The use of Hastelloy B as a typical substrate represents a compromise between the low thermal mismatch requirement and other

TABLE III

Mean Linear Thermal Expansion Coefficients, β

Material	$\beta, \times 10^{-6}/^{\circ}\text{C}$	Temperature, $^{\circ}\text{C}$	Ref.
Nb ₃ Ge (CVD layer removed from Hastelloy B)	7.7	25°-760°	This Study
Nb ₃ Sn (CVD layer on magnesium silicate ceramic substrate)	9.8	25°-700°	22
Nb ₃ Sn (diffusion grown on Nb sheet)	8.7	27°-899°	23
Nb ₃ Sn (single crystals prepared at 925°C)	8.0	15°-774°	23
Niobium	7.8	27°-900°	24
Copper	20.0	0°-1000°	25
Hastelloy B	13.0	21°-871°	26
Typical Austenitic Stainless Steel (for Type 303)	20.0	-32°-816°	27
Typical Martensitic Stainless Steel (for Type 410)	12.6	-32°-816°	27

desirable properties such as high strength, corrosion resistance, high electric resistivity, etc.

SUPERCONDUCTING PROPERTIES

Our best CVD samples on Hastelloy have superconducting transition onsets exceeding 22.5 K, i.e., they approach the value $T_c \simeq 23$ K [18-20] for sputtered Nb₃Ge. A precise T_c determination by extrapolation of the critical field $H_{c_2}(T)$ measured at liquid hydrogen range gave $T_c = 22.50 \pm .05$ K. The resistive measurements are corroborated by inductive measurements on powders and by static magnetization data. The critical field extrapolated to 0 K, $H_{c_2}(0) \simeq 360$ kOe and the temperature dependence $H_{c_2}(T)$ are also comparable with those of sputtered samples [5]. A shady area, still subject to ongoing investigation, is the correlation between the critical temperature and the composition of the specimen. Sputtered and CVD films which are Ge-deficient (18-21 at.% Ge and a correspondingly high unit cell size of $a_0 = 5.16$ -5.17 Å, (see Fig. 3) can have very high T_c 's in the 21-22.5 K range [7]. While phase inhomogeneity can be strongly suspected, no proof of it has been found to date. Stabilization of Ge-deficient high- T_c phases by impurities is another possible explanation for the above results.

The strongest indication of inhomogeneity was provided by magnetization versus temperature measurements, since the magnetic moment is a volume dependent property. The critical current density, J_c , can be derived from

magnetization by using the Fietz and Webb formula [28]. Figure 4 compares two normalized low-field critical current density versus temperature curves, one for a stoichiometric (~ 25 at.% Ge) sample and another for a Ge-deficient sample of equally high T_c as determined by inductive measurement on powder of grain size less than $100\text{ }\mu\text{m}$. Both samples were CVD grown on Hastelloy B tape, and the x-ray phase analysis revealed in both cases the A-15 phase, with traces of T2 in the stoichiometric sample. Magnetization was measured by means of a Foner magnetometer. The $J_c(T)$ curve for Nb_3Sn is also given in Figure 4 as a reference. The stoichiometric Nb_3Ge sample exhibits a temperature dependence nearly identical to that of Nb_3Sn , and fitting a $1-(T/T_c^*)^2$ curve, where T_c^* is the transition temperature obtained by extrapolating the steep portion of the curve and neglecting its tail. In contrast, the Ge-deficient sample $J_c(T)$ drops off very fast with increasing temperature, and has a deep knee strongly suggesting an A-15 phase inhomogeneity with a majority phase being Ge deficient and having low T_c . This suggestion is not corroborated, however, by the very sharp lines of the x-ray powder pattern. Also, the electron microprobe analysis of the sample section shows no evidence of macro-nonuniformity. We hope that on-going heat capacity measurements will resolve the question more definitely. The shape of the $J_c(T)$ dependence is of considerable concern from the practical conductor point of view. The aim of obtaining high critical current densities, exceeding those of Nb_3Sn and V_3Ga in the broad temperature range, is, perhaps, the strongest motivation for the

FIG. 4. Normalized low field critical current density vs. normalized temperature for stoichiometric and Ge-deficient Nb_3Ge . A curve obtained for Nb_3Sn is shown for comparison.

TABLE IV
Critical Current Densities of High- T_c Nb₃Ge

Sample Type	$\times 10^6 J_c$ A/cm ²		Measuring Method ^a	Magnetic Field Intensity kOe	Reference	Comment
Sputtered	4.2K	14K				
Sputtered	2.8(4.4)	2.1	T	(self-field)	29	Values in parentheses obtained by extrapolation or estimated.
Sputtered	0.1	-	T	210	21	
Evaporated	4-5	-	T	10	30	
CVD	(5.2)	1.8	T	(self-field)	31	
CVD	1.5	0.5	T	(self-field)	this work	
CVD	4-6	-	L	1-2	this work	
CVD	1.6	0.4	M	10	this work	
Nb ₃ Sn	5-7	1.2	T	(self-field)	} best available data	
Nb ₃ Sn	~ 0	-	T	210		

^aT, four point, transport measurement; L, deduced from low field ac loss vs. H dependence; M, magnetization measurement.

study of Nb₃Ge synthesis and properties. At 4.2 K the high critical field of Nb₃Ge allows us to attain a $J_c \geq 105$ A/cm² at 210 kOe, i.e., at a field intensity approximately equal to the H_{c2} of Nb₃Sn. Low field J_c 's of Nb₃Ge are comparable to those of Nb₃Sn. At higher temperatures, in the liquid hydrogen range, J_c 's of Nb₃Ge are expected to be superior to those of the other above-mentioned A-15 compounds. Table IV presents a selection of low (self-field) and high field J_c values found in Nb₃Ge by us and by other investigators. Improved values of J_c in both sputtered and CVD material can hopefully be obtained by metallurgical control of the microstructure and/or addition of flux pinning impurities.

The behavior of Nb₃Ge tapes in ac fields was investigated in only a very preliminary way. Low field ac losses at 60 Hz, 4.2 K are comparable to those of Nb₃Sn. The increase of losses with temperature is less sharp in Nb₃Ge than in Nb₃Sn, but it is not clear yet whether the true temperature dependence is obscured by the suspected A-15 phase inhomogeneity.

FUTURE DIRECTIONS OF STUDY

As a result of our study of Nb₃Ge grown by CVD, we obtained convincing evidence that this new material can have attractive superconducting properties when prepared in the form of a tape conductor. Additional work is needed to, for example, better elucidate the phase relations, resolve doubts

about the correlation between the composition and T_c , determine mechanical properties, and to improve the critical current density through metallurgical alterations.

While we adopted CVD as the presently most viable method of obtaining and evaluating Nb₃Ge in the tape conductor form, it is not clear what process might be best used to fabricate multifilamentary Nb₃Ge composite conductors. Hence, we are investigating the feasibility of fabricating such short samples of composites by several alternative techniques, including CVD. If successful, the continuous conductor fabrication will constitute the ultimate goal in the on-going developmental work.

The authors acknowledge the helpful technical discussions with D. W. Deis, M. Ashkin, J. R. Gavalier, and M. A. Janocko. Invaluable technical assistance was offered by M. T. Miller, P. A. Piotrowski, H. C. Pohl, and R. P. Storrick. The microprobe analysis was performed by R. W. Palmquist and the scanning electron microscopy by C. W. Hughes. This research was supported in part by AFOSR under the Contract No. F44620-74-C-0042. Part of the work was also supported by ERDA under Contract No. E(11-1)-2522.

REFERENCES

- [1] J. J. Hanak, K. Strater, and G. W. Cullen, *RCA Rev.*, **25**, 342 (1964).
- [2] A. I. Braginski and G. W. Roland, *Appl. Phys. Lett.*, **25**, 762 (1974).
- [3] L. J. Vieland and A. W. Wicklund, *Phys. Lett.*, **49A**, 407 (1974).
- [4] H. Kawamura and K. Tachikawa, *Phys. Lett.*, **50A**, 29 (1974).
- [5] J. R. Gavalier, M. A. Janocko, A. I. Braginski, and G. W. Roland, *IEEE Trans. Magn.*, **MAG-11**, 192 (1975).
- [6] L. R. Newkirk, F. A. Valencia, A. L. Giorgi, E. G. Szklarz, and T. C. Wallace, *IEEE Trans. Magn.*, **MAG-11**, 221 (1975).
- [7] G. W. Roland and A. I. Braginski, *Advan. Cryog. Eng.*, vol. 22, in press.
- [8] L. R. Newkirk, F. A. Valencia, and T. C. Wallace, *J. Electrochem. Soc.*, **123**, 425 (1976).
- [9] M. Hansen and K. Anderko, *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958; First Supplement, R. P. Elliott, McGraw-Hill, New York, 1965; Second Supplement, F. A. Shunk, McGraw-Hill, New York, 1969.
- [10] J. H. Carpenter, *J. Phys. Chem.*, **67**, 2141 (1963).
- [11] E. Parthe, B. Lux, and H. Nowotny, *Monatsh. Chem.*, **86**, 859 (1955).
- [12] H. Nowotny, A. Searcy, and J. E. Orr, *J. Phys. Chem.*, **60**, 677 (1956).
- [13] L. Brewer, A. W. Searcy, D. H. Templeton, and C. H. Dauben, *J. Am. Ceram. Soc.*, **33**, 291 (1950).
- [14] E. Parthe and J. T. Norton, *Acta Cryst.*, **11**, 14 (1958).
- [15] R. Horyń and M. Dryś, *Krist. Tech.*, **6**, K85 (1971).
- [16] F. Galasso and J. Pyle, *Acta Cryst.*, **16**, 228 (1963).
- [17] R. E. Enstrom and J. R. Appert, *J. Appl. Phys.*, **45**, 421 (1974).
- [18] J. R. Gavalier, *Appl. Phys. Lett.*, **23**, 8, 480 (1973).
- [19] L. R. Testardi, J. M. Wernick, and W. A. Royer, *Solid State Commun.*, **15**, 1 (1974).
- [20] J. R. Gavalier, M. A. Janocko, and C. K. Jones, *J. Appl. Phys.*, **45**, 3009 (1974).
- [21] S. Foner, E. J. McNiff, Jr., J. R. Gavalier, and M. A. Janocko, *Phys. Lett.*, **97A**, 485 (1974).
- [22] J. White and R. Paff, *RCA Rev.*, **25**, 342 (1964).

- [23] H. W. Schadler, L. M. Osika, G. P. Salvo, and Mrs. V. J. DeCarlo, *Trans. of Met. Soc. AIME*, **230**, 1074 (1964).
- [24] C. R. Tottle, *J. Inst. Metals*, **85**, 375 (1957).
- [25] *International Critical Tables*, vol. II, 460 (1927).
- [26] *Corrosion Resistance of Hastelloy Alloys*, Bulletin F30, 131-E, prepared by Cabot Corporation, Stellite Division.
- [27] *Metals Handbook*, prepared by American Society for Metals, 1948, p. 555.
- [28] W. A. Fietz and W. W. Webb, *Phys. Rev.*, **178**, 657 (1969).
- [29] L. R. Testardi, *Solid State Commun.*, **17**, 871 (1975).
- [30] Y. Tarutani, M. Kudo, and S. Tagushi, Proc. V. Inst. Cryo. Conf., Kyoto, 1974, p. 477.
- [31] R. J. Bartlett, H. L. Laquer, and R. D. Taylor, *IEEE Trans. Magn.*, **MAG-11**, 405 (1975).

APPENDIX II

CRITICAL CURRENT DETERMINATION FROM THE MAGNETIZATION OF TYPE II SUPERCONDUCTING DISC SAMPLES *

Michael R. Daniel and M. Ashkin
Westinghouse Research Laboratories
Pittsburgh, Pennsylvania 15235

ABSTRACT

Calculations show the demagnetizing field of a Type II superconducting sample in the form of a thin disc is small compared to an external field of 10 kG or more applied normal to the disc face. This result is confirmed by comparing the critical current density calculated from magnetization data, ignoring demagnetizing effects, with that obtained by transport current measurements. The results further show the demagnetizing field may be ignored down to external fields of 5 kG for disc thicknesses of several microns.

* This work was supported by ERDA
under Contract No. E(11-1)-2522

CRITICAL CURRENT DETERMINATION FROM THE
MAGNETIZATION OF TYPE II SUPERCONDUCTING
DISC SAMPLES

Michael R. Daniel and M. Ashkin
Westinghouse Research Laboratories
Pittsburgh, Pennsylvania 15235

Magnetization measurements are commonly used to obtain the critical current density, J_c , of materials in wire form¹ (long cylinders) and with the applied field along the wire axis. For other sample shapes, such as tapes and thin films, and with a field normal to the flat face, this technique is not commonly used. The basic difference between the wire and flat geometries is a small and large demagnetizing factor respectively.

The following discussion pertains to large κ materials, in the form of thin circular discs, with the applied magnetic field H_a normal to the disc face and $H_a \gg H_{c1}$, the lower critical field (measured in a long wire). Under these conditions, we show that J_c can be extracted from the magnetization using the same relation that holds for long wires in longitudinal fields.¹

The exact current distribution in a flat disc of a hard superconductor is difficult to determine. Instead, a uniform current is assumed to flow azimuthally throughout the disc. The magnitude of the current density is determined by the applied field, $J_c = J_c(H_a)$. The

resulting relation between J_c and M (magnetic moment per unit volume) is that given by Equation (A12) of Fietz and Webb.¹ Their analysis is for a long cylinder with a varying current and $J_c = J_c(B)$ where $B = H_a + 4\pi M_e(H_a)$ and M_e is the reversible magnetization at an applied field H_a . The Equation (A12) is the first term of an expansion and is the part for a constant current.

For a Type II superconductor, $-4\pi M_e \leq H_{cl}$, a condition still true for a thin circular disc.² Since the lower critical field, H_{cl} , for a high κ material, is less than 1 or 2 kG, the demagnetizing effect due to the equilibrium magnetization can be neglected for an applied field $H_a \gtrsim 10$ kG.

A screening field H' , due to the critical current in the critical state, contributes to the field in the material. It is calculated from an integration of the Biot-Savart law.³ A maximum $H' \sim 3$ kG is found over a small portion of the disc, the field magnitude remaining less than 1 kG over most of the disc for a $J_c = 10^6$ A/cm², .3 cm diameter, and a 10μ thickness. Thinner discs of comparable diameters and currents or the same dimension disc with lower current densities have smaller screening fields. These dimensions and the J_c value are typical of most of our samples and materials studied. Thus, for the conditions under consideration, J_c can be related to the applied field $B \simeq H \simeq H_a$.

An experimental verification was made of the applicability of the magnetization technique for obtaining the critical current characteristics of a material in a perpendicular field. Figure 1

compares the magnetization determined critical current density $\times$ film thickness against the transport or resistive values as a function of perpendicular (or normal) magnetic field for several Nb_3Sn samples. These were obtained from the IGC Company and had two, approximately 1.5μ thick, layers of diffusion-reacted Nb_3Sn separated by 50μ of unreacted Nb. Copper cladding was done on one sample to improve its stability to flux jumps. However, this was not observed to affect the results in any systematic way. Figure 2 shows results for an Nb_3Ge sample grown by chemical vapor deposition (CVD) on a Hastelloy substrate and subsequently copper plated. It had a 1.5μ layer of Nb_3Ge . In all cases circular discs of 0.32 cm diameter were cut for the magnetization measurements which were made on a Foner magnetometer (Princeton Applied Research Corporation, Model 156). For these and the resistive or transport measurements the magnetic field was normal to the sample face. The sample diameter and film thickness sizes gave a calculated $H' < 1 \text{ kG}$ for $J_c = 10^6 \text{ A/cm}^{-2}$ while H_{c1} was $< 1 \text{ kG}$.

IGC gave one value of 79 A/cm^{-1} at 100 kG for their Nb_3Sn tape, a value consistent with the extrapolated curve of Fig. 1.

In conclusion, calculations have shown that the agreement should be good between a directly measured current density and the value calculated from magnetization data for a disc sample in a normal magnetic field, provided this field is $\sim 10 \text{ kG}$. Experimental results confirm this for thin films of Nb_3Sn and Nb_3Ge but additionally show the agreement holds well down to a 5 kG field. For superconductors of technological interest the demagnetizing field of a thin disc sample may be ignored in applied fields of 5 kG or more.

ACKNOWLEDGMENTS

Appreciation is due to Dr. C. D. Henning of IGC for supplying the Nb₃Sn tape and to Dr. A. I. Braginski of Westinghouse for his continued interest in the work.

REFERENCES

1. Fietz, W. A., Webb, W. W., Phys. Rev. 178, 657 (1969).
2. Cape, J. A., Zimmerman, J. M., Phys. Rev. 153, 416 (1967).
3. Stafl, M., "Electrodynamics of Electrical Machines," (Iliffe, London, 1967), Ch. 3.
4. McEvoy, J. P., RCA Rev. 25, 533 (1964).

Fig. 1 — A comparison of the critical current density $\times$ film thickness versus applied normal magnetic field from transport current and magnetometer measurements for a thin Nb_3Sn disc

Fig. 2 — A comparison of the critical current density versus applied normal magnetic field from transport current and magnetometer measurements for a thin Nb₃Ge disc

APPENDIX III

OBSERVATIONS OF DAMAGE TO Nb₃Ge TAPE DURING SAMPLE PREPARATION

Michael R. Daniel

Westinghouse Research Laboratories
Pittsburgh, Pennsylvania 15235

INTRODUCTION

Several programs are presently concerned with the superconducting Nb₃Ge in tape form for potential application as: (1) a cryogenic transmission line and (2) a material for winding high magnetic field solenoids ≥ 20 T. The superconducting tape is presently prepared by chemical vapor deposition (CVD) on 2 mil thick Hastelloy B tape. Nb₃Ge like many other Al₅ structure superconductors is extremely brittle and the thin films (typically 10 μ thick) deposited on the Hastelloy undergo some damage when samples for measurements are cut from the tape. This memorandum describes observations of the extent of this damage and its effect upon the measurement of transition temperature (T_c) and critical current density (J_c).

RESULTS

The CVD process provides lengths of tape 1/2 inch wide and up to 2 feet in length coated with Nb₃Ge which usually ranges between 5 and 20 μ in thickness. Samples for the resistive measurement of T_c are cut with scissors and measure 1/8 inch by 1/2 inch. This same technique also prepares samples for the transport measurement of J_c and the upper critical field (H_{c2}). Usually J_c is calculated from a measurement of the magnetic field dependence of magnetization taken on a Foner-type magnetometer.

Samples for this are in the form of 1/8 inch diameter discs. The discs are cut from the tape by either punching out with a homemade punch or spark machining. Punching out is used most for reasons of speed, convenience, and precision of shape. Spark machining is an inherently more gentle process but takes time to set up and is prone to giving a non-circular disc.

Samples prepared by all three methods were examined by scanning electron microscope (SEM). As anticipated, damage in the form of cracks or fissures was observed but was confined to the samples edges. Figures 1(a) through 1(d) show the damage done by cutting with scissors. This includes chipping off the Nb_3Ge at corners [Figure 1(a)], cracking [Figures 1(b) and 1(c)], and general crazing [Figure 1(d)]. However, the damage appears to be confined to within a 5 mil wide band at worst.

Figures 2(a) and 2(b) illustrate the effects of punching. The damage is principally cracking in a well defined circumferential band round the disc. Extended radial cracks were mostly absent. The band of cracking did not exceed 3 mils in width. Figures 3(a) and 3(b) show that spark machining is not damage free although it cannot be determined whether damage occurs during machining or in the mounting and demounting of the material. Cracking ranged from being circumferential and small [Figure 3(a)] to being radial and large [Figure 3(b)]. Resolidified material is also evident from the sparking technique. This produces a more irregular edge profile.

CONSEQUENCES

Provided no crack extends across the width of a rectangular sample to electrically open circuit the material, resistive measurements of T_c will be unaffected by damage. Transport current measurements of J_c on these samples could be affected to the extent that the damaged zone subtracts from the width. Note that for cracks running parallel to a transport current flow their effect on J_c could be minimal. However,

generally their most deleterious effect would be to cause an error of up to $-(2 \times 0.005)/0.125$ or -8% in J_c since $J_c \propto 1/\text{width}$.

For the punched out disc samples also the circumferential cracks do not necessarily inhibit the circumferentially induced current flow in the magnetization measurements. However, since $J_c \propto (1/(\text{disc radius})^3)$ the maximum error in J_c could be as large as -3 (0.003/0.0625) or -14%. The consequences of the more variable damage done by spark machining are difficult to assess but could cause errors in J_c as large as those for the punched out discs (-14%).

CONCLUSIONS

Of the three methods used for cutting samples for measurement from Nb_3Ge tape, scissors do the most damage—up to 5 mils wide. Punching out causes an intermediate but regular level of damage—up to 3 mils wide—and spark machining causes the most irregular damage—0 to 5 mils wide. Cutting a 1/8 inch wide sample could result in an -8% error in J_c and punching out a 1/8 inch diameter disc could result in a -14% error in J_c from magnetization measurements.

ACKNOWLEDGEMENTS

The help of Dr. A. T. Santhanam is acknowledged in expediting some of the scanning electron microscope analysis and C. W. Hughes for performing the analysis.

FIGURE CAPTIONS

Figure 1 SEM photographs of the damage done by cutting Nb_3Ge on Hastelloy tape with scissors. (a) Sample 372-8, X200; (b) Sample 372-8, X500; (c) Sample 310-8, X500; (d) Sample 310-8, X500.

Figure 2 SEM photographs of the damage done by punching out discs of Nb_3Ge on Hastelloy tape. (a) Sample 372-8, X500; (b) Sample 310-8, X500.

Figure 3 SEM photographs of the damage done by spark machining discs from Nb_3Ge on Hastelloy tape. (a) Sample 372-8, X500; (b) Sample 310-8, X500.

(a)

(b)

(c)

(d)

Figure 1

(a)

(b)

Figure 2

(a)

(b)

Figure 3

APPENDIX IV

CRITICAL CURRENT DENSITY AND FLUX PINNING IN Nb₃Ge

A. I. Braginski,^{*} Michael R. Daniel,[†] and G. W. Roland^{*}
Westinghouse Research Laboratories
Pittsburgh, Pennsylvania 15235

ABSTRACT

High self-field critical current densities, J_c , of the order of 10^6 A/cm² between 4 and 14 K have been reported for chemical vapor deposited (CVD) films of Nb₃Ge. Our results of J_c measurements in a wide field range and film composition analyses suggest that high values of J_c are due primarily to flux pinning on dispersed tetragonal (σ) phase. Single phase (Al₅) Nb₃Ge samples exhibited lower J_c of the order of 10^4 to 10^5 A/cm². The ac loss measurements corroborate the proposed interpretation.

INTRODUCTION

High self-field and low-field critical current densities, J_c , of the order of 10^6 A/cm² between 4 and 14 K, have been observed in Al₅Nb₃Ge films having high critical temperatures, $T_c = 20$ to 23 K. Such films have been so far synthesized by sputtering,^{1,2} evaporation,³ or chemical vapor deposition (CVD).^{4,5} It is generally assumed that in the brittle Al₅ compounds the effective fluxoid pinning, leading to high J_c , occurs predominantly on grain boundaries. The purpose of this work was to determine the origin of high J_c 's in CVD-grown, Nb₃Ge thick films. These films have coarse grains, of the order of 1 μ m and above, as opposed to fine-grained sputtered Nb₃Ge films, and Nb₃Sn layers formed by the diffusion process. One could suspect, therefore, that grain boundaries alone may not insure a concentration of flux pinning centers sufficient for attaining the high J_c values.

SAMPLES AND THEIR CHARACTERIZATION

The Nb-Ge superconducting layers were deposited on 50 cm long, 1.27 cm wide, and 50 μ m thick Hastelloy B tape sections.⁶ The standard deposition temperature was $T_d = 900^\circ\text{C}$, but deposition experiments in the range 750 to 1000°C have also been performed to obtain layers differing in microstructure. At lower T_d smaller grain sizes could be anticipated. The lower temperature limit of 750°C was imposed by the chemistry of the deposition process and the upper limit by equipment limitations. The deposit thickness was in the range of 5 to 20 μ m. The chemical composition was determined by electron microprobe. For $T_d = 900^\circ\text{C}$ the average deposit composition varied along the tape such that the molar ratio $s = \text{Nb}/\text{Ge}$ in the solid monotonically increased from one end of the tape to the other. The x-ray phase analysis was performed on powdered samples removed from the substrates by dissolving Hastelloy in HNO₃. The unit cell edge of the Al₅ phase, a_0 , was determined from Debye-Scherrer photographs by taking the average of the cell sizes determined from the 622, 600, 610, and 611/532 reflections. The chemical vapor deposition conditions at $T_d = 900^\circ\text{C}$ were usually set such that distinct phase regions appeared in sequence along the tape. Starting from the Ge-richer end at the position coordinate $x = 0$, there first appeared a two-phase region (Al₅ + σ), where σ denotes the tetragonal Nb₅Ge₃ modification. In this region the cell edge of the Al₅ phase was constant. The concentration of σ depended upon s set in the vapor phase. This concentration, estimated from the x-ray intensity of characteristic lines, often fluctuated but generally decreased with increasing x .

Beyond a certain point, $x = x_b$, only the Al₅ phase was present, which extended to the Nb-richer end, $x = x_{\text{max}}$. In this single phase region the cell edge monotonically increased with x thus reflecting an increasing

Ge-deficiency in the Al₅ structure. Hence, at $x \approx x_b$, the deposit composition was closest to Nb₃Ge.

The $a_0(x)$ dependence typical of the above situation is shown in Fig. 1. While the CVD deposition may occur far from thermodynamic phase equilibrium, the $a_0(x)$ dependence for the Al₅ implies that traversing the tape from $x = 0$ to x_{max} is equivalent to traversing a corresponding section of the Nb-Ge binary phase diagram, starting in the Al₅ + σ phase field, and at the knee of the $a_0(x)$ curve crossing the boundary into the Al₅ solid solution field.

The microstructure of deposits was examined by optical microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The deposits exhibited the [100] columnar texture. The column diameter, estimated by SEM, was assumed to be the grain size, d . This d value represented the upper limit of the single crystallite size determined by TEM. In the two-phase region d was generally larger than in the single phase region. Typical data are shown in Table I. The presence of the second phase (σ) could not be detected by TEM and SEM, suggesting a high degree of dispersion in the Al₅ matrix.

CRITICAL CURRENT DENSITY DETERMINATION

Most of the critical current density data were obtained from magnetization measurements performed using a Foner-type magnetometer (P.A.R. Model 155). Measurements were made on disc samples, 3 mm in diameter, punched out from the tape. The magnetic field, H , was applied normal to the disc face. Previous calculations have shown the demagnetizing field of these discs to be less than 1 kG for film thicknesses $h < 10 \mu\text{m}$.⁷ Thus, we were able to calculate low field J_c from the magnetization after Fietz and Webb.⁸ Experiments have confirmed that excellent agreement exists with direct, transport current, measurements at $H \geq 5$ kG. The magnetometer measurements were performed in the field range up to 70 kilogauss. Self-field J_c measurements and measurements at $H > 70$ kilogauss** were performed by the four-point transport method on short tape sections. The disc sample temperatures were measured with an accuracy of ± 0.3 K between 4.2 K and the critical temperature, T_c . The four-point transport measurements were performed in liquid helium, i.e., at 4.2 K, and in the pumped liquid hydrogen range 13.8 to 20.3 K where the accuracy was ± 0.05 K.

In addition to J_c determinations the ac losses, p , were determined using the electronic wattmeter^{††} method at $f = 60$ Hz, 4.2 K, and in fields up to a peak value of $H_p = 2$ kilogauss. The tape sample section length was typically 2.5 to 4.0 cm. The short sample arrangement used was similar to that devised by Bussiere.⁹ For samples which exhibited the $p(H)$ dependence obeying Bean's model of the critical state, $p(\mu\text{Wcm}^{-2}) = (0.5f/12\pi^2) H_p^3 (G^3)/J_c (\text{Acm}^{-2})$, and thus the value of low-field J_c could also be estimated by ignoring its field dependence.

RESULTS AND DISCUSSION

To correlate the critical current density with the microstructure and grain size of nearly single phase layers having an approximately stoichiometric composition Nb₃Ge, J_c was measured for samples synthesized in the temperature range 750 to 1000°C . The results are shown in Table I. In this range of synthesis temperatures the grain size varies by less than one order of magnitude and maximum J_c 's at 4.2 K and 5 kilogauss are uniformly low, of the order of 10^5 A/cm². In contrast, much higher J_c values, of the order of 10^6 A/cm², are

TABLE I. Grain Size (from SEM), d , Critical Temperature, T_c , and Maximum Critical Current Density, J_c , Determined for Nb_3Ge Layers Deposited at Various Temperatures, T_d

T_d °C	Single Phase Al5 Deposits			Two Phase, Al5 + σ , Deposits		
	d μm	T_c (midpoint) K	J_c @ 4.2 K, 5 kG 10^6 A/cm 2	d μm	T_c (midpoint) K	J_c @ 4.2 K, 5 kG 10^6 A/cm 2
750	< 1	16.0 to 17.0	0.25	0.4 to 1	14 to 19	3.0
800	0.2 to 2	19.0 to 21.0	0.25	0.4 to 2	19 to 20	1.8
900	0.5 to 2	21.0 to 21.5	0.4	0.5 to 3	19 to 21	2.4
950	0.5 to 2	21.0 to 21.7	0.1	0.5 to 3	19 to 20	0.40
1000	1 to 3	19.0 to 20.5	0.06	2 to 5	16 to 20	0.34

characteristic of samples containing the σ phase except for $T_d = 1000^\circ C$. On the other hand, Table I shows that the σ phase is not inhibiting the Al5 grain growth so that it should not enhance the concentration of flux pinning centers through the grain size control. The data of Table I suggest, therefore, that flux pinning may occur on nonsuperconducting particles of dispersed σ phase in analogy to other known cases of superconductor hardening by precipitation.¹⁰ Flux pinning on grain boundaries may still represent a secondary contribution. However, lower J_c values for $T_d = 950$ and $1000^\circ C$ may represent the effect of analytically verified significant diffusion of nickel from the substrate rather than that of the large grain size.

The correlation of J_c with the concentration and dispersion of σ phase was difficult to establish. All attempts failed to visualize the dispersed σ phase by the etching or anodizing of micrographic sections. Electron microscopy (TEM and SEM) was of no help either. This lack of success could be only tentatively attributed to a high degree of dispersion. The average concentration of the σ phase has been estimated from the powder x-ray diffraction data. However, electron microprobe traces of tape sections indicated that an upper layer of these σ -phase-containing deposits, ($\sim 10\%$ of the total thickness) was generally richer in germanium and consisted mostly of σ phase. This stratification resulted from the deposition shut-off procedure. Hence, the average concentrations measured represent only an upper bound to the amount of σ phase dispersed in the Al5 matrix. For σ -phase-containing samples of Fig. 1, and high- J_c samples in general, such upper bound was 10 ± 5 vol. %.

An indirect but meaningful correlation could be established, however, due to the fact that the average Nb/Ge ratio in deposits grown at $T_d = 900^\circ C$ increased monotonically with x , as already discussed. Figure 1 shows a typical dependence of a_0 , T_c , the upper critical field, H_{c2} , and J_c upon x . One can assume that the dramatic decrease of J_c with increasing x in the two-phase region reflects a correlation with the amount of σ phase dispersed such that effective pinning of the fluxoid lattice becomes possible either through direct perturbation of the superconducting parameters or through the associated internal stresses. The region of pure, nearly stoichiometric Nb_3Ge at $x \sim x_b$ is at the knee of the $a_0(x)$ curve. Accordingly, H_{c2} and T_c reach a maximum there. These H_{c2} values (at 4.2 K) were extrapolated from data collected at the pumped hydrogen temperatures by using the Werthamer expression for a dirty Type II superconductor with no paramagnetic limiting.¹¹ The variations of H_{c2} and T_c vs. x are too slight to significantly affect J_c . They are inconsistent with the observed sharp drop of $J_c(x)$, but may be responsible for the local maximum of J_c at $x \sim x_b$ (Fig. 1), a feature only occasionally observed.

Since both the precipitate concentration and dispersion (pinning center size and spacing) affect J_c ,

the determination of an "optimum" average σ concentration for a highest J_c was not attempted. However, as could be expected, at high σ concentrations J_c is degraded. This is caused not only by the reduction of the net content of the superconducting medium (which would imply a linear J_c decrease) but also by the deterioration of superconducting parameters due, e.g., to the internal stress. The degradation is seen in Figure 2, which shows the variation of J_c and T_c over a

Fig. 1. The Al5 phase cell edge, a_0 , midpoint critical temperature, T_c , upper critical field, H_{c2} , and critical current density, J_c , vs. the Nb-Ge tape position coordinate, x . The T_c bars represent the superconducting transition temperature range, from onset to tail. Sample series 201, $T_d = 900^\circ C$.

Fig. 2. The critical current density, J_c , and critical temperature, T_c , vs. the maximum concentration (upper bound) of σ -phase. Line drawn to guide the eye. The T_c bars represent the superconducting transition temperature range, from onset to tail. Sample series 279 and 86, $T_d = 750^\circ\text{C}$.

wide range of σ concentration. With regard to the "optimum" σ phase particle size, one can expect it to be of the order of the coherence length ξ . In Nb_3Ge a high- κ material, $\xi \sim 30 \text{ \AA}$.

The highest values of low field J_c (5 kG) so far observed in this study were $\sim 3 \times 10^6 \text{ A/cm}^2$ at 4.2 K and $\sim 1 \times 10^6 \text{ A/cm}^2$ at 14 K. The highest self-field values were 5 to $8 \times 10^6 \text{ A/cm}^2$ at 4.2 K. Further J_c optimization can be anticipated.

The 60 Hz loss characteristics at 4.2 K in low fields are consistent with the proposed interpretation. Losses in single phase Nb_3Ge exceeded greatly those of two-phase deposits. The σ -phase doped samples exhibited a cubic field dependence of losses thus conforming to Bean's model of the critical state. Values of J_c calculated from loss data using Bean's expression are shown in Fig. 1. With the amount of σ phase decreasing to zero, the power exponent of the peak field increased to 4 and above, thus indicating a strong J_c (H_p) dependence characteristic of weak flux pinning.

CONCLUSION

In coarse-grained Nb_3Ge deposited by chemical vapor deposition high critical current densities are characteristic of samples containing several volume percent of the precipitated tetragonal Nb_5Ge_3 (σ) phase. While the quantitative correlation of J_c with the second phase dispersion and concentration is yet to be determined, the present results strongly suggest

that flux pinning occurs primarily on dispersed, non-superconducting σ particles. The presence of this σ phase does not inhibit the grain growth of Nb_3Ge , and flux pinning on grain boundaries plays a secondary role, perhaps more significant at lower deposition temperatures. Further enhancement of J_c through the control of precipitate dispersion, concentration, and also of Al grain size, can be anticipated.

ACKNOWLEDGMENT

We acknowledge the contribution of M. A. Janocko and A. T. Santhanam in the H_{c2} measurement and electron microscopy, respectively. M. T. Miller, P. A. Piotrowski, H. C. Pohl, R. P. Storrick, D. Sunseri, and A. L. Foley offered valuable technical assistance.

REFERENCES

- * Supported by ERDA under Contract No. E(11-1)-2522.
- † Supported in part by AFOSR under Contract No. F44620-74-C-0042.
- ** At the National Magnet Laboratory.
- *† Low power factor wattmeter, Model IH744, constructed by the Brookhaven National Laboratory.
1. J. R. Gavaler, *Appl. Phys. Lett.* **23**, 480 (1973).
2. L. R. Testardi, J. H. Wernick, and W. A. Royer, *Solid State Comm.* **15**, 1 (1974).
3. Y. Tarutani, M. Kudo, and S. Taguchi, *Proc. 5th Int. Cryo. Eng. Conf., ICEC5, IPC Sci. & Tech. Press, London (1974)*, p. 477.
4. L. R. Newkirk, F. A. Valencia, A. L. Giorgi, E. G. Szklarz, and T. C. Wallace, *IEEE Trans. MAG-11*, 221 (1975).
5. A. I. Braginski and G. W. Roland, *Appl. Phys. Lett.* **25**, 762 (1974).
6. G. W. Roland and A. I. Braginski, in *"Advances in Cryo. Eng."* Vol. 22 (in press).
7. Michael R. Daniel and M. Ashkin (Westinghouse Research Laboratories) - submitted to *Cryogenics*.
8. W. A. Fietz and W. W. Webb, *Phys. Rev.* **178**, 657 (1969).
9. O. Horigami, J. F. Bussiere, and Y. Tanaka, *Cryogenics* **15**, 660 (1975).
10. A. M. Campbell and J. E. Evetts, *Adv. Phys.* **21**, 199 (1972).
11. N. R. Werthamer, E. Helfand, and P. Hohenberg, *Phys. Rev.* **147**, 295 (1966).

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

THE TEMPERATURE DEPENDENCE OF J_c IN SUPERCONDUCTING Nb_3Ge

Michael R. Daniel,[†] A. I. Braginski,^{*}
G. W. Roland,^{*} and J. R. Gavaler[†]

Westinghouse Research Laboratories
Pittsburgh, Pennsylvania 15235

R. J. Bartlett^{*} and L. R. Newkirk^{*}

Los Alamos Scientific Laboratory
Los Alamos, New Mexico 87544

ABSTRACT

Measurements are presented of the temperature variation of the critical current density (J_c) for superconducting Nb_3Ge in the field range from 0 to 65 kilogauss. Samples prepared either by sputtering or chemical vapor deposition (CVD) show a behavior similar to that exhibited by Nb_3Sn . The data can be approximated by the relationship $J_c \sim \{H_{c2}(t)\}^n$. The n values range from 1 for self field J_c to 5 at a field intensity of 50 kG.

I. INTRODUCTION

The advantage of a Nb_3Ge superconductor is its ability to support a large critical current density, J_c , at high temperatures ($T \geq 14$ K) or high magnetic fields ($H \geq 200$ kG). At these temperatures and fields Nb_3Ge appears superior to the commercially available superconductors such as NbTi , V_3Ga or Nb_3Sn . There is thus a need to know how J_c depends on temperature both from an application point of view and the intrinsic research interest.

The temperature dependence of self-field J_c between 4.2 K and the critical temperature, T_c , was investigated by Testardi on thin, sputtered Nb_3Ge films.¹ His functional $J_c(T)$ dependence differs considerably from those found in other A15 superconductors, such as Nb_3Sn .²⁻⁶ Measurements on chemical vapor deposited Nb_3Ge were limited to the pumped hydrogen temperature range (13.8 to 20.3 K)⁷ so that proper comparison with Testardi's data could not be made. The purpose of this study was to determine $J_c(T)$ for both sputtered and vapor deposited Nb_3Ge over the range of temperatures between 4.2 K and T_c . Our results presented below will be seen to be quite different from Testardi's and to more closely resemble those obtained for Nb_3Sn .

II. EXPERIMENTAL

Two J_c measuring methods have been used. In magnetic fields up to 65 kilogauss J_c has been obtained from magnetization data, while the

self-field J_c has been measured directly, i.e., by the transport method. The magnetization measurements were made using a Foner-type magnetometer (P.A.R. model 155). Disc-shaped samples 3 mm in diameter were used with the magnetic field derived from a superconducting solenoid and applied normal to the disc faces. Previous results and calculations⁸ have shown the demagnetizing field of these disc samples is ≥ 1 kG for film thickness $\leq 10\mu$. Thus we were able to ignore it at fields of interest and calculate the critical current from the magnetization after Fietz and Webb.⁹ The sample temperatures were measured to an accuracy of ± 0.3 K.

The self-field critical currents were determined from 4-point dc transport measurements at 4.2 K, and in the temperature range of pumped liquid hydrogen. In this latter temperature range the absolute temperature accuracy was ± 0.05 K. The samples were in the form of lengthwise split tube sections or tape. The sample length was ~ 20 cm. A voltage of $0.2 \mu\text{V}$ across 1 cm of the sample was used to define the transition to normalcy. Experimental details are given in Reference 7.

Four types of Nb_3Ge samples were chosen for measuring.

1. Four samples, chemical vapor deposited on copper substrates, and in which flux pinning is believed to occur on dispersed Nb_5Ge_3 (σ) phase particles.
2. Two samples grown on Hastelloy B tape by CVD, and in which flux pinning is, again, believed to occur on σ -phase particles.
3. One sample grown on Hastelloy B by CVD but doped with nitrogen to precipitate NbN , and inhibit grain growth.

It is believed that flux pinning occurs here on NbN particles and/or grain boundaries.

4. One, sputtered on a sapphire substrate, and in which flux pinning is believed to occur predominantly on grain boundaries.

A listing of all the samples, including their T_c and J_c values is given in Table I.

The results of J_c measurements are given in Figures 1 through 4.

Figure 1 shows the reduced critical current density, j_c , vs the reduced temperature, t , as obtained from the magnetization data at 5 kilogauss. Figure 2 shows $j_c(t)$ at 50 kilogauss. Figure 3 presents the self-field $j_c(t)$. Finally, Figure 4 gives an example of $j_c(H, t)$ to define a segment of the critical HJT surface.

III. DISCUSSION

Figure 1 demonstrates that the temperature dependence of low field J_c is similar for samples prepared either by sputtering or CVD, and apparently independent of the flux pinning mechanism. However, samples grown on copper (LASL) show a slightly lesser tail at high t , and low fields, than do the Westinghouse samples deposited on Hastelloy B or sapphire. This is also seen in Figure 3. The cause of that difference is unknown at present. We speculate that the compositional homogeneity of the LASL samples is slightly better than that of the Westinghouse samples. In higher fields the difference virtually disappears, as shown in Figure 2.

Table I
Measured Samples

Sample Designation	Sample Grown At	Sample Formation	T_c Mid-Point (K)	Assumed Flux Pinning Centers	Film Thickness (μm)	Shape	J_c , 10^6 A cm^{-2} at 4.2 K		
							Self-field	5 kG	50 kG
154-M12	LASL*	CVD	20.0	σ -phase	19.5	disc	---	0.85	0.27
274-B6	LASL	CVD	19.0	σ -phase	13.5	disc	---	0.23	0.025
201-5	Westinghouse	CVD	20.2	σ -phase	14.2	disc	---	1.5	0.38
310-9	Westinghouse	CVD	20.7	NbN precipitates, grain boundaries	5.6	disc	---	1.8	0.65
19-6	Westinghouse	Sputtered	21.5	grain boundaries	0.63	disc	---	1.6	0.13
47	Westinghouse	CVD	20.0	σ -phase	1.5	tape	1.5	---	---
414 M10T	LASL	CVD	20.6	σ -phase	12.5	split tube	4.5	---	---
377.2	LASL	CVD	20.5	σ -phase	11.7	split tube	2.0	---	---

* Los Alamos Scientific Laboratory.

The results of Figures 1 and 3 differ substantially from those published by Testardi,¹ and resemble those of Nb₃Sn.²⁻⁶ Close similarity to Nb₃Sn is also indicated by high field data of Figures 2 and 4. Empirically we find we can represent the temperature dependence of J_c by the expression:

$$J_c(t) = J_c(o) [H_{c2}(t)]^n \quad (1)$$

where H_{c2} is the upper critical field. In Figures 1, 2 and 3 the data are bounded by curves defined for n = 1 and 2 at self field and for n = 1.5 and 3 at 5 kG. The results at 50 kG are approximated by an n = 5 curve. We assumed the Ginzberg-Landau parameter κ as temperature independent and set H_{c2}(t) = H_{c2}(o) (1 - t²) which is the simplest form for the temperature dependence of H_{c2}.

The analysis of Fietz and Webb,⁹ derived from their measurements on Nb-Ti alloys can be applied only very approximately to Nb₃Ge and also, we believe, to Nb₃Sn. A careful re-examination of the data of Aron and Ahlgren³ and also Haller and Belanger⁵ for Nb₃Sn shows the normalized pinning force (F_p/F_{pmax} where F_p = J_c H is the Lorentz force) versus reduced field (h = H/H_{c2}) to consist of a series of curves whose maxima shift to lower h with increasing temperature. This appears to contradict the contention of Kramer¹⁰ regarding the existence of a universal scaling law for Nb₃Sn. Our data for Nb₃Ge and also measurements taken on commercial Nb₃Sn tape show a pronounced shift in the pinning force maxima typically by about a factor of 3 between 4.2 K and 12 K. This is noticeably in excess of that for the data of references 3 and 5

where the factor is approximately 1.3. This smaller factor probably accounts for the belief by Kramer¹⁰ that Nb₃Sn did obey the universal scaling law of Fietz and Webb.⁹

The failure of scaling law has in fact been noted in at least one publication for Nb₃Sn¹¹ and was attributed to a compositional inhomogeneity. Whether in fact the scaling law is valid, and the results for Nb₃Sn and Nb₃Ge, which are in disagreement, indicate materials' inhomogeneity or sample preparation problem (damage for instance) is a moot point; it is being further investigated by the present authors. One immediate consequence for Nb₃Ge (and Nb₃Sn) is a restricted usefulness of Kramer's¹² suggestion for obtaining J_c at 4.2 K from data taken closer to the transit on temperature T_c.

In conclusion, we find the temperature dependence of J_c for Nb₃Ge to be similar to that for Nb₃Sn. The scaling law analysis of Fietz and Webb⁹ gives only an approximate description of the behavior of Nb₃Ge. Whether this is a consequence of sample non-uniformity or a true characteristic of the A15 materials investigated remains to be established.

REFERENCES

- † Supported in part by AFOSR.
- * Supported by ERDA, work at LASL additionally supported in part by EPRI.
1. L. R. Testardi, Solid State Comm., 17 871 (1975).
 2. R. Hancox, Appl. Phys. Letters, 7, 138 (1965).
 3. P. R. Aron and G. W. Ahlgren, Adv. in Cryogenic Eng., 13, 21 (1968).
 4. S. Matsunaga and K. Ueda, Jap. J. Appl. Phys., 10, 480 (1971).
 5. T. R. Haller and B. C. Belanger, IEEE Trans. Nucl. Sci., NS-18, 671 (1971).
 6. J. E. Crow and M. Suenaga, Proc. of 1972 Applied Supercond. Conf. IEEE 72CHO682-5-TABSC, p. 472 (1972).
 7. R. J. Bartlett, H. L. Laquer, and R. D. Taylor, IEEE Trans. MAG-11, 2, 405 (1975).
 8. Michael R. Daniel and M. Ashkin, "Critical Current Determination from the Magnetization of Type II Superconducting Disc Samples," to be published in "Cryogenics".
 9. W. A. Fietz and W. W. Webb, Phys. Rev. 178, 657 (1969).
 10. Edward J. Kramer, J. Appl. Phys. 44, 1360 (1973).
 11. M. P. Mathur, M. Ashkin, D. W. Deis, and B. J. Shaw, IEEE Trans. Magnetics MAG-11, 255 (1975).
 12. Edward J. Kramer, J. Electronic Mat., 4, 839 (1975).

FIGURE CAPTIONS

Figure 1 Reduced critical current density versus reduced temperature for Nb_3Ge at 5 kG.

Figure 2 Reduced critical current density versus reduced temperature for Nb_3Ge at 50 kG.

Figure 3 Reduced critical current density versus reduced temperature for Nb_3Ge in self field from transport measurements.

Figure 4 Reduced critical current density versus reduced temperature for Nb_3Ge at various magnetic field values.

Fig. 1—Reduced critical current density versus reduced temperature for Nb_3Ge at 5kG

Fig. 2—Reduced critical current density versus reduced temperature for Nb₃Ge at 50kG

Fig. 3 — Reduced critical current density versus reduced temperature for Nb_3Ge in self field from transport measurements

Fig. 4 — Reduced critical current density versus reduced temperature for Nb_3Ge at various magnetic field values

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

APPENDIX VI

Applied Superconductivity Conference
Palo Alto 1976
Paper J1 - Final Version

PROGRESS TOWARD A PRACTICAL Nb-Ge CONDUCTOR*

A. I. Braginski, J. R. Cavalier, G. W. Roland, **
Michael R. Daniel, M. A. Janocko, and A. T. Santhanam

ABSTRACT

Properties of high- T_c Nb-Ge films deposited by sputtering and by chemical vapor deposition (CVD) have been investigated. Results of sputtering in the presence of controlled levels of O_2 , N_2 , Si, and of reactive sputtering in Ar- GeH_4 , suggest that the high- T_c Al5 phase is impurity- or defect-stabilized. In CVD deposits two tetragonal modifications were found: σ and T2, the latter probably stabilized by Cl_2 . High critical current densities, J_c (H, T) of fine-grained sputtered films are attributed to flux pinning on Al5 grain boundaries. In coarse-grained CVD films high self-field J_c 's, 10^6 to 10^7 A cm $^{-2}$ at $T = 4.2$ K, are attributed to pinning on dispersed σ -phase. Comparably high J_c 's were also obtained in CVD Al5 films doped with impurities. Low field ac losses p (H, T) were correlated with J_c and coating geometries. The feasibility of fabricating multifilamentary composite conductors by CVD was demonstrated experimentally and a fabrication process for long Nb_3Ge CVD tapes is being developed.

I. INTRODUCTION

The purpose of this paper is to review the progress in the study and development of the Nb_3Ge superconductor as accomplished by our group since the 1974 Applied Superconductivity Conference. We address the phenomenology of the high critical temperature Al5 phase, and the characterization and understanding of the superconductor properties which are relevant for potential applications. On this basis we briefly characterize the status of our work aimed at fabricating practical Nb_3Ge conductors.

To synthesize Nb_3Ge we are using two methods: low energy sputtering^{1,2} and chemical vapor deposition (CVD).^{3,4} The first is being used primarily as an investigation tool, while the second is being developed as a process leading to conductor fabrication. The details of these synthesis methods were given previously.¹⁻⁴ In this paper we compare the behavior and properties of sputtered and CVD films.

The paper encompasses work performed under several programs and includes contributions of many individuals. By necessity, we present a rather general overview and refer the reader to more specific publications.

II. THE HIGH CRITICAL TEMPERATURE Al5 Nb-Ge PHASE

Composition and Stability

The cell edge, a_0 , of the Al5 phase has been determined by x-ray diffractometer in the case of films sputtered on sapphire or alumina, and by powder camera for CVD layers removed from the substrate. The a_0 range is typically 5.14 to 5.18 Å. Using the previously determined curve for cell edge versus Al5 composition,⁵ this range in cell size would correspond to a compositional variation from nearly stoichiometric Nb_3Ge (~ 25 at.% Ge) to a Ge-deficient phase containing about 14 at.% Ge. It is well verified that at high tempera-

tures the solid solution limits of the Al5 phase do not reach the ideal 3:1 ratio; at $\sim 1600^\circ\text{C}$, for example, the homogeneity limits are reported⁶ as $NbGe_{0.15} \pm 0.01$ (13 at.% Ge) and $NbGe_{0.22} \pm 0.01$ (18 at.% Ge). There are no data on the solubility limits as a function of temperature below 1600°C , although the position of the Ge-rich boundary assumes considerable importance since it has generally been believed that the highest critical temperature, T_c , for any Al5 compound will occur in the ordered stoichiometric phase. If the phase stability situation as related to T_c is considered for the series of Nb_3X compounds, where $X = \text{Sn, Al, Ga, or Ge}$, it is evident that there are two trends operative: As the size of the X-atom decreases (in the order listed), the T_c of the ordered stoichiometric Al5 phase becomes higher. At the same time, however, this high- T_c phase becomes increasingly more difficult to prepare. In the Nb-Ge system, attempts to grow the high- T_c stoichiometric Al5 phase from the melt are not successful. In fact, high T_c Al5 material is not obtained at a deposition temperature, T_d , much greater than 1000°C .

There are three possible explanations for the occurrence of stoichiometric, or nearly stoichiometric, Nb_3Ge in Al5-films: (1) a stoichiometric Nb_3Ge phase (25 at.% Ge) is thermodynamically stable at $T \leq 1000^\circ\text{C}$, (2) the Nb_3Ge (25 at.% Ge) is a thermodynamically metastable phase when deposited in the same temperature range, or (3) impurity stabilization results in deposition of high- T_c Nb_3Ge which otherwise cannot be obtained in the pure Nb-Ge chemical system. The conditions under which Nb-Ge is formed by low energy sputtering, CVD, or evaporation differ in at least two essential ways from those present when using ordinary bulk melting methods. First, the temperature of formation is low compared to the melting temperature, thus phases which are stable only at lower temperatures can be prepared. Second, the planar geometry of the deposition process is more favorable than the bulk geometry of melting for the accidental or deliberate introduction of impurities into the growing film.

X-ray and T_c data on sputtered films, which were grown in the presence of controlled levels of impurities, indicate that the high- T_c phase is impurity stabilized. These data⁷ show that the three impurity elements which were investigated (oxygen, nitrogen, or silicon) are each capable of acting as the stabilizing agent. Nb-Ge films were also sputtered under conditions designed to minimize or eliminate residual gas contamination. This was done by sputtering Nb in an argon-germane (GeH_4) atmosphere in which the germane pressure was adjusted to deposit stoichiometric Nb_3Ge . Using otherwise optimum conditions, films were sputtered which had the Nb body-centered cubic structure with a greatly contracted cell edge of 3.25 Å whereas the normal cell edge for Nb is 3.31 Å. This result indicates that without the presence of impurities an Nb-Ge solid solution is formed which contains a substantial amount of Ge. According to the Nb-Ge phase diagram which was constructed from bulk data, the equilibrium solubility of germanium in niobium is less than 5% at all temperatures.

A detailed study of the possible impurity stabilization of the Al5 phase in CVD films has not been done, but analytical data indicate that, if it does occur, the amount of impurity is small. We examined several of our films using an x-ray analyzer (EDAX) attachment to a scanning electron microscope but were unable to detect any metallic elements other than Nb and Ge in the films, except at the Hastelloy substrate-film interface where a diffusion layer is present. The detection limit of the EDAX unit is ~ 1 wt.%. A spark source mass spectroscopic analysis of a pure Al5-phase film grown at 900°C showed $Cl < 0.0120$, $Si \sim 0.005$, $Al < 0.0015$ at.%. Vacuum

Manuscript received August 17, 1976.

* Review of programs supported by: AFOSR Contract No. F44620-74-C-0042 (in part); ERDA Contract No. E(11-1)-2522; NASA Contract No. NAS 3-20233. Part of this work was done at the Francis Bitter National Magnet Laboratory supported at MIT by NSF.

** Westinghouse Research Laboratories, Pittsburgh, PA 15235

fusion analyses for oxygen in Nb₃Ge powders removed from the Hastelloy substrate showed oxygen contents from 0.67 wt.% (6.7 at.%) to 1.28 wt.% (12.5 at.%) with an average of 12 samples of 0.85 wt.% (8.6 at.%). This oxygen is, however, probably a result of the acid treatment used to remove films from Hastelloy, because Auger analyses of films on Hastelloy always showed less than 0.1 at.% O₂ (the detection limit).

There is evidence that at least one Nb-Ge phase, a tetragonal (T2) phase with $a = 6.63$, $c = 11.96$ Å is impurity stabilized in the CVD process. This phase contains about 33 at.% Ge, i.e., it has essentially the same composition as the more usually encountered Nb₅Ge₃ σ phase, but has a different structure.⁵ The occurrence of the T2 phase rather than σ Nb₅Ge₃ is a function of CVD parameters as shown in Fig. 1. It is favored by low temperature and/or low H₂ content in the gas phase.

Fig. 1. Tetragonal phase occurrence vs. deposition temperature, T_d , and hydrogen to chloride ratio, r ; o-T2 tetragonal phase present, •- σ -tetragonal phase present.

We define the H₂ content by the value of the molar ratio $r = \text{H}_2/(\text{NbCl}_4 + \text{GeCl}_2)$. Spark-source mass spectroscopy analyses showed high contents of Cl₂ in T2-containing samples, e.g., a sample of T2 prepared at 900°C in conditions $r = 10$ contained 20.0 at.% of Cl₂ as compared to a content of 0.19 at.% in a σ phase sample prepared at 900°C but with $r \approx 300$. A marked, but less striking, difference was observed also for samples prepared at 800°C: 1.6 at.% Cl₂ in T2 prepared at $r = 80$ vs. less than 0.2 at.% Cl₂ in σ phase prepared at $r = 200$. Some of the chloride content of the chloride-rich samples is undoubtedly due to included unreduced niobium or germanium chlorides; nevertheless, T2 samples always contained at least twice the amount of Cl₂ as A15 samples prepared under the same T_d and r conditions (but different Nb/Ge gas ratio) or σ samples prepared at the same T_d but higher r .

Critical Temperature

Critical temperatures were measured by the standard four-point resistive method and by the inductive (susceptibility) method at 17 Hz. Also, linear extrapolation of upper critical field $H_{C2}(T)$ has been employed at liquid hydrogen temperatures. The temperature measurement accuracy was ± 0.05 K for precise measurements and ± 0.2 K for routine characterization. The width of the Nb₃Ge superconducting transition was often as narrow as $\Delta T = 0.4$ to 0.7 K. More typically, however, it was of the order of $\Delta T = 1$ to 2 K especially in CVD films. This suggests the existence of compositional inhomogeneity in the A15 phase.

Both sputtering and CVD resulted in critical temperature onsets approaching 23 K. The question whether

further enhancement of T_c would be achieved by improved atomic ordering was addressed by Blaugher.⁸ Low-temperature annealing of CVD samples resulted in a measurable increase of the T_c onset. However, no direct measurements of the order parameter were performed due to the similarity of the x-ray atomic scattering factors for Nb and Ge. For as-deposited sputtered samples, onsets in excess of 22 K were recorded for a relatively wide range of T_d , 750 to 1000°C, in agreement with the results of Sweedler et al.⁹ Below 900°C the critical temperature of CVD samples decreased with T_d as shown in Fig. 2. This decrease might be caused by the incorporation of unreduced Nb chlorides.

Fig. 2. Highest transition temperature, T_c , achieved for sputtered and CVD films versus deposition temperature, T_d . Bars indicate width of superconducting transition.

The highest T_c 's were observed in single phase (A15) sputtered and CVD samples having a_0 between ~ 5.14 and 5.17 Å. This indicated Ge-concentrations in the range from nearly 25 at.% down to only 16 at.%. Insufficient accuracy of our analytical techniques prevented a precise determination of sample composition independent of the x-ray diffraction data.

Since Ge-deficiency implies disorder and a correspondingly degraded critical temperature, we believed initially that compositional inhomogeneity in the A15 phase is responsible for the high-temperature "filamentary" superconductivity. However, on the basis of good agreement between resistive and inductive (susceptibility) T_c measurements, and in the light of preliminary low temperature specific heat measurements,¹⁰ we now admit the possibility that an A15 solid solution somewhat off stoichiometry can indeed have high T_c , perhaps due to a not-yet-understood defect ordering process. We hope that additional specific heat measurements will eventually resolve the question.

III. CRITICAL FIELDS, CURRENTS AND AC LOSSES

Upper Critical Field

The upper critical fields, H_{C2} , of Nb₃Ge samples prepared by sputtering and CVD in a variety of conditions, and covering a T_c range between 17 and 22.5 K, have been determined between 14 and 20 K. The H_{C2} values at 0 K have been calculated from dH_{C2}/dT at $T \rightarrow T_c$ ¹¹ using 90% of normal state resistivity, ρ_n , as a criterion for defining H_{C2} at a temperature T . Figure 3 presents the $H_{C2}(0)$ data vs. T_c and indicates that the

highest- T_c sputtered films have higher H_{c2} than the CVD samples. Since the superconducting transitions of the latter are broader, their 90% ρ_n T_c 's are somewhat lower. This is not sufficient, however, to account for the H_{c2} difference.

Fig. 3. Upper critical field at 0 K vs. transition temperature, T_c^* extrapolated from dH_{c2}/dT . Field applied perpendicular to the film plane. The H_{c2} (T_c^*) curve represents Usui's relation.¹²

Measurements show that the low temperature resistivity of sputtered fine-grained samples, $\rho_{25} \sim 100$ to $150 \mu\Omega\text{cm}$, is always substantially higher than that of CVD coarse-grained samples, $\rho_{25} \sim 40$ to $60 \mu\Omega\text{cm}$, independent of the deposition conditions. If $H_{c2} \propto \gamma T_c$ where γ is the specific heat coefficient, then we can infer that the difference in ρ defined by the microstructure is more significant than ρ and γ variations with composition, defect concentration, etc., resulting from various deposition conditions. The scatter of H_{c2} (T_c) data reflects these variations. It can be noted that the trend of H_{c2} (T) data is approximated by the empirical H_{c2} (T_c) relation of Usui.¹² The results of Fig. 3 imply that for very high field applications sputtered Nb_3Ge may be preferred over the CVD material unless the resistivity of the latter is enhanced, e.g., by a modification of microstructure. However, even the present H_{c2} level of CVD materials should be adequate for applications up to the 200 kilogauss level.

Critical Current Density and Microstructure

The critical current densities, J_c , have been determined from magnetization¹³ and transport measurements of small samples in fields ranging from zero up to 200 kilogauss at 4.2 K, and in a narrower field range between 4.2 K and the critical temperature. Our earlier results^{4,14,15} and those of other authors¹⁶⁻¹⁸ demonstrated that Nb_3Ge films, prepared by various methods, can support high critical current densities in a broad range of fields and temperatures. Our main interest here is to compare J_c characteristics of sputtered and CVD samples. Previous comparison of high field J_c 's

with the field, H_1 , perpendicular to the film plane, indicated that sputtered films exhibit J_c 's at least an order of magnitude higher than those of CVD layers. Assuming that flux pinning in Nb_3Ge occurs primarily on grain boundaries we attributed the above result to differences in microstructure.¹⁵ Grain size estimates, based on scanning electron microscopy (SEM) of fractured films, indicated that CVD layers have coarse columnar grains from several thousand angstroms up to above $1 \mu\text{m}$ in diameter whereas grains in the $1000 \text{ \AA}$ range are typical of sputtered Nb_3Ge . Recent microstructure studies by transmission electron microscopy (TEM) generally confirm the SEM observations. The grain size dependence upon T_d in the range from 750 to 1000°C is significant but insufficient to offset the difference. Two examples of CVD sample microstructure are shown in Fig. 4.

Fig. 4. TEM micrographs of (a) single phase Al5, $T_d = 950^\circ\text{C}$, and (b) Al5 + σ , $T_d = 900^\circ\text{C}$. Small grains in (b) are the σ -phase precipitates.

The proposed correlation of J_c with microstructure, although plausible, cannot explain why some CVD samples exhibit at 4.2 K high critical current densities, 5×10^6 to 10^7 A cm^{-2} in zero field, and $\sim 1 \times 10^6 \text{ A cm}^{-2}$ in $H_1 = 50 \text{ kG}$, in spite of the large grain size. A more detailed study of CVD films revealed that in a wide field range the critical current densities depend upon the concentration and dispersion of the tetragonal σ -phase, Nb_5Ge_3 , present in some deposits.¹⁹ Pure, single phase Al5 layers exhibit relatively low J_c 's, while the presence of several volume percent of Nb_5Ge_3 results in J_c up to one order of magnitude higher, as shown in Fig. 5 which compares the J_c (H) characteristics at 4.2 K. However, with further increasing σ -concentration, the critical current density decreases sharply, probably due to internal strains and discontinuities in the Al5 matrix. The critical temperature of σ -rich layers is also depressed. An example of J_c dependence upon the σ -phase concentration is shown in Fig. 6. The upper limit to the σ -phase concentration shown in the figure was estimated from Debye-Scherrer powder patterns. Only most recently the first TEM determination of σ concentration was achieved indicating satisfactory agreement with x-ray results. In a sample containing $10 \pm 5 \text{ vol.}\%$ of σ (measured by x-rays) TEM indicates 9 to 11%. The Nb_5Ge_3 particles have a mean size of $600 \text{ \AA}$ with a mean spacing of $1600 \text{ \AA}$. It is not yet known how the σ dispersion depends upon its concentration and the deposition conditions. Since the mean size and spacing of σ precipitates should affect J_c , the "optimum" σ -concentration of $5 \pm 2 \text{ vol.}\%$ at the J_c peak in Fig. 6 may be rather accidental. Nonetheless, the peak reflects a trade-off between the enhanced flux

pinning and strain or defect level introduced by the σ -phase.

Fig. 5. Critical current density at 4.2 K vs. the perpendicular magnetic field intensity, $H_{\perp}$, for CVD and sputtered films. Results derived from magnetization measurements.

In the case of CVD layers the high critical current densities can be obtained not only by σ -doping but also by introducing impurities. In analogy to earlier studies of Nb_3Sn ^{20,21} we have used nitrogen, CO_2 and C_2H_6 doping to enhance flux pinning in single-phase Al5 deposits. Various doping methods result in comparable critical current densities, as shown in Fig. 5. The critical temperatures of doped, high- J_c samples are depressed by 1 to 4 K compared to the T_c of a pure Al5 phase. The most detrimental to T_c and least effective is doping with CO_2 . Results of the impurity-doping study will be reported and discussed elsewhere.²²

Fig. 6. Maximum achieved critical current density vs. the upper limit of σ -phase concentration.

Comparison with sputtered samples shows that in the low and moderate field range, below 100 kilogauss, similar levels of J_c 's can be achieved in coarse-grained σ - or impurity-doped Nb_3Ge prepared by CVD, and in single Al5 phase sputtered films which are fine grained. Indeed, we have no evidence of any further J_c enhancement due to the presence of σ -phase in sputtered samples. This indicates that in sputtered films flux

pinning occurs predominantly on grain boundaries, as anticipated earlier.¹⁵

At very high fields and at temperatures near T_c , the J_c 's of sputtered films exceed those of CVD layers. The early figure of $J_c = 10^5 \text{ A cm}^{-2}$ at 200 kilogauss, 4.2 K¹⁴ for a thin ($< 1 \mu\text{m}$) sputtered sample still remains unsurpassed. For CVD layers the extrapolation from lower field J_c data to 200 kG, 4.2 K, (by using the scaling laws,²³ and available H_{c2} values) gives J_c 's of approximately $5 \times 10^4 \text{ A cm}^{-2}$. The direct resistive measurement of small, but relatively thick (5 to 10 μm), CVD samples is difficult due to high measuring currents, and resulting heating effects. Based on the extrapolation we believe that sputtered samples have higher J_c 's due to their better uniformity and higher H_{c2} values discussed above. Improvements in high field properties of CVD materials are feasible.

The temperature dependence, $J_c(T)$, of Nb_3Ge has been determined in the low and moderate field range, up to 65 kilogauss. At self- and low-fields it can be approximated by

$$J_c(t) = J_c(1 - t^2)^m \quad (1)$$

where $t = T/T_c$ is the reduced temperature, and $m \sim 1 - 4$.²⁴ With increasing field the functional dependence gradually changes, and becomes more linear with a pronounced tail. The relevant segment of the JHT surface can be expressed by (1) with m becoming an increasing function of H . Reduced $J_c(t)$ curves for $H_{\perp}$ equal 5 and 50 kG with $m \sim 4$ and 6 are shown in Fig. 7. We suspect that the $m(H_{\perp})$ scatter is due to inhomogeneity of the Al5 phase.

Fig. 7. Reduced critical current density vs. reduced temperature for sputtered and CVD films at $H_{\perp} = 5$ and 10 kG. The J_c values are derived from magnetization measurements.

What are the ultimate upper limits to $J_c(H, T)$ of Nb_3Ge , and what are the advantages over Nb_3Sn or V_3Ga ? Assuming the plastic flux lattice shear mechanism,²³ with $H_{c2} \sim 380 \text{ kG}$ and $J_c(200 \text{ kG}) = 10^5 \text{ A cm}^{-2}$, one obtains at 4.2 K, in low fields, J_c of the order of 10^7 A cm^{-2} , but even higher values are projected for Nb_3Sn and V_3Ga .²⁵ The J_c 's of Nb_3Ge win out either at very high fields ($\geq 200 \text{ kG}$) or at high temperatures, above 10 to 14 K.

Losses

The ac losses in a given superconductor depend, among other factors, upon its shape and configuration with respect to the external field. Thus far, we have investigated only planar Nb₃Ge CVD films deposited on one side of short (2.5 to 5 cm) sections of Hastelloy B ribbon, typically 1.3 cm or 0.6 cm wide. Such tapes can be envisaged for application in superconducting power transmission lines (SPTL). We measured 60 Hz surface current losses with $H_{||}$ in plane conforming to the geometry of Bean's model of the critical state.²⁶ The samples were too short to permit loss measurements in a hairpin or shorted-turn sample configuration where the flux is excluded from the substrate. Hence, we used the short sample technique,²⁷ and our loss data included the hysteretic and eddy-current contribution of the substrate, as well as losses originating at the substrate/superconductor interface where a non-uniform diffusion layer exists, as mentioned before.

The 60 Hz loss p (H , T) measurements have been performed using an electronic low power factor wattmeter.²⁸ Standard measurements were performed at 4.2 K, but p (T) characteristics were also determined. Losses in high- J_c samples, doped with σ -phase or gas impurities, conform well to the Bean's model, $p \sim H_{||}^n$, with $n \sim 3$, since J_c is not too field-dependent. A typical p (H) dependence is shown in Fig. 8a for a σ -doped sample. For samples with sufficient flux pinning, losses scale well with $1/J_c$, i.e., J_c calculated from loss data at a peak field of ~ 2 kilogauss agree well with those obtained from static, magnetization measurements. For such samples one observes:

$$p(t) \sim (1 - t^2)^{-m} \quad (2)$$

or a less steep loss increase with temperature up to $t = 0.6 - 0.9$, depending upon the material uniformity.

In pure Al5 samples with a low level of flux pinning, and steep $J(H_{||})$ dependence, losses increase dramatically with H such that $n = 4$ to 6 up to the region of flux penetration between $H_{||} = 1000$ and 2000 gauss (peak) where $n \rightarrow 1$ as shown in Fig. 8b. In such samples losses increase very gradually with temperature, or even decrease at higher fields. The Al5 samples with significant Ge-deficiency exhibit $n < 3$ (Fig. 8c) from very low fields up, suggesting easy flux penetration due to the material non-uniformity.

In all the above results a surface field barrier, ΔH , evidenced by very low losses at $H < \Delta H$, could not be observed.

Thompson et al. demonstrated recently that Nb₃Ge losses in the Kim tube geometry can be extremely low after an appropriate treatment of the tube surface.²⁹ Proper surface topography and pinning seem to greatly enhance the surface field barrier as shown by Bussière et al. for Nb₃Sn tubes.³⁰ Tubes of both materials show 60 Hz losses at 4.2 K as low as $p < 1 \mu W/cm^2$ for a surface current $\sigma = 500$ A/cm, while the SPTL requirements allow up to $10 \mu W/cm^2$. For our sample geometry we were not in a position to observe the surface barrier even in samples with sufficient flux pinning since losses at $\sigma < 500$ A/cm were dominated by the diffusion layer and Hastelloy substrate contributions (Hastelloy alone contributes 10 to $15 \mu W/cm^2$ at 500 A/cm). The losses at 500 A/cm, rms were typically in the range of 30 to $100 \mu W/cm^2$, depending upon the J_c value and the deposition temperature. From loss data for Nb₃Ge deposited on various metallic substrates (Nb, Hastelloy, stainless steel and copper), and after Nb₃Ge surface treatment analogous to that of Refs. 29 and 30 we concluded that the dominant loss component is that of the superconducting diffusion layer. In the case of Hastelloy the layer forms by diffusion of nickel into Nb₃Ge, and is up to $1 \mu m$ thick as revealed by Auger spectroscopy.³¹ The diffusion of copper from Cu substrates is even more pronounced. To properly measure surface current losses on short samples a different geometry of coating is re-

quired. The Nb₃Ge layer should be deposited on all substrate surfaces, and around the edges, to approximate the Kim tube situation, and permit flux exclusion from the diffusion region and the substrate. This tape geometry is also necessary for the double helix SPTL cable where the magnetic field is present on both sides of the tape. Development of such tape conductor represents one of our present goals.

Fig. 8. Low frequency losses at 4.2 K vs. rms surface current density calculated from field intensity. Comparison of CVD samples of different composition and flux pinning level. The J_c values @ 5 kG were obtained from dc magnetization measurements.

IV. PROGRESS TOWARDS A PRACTICAL CONDUCTOR

Composite Tape Conductors

Tapes of Nb₃Ge can find application in SPTL at temperatures up to 14 to 16 K and in high field dc magnets producing fields in the range of 200 to 250 kilogauss. The planar tape configuration is best suited for superconductor deposition from a vapor phase. Flexible, high strength metallic ribbon is used as a substrate. Its thermal expansion coefficient β should exceed that of Nb₃Ge ($\beta \sim 7.7 \times 10^{-6}/^\circ C$ in the 20 to 760°C temperature range⁵), so that the superconductor would be in compression. Coating of equal thickness should be applied to both surfaces to avoid ribbon deformation. For applications such as the double helix SPTL cable, the superconductor should enclose the ribbon entirely. The outer surfaces of Nb₃Ge should be coated by flux jump stabilizing layers of copper having a high resistance ratio. We have previously fabricated⁴ short tape sections, up to 30 cm in length with Nb-Ge layers 2 to 5 μm thick, grown by CVD on one side of 1.27 cm wide, stationary Hastelloy B ribbon substrate ($\beta \sim 13 \times$

$10^{-6}/^{\circ}\text{C}$). Flux-jump stabilization was provided by first sputtering copper on the Nb_3Ge and then electroplating to final thickness. Superconducting properties of these tapes were reported.⁴ Mechanical testing indicated bend radius values similar to Nb_3Sn tapes with a strain limit $\epsilon > 0.2\%$.³² Unfortunately, the tape sections exhibited marked longitudinal non-uniformity of thickness and composition caused by longitudinal gas-phase composition gradients in the CVD reactor tube. Hence, material characteristics reported here have been determined on short samples only. Recently we constructed a moving tape CVD system capable of producing lengths of tape, either one-, two-side, or around-the-edge-coated with the Nb_3Ge superconductor of acceptable uniformity. The system is analogous in principle to that developed by Hanak *et al.*³³ for producing Nb_3Sn tapes by CVD. Initial Nb_3Ge coating tests are now in progress. Cladding of Nb_3Ge will be achieved probably by E-beam evaporation of high resistance ratio copper. Firm adhesion to the Nb_3Ge surface has been already demonstrated.³⁴

Filamentary Conductors

In the absence of metallurgical methods for processing multifilamentary Nb_3Ge , the use of CVD was proposed to form composite wire analogous to fiber reinforced structural composites.³⁵ In particular, alumina fiber reinforced composites, $\text{Al}_2\text{O}_3/\text{Al}$, could be contemplated since Al_2O_3 fibers offer a good thermal expansion match with Nb_3Ge and have very high longitudinal and transverse moduli (although low tensile strength). A 200 filament Al_2O_3 yarn (DuPont Fiber FP) with a filament diameter of 20 μm was coated with Nb_3Ge . Simultaneous coating of individual filaments was achieved with satisfactory uniformity as shown in Fig. 9. The Nb_3Ge filaments and filament bundles were

Fig. 9. SEM photograph of Nb_3Ge filaments formed by CVD on alumina yarn fibers 20 μm in diameter.

electroplated with copper to allow measurements of superconducting properties, and to insure wetting in the next processing step consisting of vacuum infiltration of liquid aluminum to form a composite wire. The filament critical temperature was 21 K with onset at 21.5 K. The upper strain limit figure indicates that a multifilamentary wire could be made with a twist pitch of the order of a few centimeters. Wires could then be cabled to achieve the desired current carrying capability. Approximate loss calculations suggest that such a type of conductor could be successfully used in Tokamak fusion reactors to produce high dc fields in the presence of superposed transverse and longitudinal pulsed fields since the dominant losses in the composite cable would be due to eddy currents in the normal matrix.³⁶

Fabrication Methods

Assuming that fabrication of Nb_3Ge will be limited to low-temperature deposition from a vapor phase, it is desirable to define the preferred deposition method. Should it be a PVD (physical vapor deposition) or CVD? Thus far, high- T_c Nb_3Ge has been synthesized by low energy, low deposition rate sputtering, by E-beam evaporation,^{16,37} and by CVD. Of these, CVD and E-beam evaporation are amenable to mass fabrication. Sputtering could also work if a high rate, low energy process such as magnetron sputtering were successfully developed for Nb_3Ge . The CVD process offers conductor geometry flexibility, especially in the case of filamentary deposition, and calls for the lowest capital investment, if performed at atmospheric pressure. It is, however, an inherently impure and complicated process. The control of the deposit microstructure is limited. E-beam evaporation offers the advantage of very high deposition rates, and it is cleaner, but the composition control is relatively difficult, and the deposit microstructure similar to that obtained by CVD. In both cases impurity doping or layering will probably be necessary to achieve high J_c 's and low losses, thus resulting in some degradation of T_c and conductor uniformity. As shown above, the best results for small, thin Nb_3Ge samples especially at very high fields, have been achieved by low energy, low rate sputtering, without necessitating any doping or microstructure control. It is thus desirable to continue efforts aimed at developing high deposition rate sputtering of Nb_3Ge . Unless this is achieved, CVD will be the preferred method since it is already reaching a stage where fabrication of long conductors becomes possible. Eventually, sputtering may win out for planar conductors, while for filamentary wire fabrication CVD will be preferred.

Economics

Deposition from a vapor phase is usually more costly than metallurgical processing. Also, Ge is substantially more expensive than, for example, Sn. Cost estimates were made for mass production of Nb_3Ge tape using CVD on Hastelloy B substrates. Prior to the copper cladding (laminating) operation, the cost per unit tape length was found to be approximately 50% higher than for Nb_3Sn tape of identical dimensions. Assuming that in applications above a certain temperature, or field intensity, the current carrying capability of the conductor will exceed that of Nb_3Sn or V_3Ga by more than 50%, the cost per kA-unit length will become economically attractive.

With respect to the availability of raw materials, we note that the massive use of Ge would significantly exceed the present supply. A lead-time of several years would be required to open or reopen additional primary Ge sources. Such sources are, however, available up to the limit of the order of 100 to 200 metric tons a year.^{38,39} For small scale applications such as high-field laboratory magnets, the present Ge supply is adequate.

CONCLUDING REMARK

The studies performed over the past two years advanced the characterization and understanding of Nb_3Ge material properties to the point where a practical conductor can be envisaged. The possibility of fabricating both tape and filamentary conductors exists. In the near term, tape conductors should first become available.

REFERENCES

1. J. R. Gavaler, *Appl. Phys. Lett.* 23, 480 (1973).
2. J. R. Gavaler, M. A. Janocko, and C. K. Jones, *J. Appl. Phys.* 45, 3009 (1974).
3. A. I. Braginski and G. W. Roland, *Appl. Phys. Lett.* 25, 762 (1974).

4. G. W. Roland and A. I. Braginski, Adv. Cryo. Eng. Vol. 22 (1976), in press.
5. A. I. Braginski, G. W. Roland, and Michael R. Daniel, Appl. Polymer Symp. No. 29, 93 (1976).
6. J. H. Carpenter, J. Phys. Chem. 67, 2141 (1963).
7. J. R. Gavaler, AIP Conf. Proc. - 2nd Conf. on Superconductivity in d- and f-Band Metals, 1976 (in press).
8. R. D. Blaugher (Westinghouse Research Labs) - unpublished results.
9. A. R. Sweedler, D. E. Cox, S. Moehlecke, R. H. Jones, L. R. Newkirk, and F. A. Valencia, J. Low Temp. Phys. 24, 5/6 (1976).
10. G. R. Stewart (Stanford University) - unpublished results.
11. N. R. Werthamer, E. Helfand, and P. C. Hohenberg, Phys. Rev. 147, 295 (1966).
12. N. Usui (Nihon University), Manuscript NUP-A-75-14.
13. Michael R. Daniel and M. Ashkin, Cryogenics, 1976 (in press).
14. J. R. Gavaler, Science 183, 293 (1974).
15. J. R. Gavaler, M. A. Janocko, A. I. Braginski, and G. W. Roland, IEEE Trans. MAG-11, 172 (1975).
16. Y. Tarutani, M. Kudo, and S. Tagushi, Proc. V Int. Cryo. Eng. Conf., Kyoto, (1974), p. 477.
17. R. J. Bartlett, H. L. Laquer, and R. D. Taylor, IEEE Trans. MAG-11, 405 (1975).
18. L. R. Testardi, Solid State Comm. 17, 871 (1975).
19. A. I. Braginski, Michael R. Daniel, and G. W. Roland, IEEE Trans. MAG-12 (1976), in press.
20. R. E. Enstrom and J. R. Appert, J. Appl. Phys. 43, 1915 (1972).
21. G. Ziegler, B. Blos, H. Diepers, and K. Wohlleben, Z. Ang. Phys. 31, 184 (1971).
22. G. W. Roland, Michael R. Daniel, A. I. Braginski, and A. T. Santhanam, AIME Symposium on Superconducting Materials and Applications IV, Niagara Falls, September 1976.
23. E. J. Kramer, J. Appl. Phys. 44, 1360 (1973), and J. Electronic Mat. 4, 839 (1975).
24. Michael R. Daniel, A. I. Braginski, G. W. Roland, J. R. Gavaler, R. J. Bartlett, and L. R. Newkirk, (submitted to J. Appl. Phys.).
25. Michael R. Daniel, to be published in Cryogenics.
26. C. P. Bean, Rev. Mod. Phys. 36, 31 (1964).
27. O. Horigami, J. F. Bussière, and Y. Tanaka, Cryogenics 15, 660 (1975).
28. Low power factor wattmeter Model IH744, constructed by the Brookhaven National Laboratory.
29. J. D. Thompson, M. P. Maley, L. R. Newkirk, and F. A. Valencia, Los Alamos Sci. Lab, preprint LA-UR 76-555.
30. J. F. Bussière and M. Suenaga, J. Appl. Phys. 47, 707 (1976).
31. J. Schreurs (Westinghouse Research Laboratories) - unpublished results.
32. C. J. Klamut (Brookhaven National Laboratory) - unpublished results.
33. J. J. Hanak, K. Strater, and G. W. Cullen, RCA Rev. 25, 342 (1964).
34. E. Adam (AIRCO) - private communication.
35. D. W. Deis (Westinghouse Research Labs, now at Lawrence Livermore Laboratory).
36. J. H. Murphy (Westinghouse Research Laboratories) - unpublished results.
37. A. B. Hallack, R. H. Hammond, and T. H. Geballe, Appl. Phys. Lett. 29, 314 (1976).
38. J. Adams (Eagle-Picher Ind.) - private communication.
39. H. R. Babitzke, Bureau of Mines Bull. 677 (1975).

DISTRIBUTION LIST

<u>Name and Address</u>	<u>No. of Copies</u>
Mr. Nelson P. Laguna Division of Electric Energy Systems Office of Conservation U.S. Energy Research and Development Administration Washington, D.C. 20545	10
Mr. Eric B. Forsyth Brookhaven National Laboratory Upton, New York 11973	2
Dr. Fred Edeskuty Los Alamos Scientific Laboratory P. O. Box 1663 Los Alamos, New Mexico 87545	3
Dr. Robert Meyerhoff Union Carbide Linde Division Tarrytown Technical Center Tarrytown, New York 10591	1
Dr. Ted Geballe Microwave Laboratory W. W. Hanson Laboratories of Physics Stanford University Stanford, California 94305	1
Dr. Mario Rabinowitz Electric Power Research Institute 3412 Hillview Avenue P. O. Box 10412 Palo Alto, California 94303	1
Dr. Michael Jones National Bureau of Standards Cryogenics Division Boulder, Colorado 80303	1

Dr. David Hartmann
U. S. Department of Interior
Bonneville Power Administration
P. O. Box 3621
Portland, Oregon 97208

1

Mr. Aldo Zanona
Commonwealth Edison Company
1319 South First Avenue
Maywood, Illinois 60153

1

Mr. Carl Hoogerhyde, Jr.
Public Service Electric & Gas Company
P. O. Box 570
Room 11330 M35
Newark, New Jersey 07101

1

Dr. Michael Mulcahy
Department of Research & Environmental
Affairs
Boston Edison Company
800 Boylston Street
Boston, Massachusetts 02199

1

Mr. Isadore Mockrin
Kawecki-Berylco Industries Inc.
P. O. Box 567
Boyertown, Pennsylvania 15235

1

Mr. Carl Rosner
Intermagnetics General Company
New Karner Road
P. O. Box 566
Guilderland, New York 12084

1

Dr. Eric Gregory
Airco, Inc.
Murray Hill
New Providence, New Jersey 07974

1

Dr. Shelly Dahlgreen
Battelle-Pacific Northwest Laboratories
Battelle Boulevard
Richland, Washington

1

Dr. A. E. Austin
Battelle-Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

1

Dr. Max Swerdlow
Air Force Office of Scientific Research
AFOSR/NE
Building 410
Bolling Air Force Base
Washington, D.C. 20332

1

Dr. Charles Oberly
Air Force Aero Propulsion Laboratory
AFAPL/POD-1
Wright-Patterson AFB, Ohio 45433

1

Dr. Alan Clark
National Bureau of Standards
Cryogenics Division
Boulder, Colorado 80303

1

Dr. Frederick Fickett
National Bureau of Standards
Cryogenics Division
Boulder, Colorado 80303

1

Dr. Louis Iannillo
Division of Physical Research
MS J. 309
U.S. Energy Research & Development
Administration
Washington, D.C. 20545

1

Dr. Carl Henning
Division of Magnetic Fusion Energy
MS G-234
U.S. Energy Research & Development
Administration
Washington, D.C. 20545

1

Mr. Edgar Edelsack
Office of Naval Research
Code 427
800 North Quincy Street
Arlington, Virginia 22217

1