AN IMPROVED SUPERCONDUCTOR FOR
TRANSMISSION LINE APPLICATIONS, PHASE I

Final Report

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January 1, 1975 - June 30, 1975

Prepared for

U.S. Energy Research & Development Administration
under Contract No. E(11-1)-2522

Effective Date: January 1, 1975
Expiration Date: June 30, 1975

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Notation

A15	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
i	the current per unit width of the tape surface, or surface current (A/cm)
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 onset of the normal-to-superconducting transition
ΔT	the width of the superconducting transition (also, the temperature difference between the inlet and outlet of a cable refrigeration circuit)
T_c^*	the transition temperature assumed for normalizing the $J_c(T)$ dependence
d_x	X-ray density (g/cm^3)
a_0	unit cell edge (lattice parameter) in $\text{\AA}$
β	linear thermal expansion coefficient ($^{\circ}C^{-1}$)
ϵ	strain
h	superconducting deposit thickness
®	Westinghouse Electric Corporation
BNL	Brookhaven National Laboratory
LASL	Los Alamos Scientific Laboratory

Additional notation is explained in text.

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ABSTRACT

The analysis of an existing superconducting power transmission cable design indicated that economic benefits in the area of refrigeration can be derived from the substitution of Nb_3Ge superconductor for the presently planned Nb_3Sn . However, the cost of Nb_3Ge must be comparable to that of Nb_3Sn , which is achievable when preparing Nb_3Ge by the chemical vapor deposition. Alternatively, technical benefits can be obtained. The most essential and prerequisite requirement is that the Nb_3Ge critical current density be improved significantly over the present state-of-the-art. Other properties of Nb_3Ge are generally suitable for the transmission line application and/or require only moderate improvements.

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This project, Contract No. E(11-1)-2522, was monitored by Mr. Nelson Laguna, Division of Electric Energy Systems, U.S. Energy Research and Development Administration, Washington, DC 20545.

1. INTRODUCTION

1.1 Program Objective

The study reported here represents the first phase of a program directed towards the exploitation of the superconducting niobium-germanium compound Nb_3Ge as a conductor in electric power transmission cables. It was discovered recently (1973) that Nb_3Ge has the highest known superconducting transition temperature, and therefore, presents a new perspective of utilization at cryogenic temperatures higher than those previously contemplated. The objective of this first phase was to define the requisite properties, and economic feasibility of a potential conductor based upon Nb_3Ge , for it to be competitive with respect to niobium-tin, Nb_3Sn , the presently most likely conductor candidate. Relevant physical parameters of state-of-the-art Nb_3Ge were compared with the projected required values so as to provide an indication of the magnitude of any necessary improvements in these properties.

1.2 Tasks of the Program

The tasks of the program were originally formulated as follows:

1. Perform a cost benefit analysis comparing existing conductors based upon Nb_3Sn to potential Nb_3Ge conductors. Computer programs developed at the Brookhaven National Laboratory (BNL) for ac transmission line design studies should provide

a base for this analysis. The LILCO (Long Island Lighting Company) cable design, Plan 3A, should be used as a specific exhibit. Additional input with respect to the dc transmission line analysis will be provided by the Los Alamos Scientific Laboratory (LASL).

2. Determine the necessary physical parameters of state-of-the-art Nb_3Ge prepared by CVD for the purpose of Task 1. To accomplish this task Nb_3Ge samples should be prepared in form of tape sections or short cylinders allowing the measurement of relevant parameters, particularly of the ac loss.

While the initial plan called for including the dc power transmission aspect, it soon became clear that the program should concentrate on the better defined ac transmission line problems. Also, the LASL dc transmission line effort is coupled with an in-house study of Nb_3Ge , so that possible external inputs, such as this study, are less critically needed. Hence, in executing the above formulated first task we limited our study to the BNL design analysis. The work was performed in a very close collaboration with BNL, and we were offered a most substantial assistance. Without the BNL participation the completion of this phase of the program would have not been possible. In addition, LASL also provided substantial help in form of information and sample exchange, and also by performing measurements. This was, and still is, a truly cooperative program.

1.3 Summary of Results

The refrigeration requirements analysis for the LILCO cable, Plan 3A, demonstrated that cable operation at 11-14 K, when made possible through the use of Nb_3Ge , leads to reduced refrigeration cost (14% of the total) or reduced cryogenic enclosure cost (8 to 10% of the total). However, the economic competitiveness of Nb_3Ge material and fabrication cost with that of Nb_3Sn is a necessary prerequisite. The analysis of these cost components shows that such competitiveness can be achieved when using a CVD process. The key requirement here resides in a substantial reduction of gross material consumption, since both metals, Nb and Ge, are expensive and so are the auxiliary gases used in the process.

As an alternative to savings related to refrigeration, technical benefits can be derived in the area of fault current handling and/or Nb_3Ge conductor handling capability. These benefits are probably exclusive with the refrigeration benefits. Definite answers cannot be provided since all depends upon the Nb_3Ge conductor potential for future improvement. The key parameter here is the self-field critical current density, J_c . The state-of-the-art material has J_c at 4.2 K comparable with that of commercial Nb_3Sn , and by a factor of ~ 2 higher at 14 K. If $J_c > 10^7$ amps/cm² could be achieved in a broadest possible temperature range, up to 14 K, then both, technical and economic benefits would be derived simultaneously. Were the J_c improvement such that operation above 14 K became feasible, then cable designs achieving conformance to utility systems through terminal equipment may be attractive. The ultimate promise and challenge of Nb_3Ge resides in the chance

of utilization of liquid hydrogen as an insulating and cooling fluid for operation above 14 K. Its high dielectric strength can make feasible very high voltage ratings and offer an additional degree of freedom in the cable design. The hydrogen synergistic energy transport capabilities may dramatically improve the cable economics.

The path towards substantial J_c improvement leads through metallurgical control of the microstructure and of the impurities to enhance the flux pinning. The preliminary step consists of achieving an improved A15 phase homogeneity. The theoretical upper limit for J_c is much higher than the 10^7 amp/cm² level, so that a substantial margin for improvement appears to exist. A review of other pertinent characteristics of Nb₃Ge has not revealed any properties which could be detrimental to the intended application. The least understood at present is the temperature dependence of losses.

The present study has provided proof of potential Nb₃Ge superiority over Nb₃Sn with regard to transmission lines. Also, it formulated possible benefit options, and has shown that the step preceding any application effort should consist of determining the upper limit of the Nb₃Ge critical current density improvement over the present state-of-the-art.

1.4 Contributors to the Program

The cable analysis defined in Task 1 was performed by S. F. Mauser, R. R. Burghardt and R. P. Corcoran of the Westinghouse Power Systems Planning (now Advanced Systems Technology), East Pittsburgh,

Pennsylvania. They were offered most essential assistance by J. Jensen and G. Morgan of BNL.

The economic analysis of the Nb_3Ge fabrication, and the conductor sample preparation were performed by A. I. Braginski and G. W. Roland at the Westinghouse Research Laboratories, Pittsburgh, Pennsylvania. In the Nb_3Ge characterization participated, in addition to the above, M. A. Janocko, J. R. Cavaler, M. R. Daniel and W. E. Kramer, also of the Westinghouse Research Laboratories. Other contributors were: M. Garber, M. Suenaga and J. Bussiere of BNL -- preliminary measurements of Nb_3Ge ac losses, and assistance in follow-up measurements, R. Bartlett of LASL -- self-field critical current measurement of a Nb_3Ge tape section, C. Klamut of BNL -- the Nb_3Ge tape bending test. A. I. Braginski was Principal Investigator of the program.

1.5 Organization of the Report

The cable analysis is presented in Section 2, and the conclusions with regard to possible benefits of substituting Nb_3Ge for Nb_3Sn are formulated in 2.6.

These conclusions take into account the results of the economic analysis of Nb_3Ge presented in Section 3, and the properties of the state-of-the-art Nb_3Ge defined in Section 6. Conclusions with regard to the necessary Nb_3Ge improvements are presented in 6.9. General conclusions from this study are formulated in Section 7, and the recommendations for the next phase are given in Section 8. References are listed separately for each section.

Section 2 is authored by S. F. Mauser and R. R. Burghardt with the cooperation of A. I. Braginski. Sections 3 through 8 are authored by A. I. Braginski and G. W. Roland. M. A. Janocko and M. R. Daniel contributed to Section 6.

2. CABLE ANALYSIS

2.1 Scope

As already stated in Section 1 a comparison of the performance of a niobium-germanium (Nb_3Ge) superconducting cable with a niobium-tin (Nb_3Sn) cable was made based on the BNL design. The particular cable design chosen for this comparison has been detailed in References 1 through 4. The cable is rated at 345 kV and 4800 MVA and has been referred to as Plan 3A. Table 2-1 presents the characteristics of this cable.⁽⁴⁾

In the performance of this study, the scope was confined to an examination of the benefits derived from the direct replacement of the Nb_3Sn conductors with Nb_3Ge conductors. The following tasks have been performed:

1. Familiarization with the electrical design of the BNL Plan 3A cable and the verification of the electrical performance for an Nb_3Ge cable;
2. Approximate heat transfer calculations to investigate the fault performance of the cable at 14-16 K;
3. Investigation of the refrigeration requirements at temperatures above 8 K;

4. Forecast of the potential of Nb_3Ge as a conductor based on the anticipated property improvements obtainable in Nb_3Ge .

2.2 Steady State Performance

In Plan 3A, the Nb_3Sn cable was designed to have ≈ 1.0 per unit surge impedance loading (SIL) and a reactive impedance ($X_L = j.136$ per unit, Figure 2-1) such that the cable would carry rated current without the use of auxiliary equipment at the terminals when installed in the LILCO power system. Reference 5 discusses the design of cables to meet the impedance constraints, and demonstrates that the SIL and impedance are determined from the surface current density in the superconductor and the electrical stress in the insulation. Since the Nb_3Ge cable must have the same SIL and impedance as the Nb_3Sn cable in Plan 3A, the surface current density in the Nb_3Ge cable is also the same, i.e. 426 A/cm, rms. This value represents the continuous contingency rating, i.e. the double of the normal rating given in Table 2-1.

The Nb_3Ge ac loss test data, and the discussion presented in Section 6 indicate that at the 426 A/cm level the losses increase only slowly up to at least 14 K. While further testing should still be performed, it appears that the steady state cable performance at high temperatures, up to a few degrees below T_c , will not be affected by the Nb_3Ge losses.

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Fig. 2-1—One-line diagram for LILCO, plan 3A (4)

Table 2-1. Characteristics of Superconducting Cable Design, Plan 3A⁽⁴⁾

Electrical radius of inner conductor, r_1 , cm	3.01
Electrical radius of outer conductor, r_2 , cm	5.83
$\text{Log}_e r_2/r_1$	0.66
Outer diameter of cable, cm	12.4
Inner diameter of cryostat, cm	28.5
Maximum stress at r_1 , rms, kV/cm	100
Mean rms stress, kV/cm	71
Per unit series reactance, $\bar{Z}_L$, * km^{-1}	0.002
Per unit shunt reactance, $\bar{Z}_C$, * km	580
Cable current at normal rating, kA	4.0
Base voltage, V, kV	345
Normal rating, MVA per circuit	2400
Linear current density at normal rating σ , A/cm	213
Continuous contingency rating, MVA per circuit	4800
Dielectric constant, ϵ_r	2.2
Dissipation factor, $\tan \delta$,	2×10^{-5}
Load per SIL, $\bar{Z}_O$, *	1.08
Length of circuit, km	68.4
Hysteretic loss at normal rating, W/km^+	8
Hysteretic loss at contingency rating, W/km^+	42
Dielectric loss at rated voltage, W/km^+	165

* Figure 2-1 shows the base diagram used

+ Value at operating temperature of 6 to 9 K, per circuit

2.3 Fault Performance

Approximate calculations, based on those in Reference 5, were performed to investigate the fault recovery characteristics of the Nb_3Ge cable to determine if any significant differences would exist between the fault performance of the Nb_3Sn and the Nb_3Ge cables. These calculations were performed assuming a 14-16 K normal operating temperature and the two fault conditions investigated by BNL. These fault conditions were:⁽⁵⁾ 1) A through fault of ten times normal current for four cycles (67 msec.), and; 2) The same fault for 30 cycles (0.5 sec). Both of these fault conditions can be assumed to have a full dc offset which gives rise to an initial 20-times normal fault current which decays to 10-times normal for a steady state, long-time fault. Temperature rises were calculated with and without the dc offset.

In this calculation we deviated from Plan 3A and used the BNL cable design described in Reference 6, with a 2.34 cm inner diameter, and a 10-mil aluminum backing layer. However, the normal helium temperature range was increased to 14-16 K. It was assumed that during the fault all the current was carried in the aluminum backing. A range of heat transfer coefficients, h , in turbulent flow⁽⁷⁾ was used to determine the possible temperature rise of the conductor assembly that would occur in steady-state, and would permit transfer of all the increased heat load to the helium. The results of these calculations are shown in Table 2-2, along with the BNL values obtained for normal operating temperatures of 6-8 K.

Table 2-2. Helium Temperature Rise
 ΔT for Fault Conditions

Condition	Heat Transfer Coefficient	Nb ₃ Ge	Nb ₃ Sn ⁽⁶⁾
	h (W/cm ² -K)	ΔT (K)	ΔT (K)
AC fault ¹	0.23	4.6	-
AC fault plus dc offset ²	0.23	14.8	-
AC fault	0.335	3.1	2.3
AC fault plus dc offset	0.335	10.2	7.0
AC fault	1.4	0.8	-
AC fault plus dc offset	1.4	2.4	-

¹Ten times normal current = 27,540 amp for 4 cycles.

²18 times normal current = 49,570 amp, for 4 cycles.

The total amount of heat that could be absorbed by the helium was evaluated by calculating the rate of rise of the helium temperature if all heat generated in the aluminum were absorbed by the helium within the conductor tube. For the ac fault considered, the helium temperature would increase 0.3 K in four cycles and 2.5 K in 30 cycles.

As a limiting condition, the assumption was made that heat would be transferred to the core of helium by convection only, with a natural convection heat transfer coefficient. This provided inadequate cooling, emphasizing the need for turbulent helium flow to provide good thermal contact with the conductor materials.

The results of these approximate calculations indicate that faults in an Nb_3Ge cable operating at 14-16 K produce only slightly higher temperature rises than found in an Nb_3Sn cable operating at 6-8 K. The normal metal backed Nb_3Ge conductor behavior will be similar to that of Nb_3Sn . The He pressure increase at fault will be negligible. Current sharing with the superconductor (case (b), Section 3) can further reduce the temperature rise as discussed in Reference 2. This case, however, was not calculated in this study.

The possibility of carrying the fault current in the superconductor alone is very attractive since it can greatly simplify the conductor and cable manufacture and should also lead to substantial material savings (Reference 4, Table 2-7). Unfortunately, the presently demonstrated critical current densities, J_c , of Nb_3Ge do not justify such an approach, even with the conceivable upper limit of the superconductor thickness, $h = 20 \mu\text{m}$ (Reference 2, Section 1.2 and Section 3, this report). For

this h value the continuous contingency current density in the inner conductor ($r_1 = 3.01$ cm) equals $J = 0.2 \times 10^6$ amps/cm.^{2*} This represents ~10% of the highest self-field J_c so far observed at 14 K (the temperature chosen based on calculations of Section 2.4). Hence, an improvement of the material J_c by a factor of five ($J_c = 10^7$ amps/cm² at 14 K) or more would be necessary. This is a noble goal for the conductor development but cannot be assumed as a safe projection.

Carrying the faults by the superconductor itself appears more realistic if considered as a trade-off against the refrigeration savings achieved due to the higher temperature of operation. Assume the Nb₃Ge temperature of operation to be maintained on the level chosen for Nb₃Sn, i.e. 6 to 8 K. The value of J_c (6-8 K) extrapolated from the present data (Section 6) is, respectively, (5 to 4) $\times 10^6$ amps/cm² for a pure, undoped material. An improvement by another factor of 2-3 is probable so that J_c (6-8 K) $\geq 10^7$ amps/cm² can be reached. We note also that at the presently demonstrated level of J_c the Nb₃Ge layer must be much thicker than the 2 μ m assumed for normal (continuous contingency) operation in Section 3, since at 2 μ m $J = 2 \times 10^6$ amps/cm.² Significant improvement in the Nb₃Ge critical current capability is a pre-requisite for any implementation in a superconducting cable such as designed in Plan 3A but operating at higher temperature.

2.4 Refrigeration Requirements

The higher critical temperature of Nb₃Ge compared with Nb₃Sn permits a Nb₃Ge cable to be operated at higher helium temperatures, as long as the ac losses are not prohibitive, and the critical currents are sufficiently high.

* Here, and in the following we assume for simplicity that the self-field J_c scales linearly with thickness of the layer.

Since the refrigeration requirements decrease rapidly as the minimum helium temperature rises, the possibility of reduced refrigeration costs exists. This was investigated with the assistance of J. Jensen and G. Morgan of the Brookhaven National Laboratories.

Two BNL computer programs as described in Reference 3 were used in this study. The two programs separately determine the requirements of the superconducting line and the refrigeration unit. The helium temperatures and flow rate must be balanced between the two units.

In order that comparison could be made between the two conductor materials, all physical dimensions of the LILCO Plan 3A were retained. The basic refrigerator design was also assumed to be the same. Changes were made only in the temperature and pressure of the helium and in the hysteretic losses of the conductor. The inlet pressure was established at 18 atmospheres, slightly below the limit of 20 atmospheres at which substantial changes in the size of various system components would be required.

With the maximum pressure fixed, the maximum helium temperature was set by the dielectric strength of the helium, which varies with density as shown in Figure 2-2. An acceptable BIL^{*} level for 345 kV equipment is 1050 kV. In order to achieve this impulse level in the cable insulation, a minimum breakdown strength of 375 kV/cm is required. In order to reduce the sensitivity of the cable to variations in helium densities, it is advisable to operate on the plateau of the curve, which requires a minimum design helium density of about 70 g/liter. This is

* Basic impulse level.

Fig. 2-2—Breakdown stress of supercritical helium at various temperatures as a function of density (2)

equivalent to 14 K at the established pressure of 18 atm. This temperature also satisfies the requirement for operation of the Nb_3Ge conductor sufficiently below its critical temperature of 21.5 K (100% superconductive state) to provide a margin for temperature increases during fault conditions. Since 14 K satisfies both of these criteria, it was used as the outlet temperature of the coolant for all calculations.

Data of Section 6 show that the hysteretic losses of Nb_3Ge tested to date are comparable to those of average commercial Nb_3Sn , although substantially higher than those of best Nb_3Sn specimens. A margin for the material loss reduction is available, and the temperature dependence is not prohibitive. Hence, it is reasonable to assume that losses in Nb_3Ge at 14 K may not exceed those of Nb_3Sn at 8 K. However, to assess the effect of higher loss, hysteretic losses (1) equal to those of Nb_3Sn and (2) approximately 11 times those of Nb_3Sn were used in the calculations. The other losses, dielectric and enclosure in-leak, were assumed to be the same as those used in the previous LILCO study. The hysteretic losses in the two cases, on a per-conductor basis, were 14 W/km and 152 W/km. Addition of per-conductor dielectric losses of 55 W/km and total enclosure in-leak of 55 W/km gave total losses (for all three conductors) of 262 W/km and 676 W/km respectively, a ratio of about 2.6.

Inlet temperatures of 12, 11, 10, 8, and 6 K were used and mass flow rates were adjusted to give the 14 K outlet temperature at each level of losses. At the lower values of inlet temperature it was not possible for a refrigerator of the assumed design to provide the required

Table 2-3. Refrigeration Costs(LILCO Plan 3A - 6 km Length of Single Circuit - Nb₃Ge Conductor)

Calc. No.	Hysteretic Losses W Cond.-km	Total Cable Losses W Cond.-km	Total System Heat Load (W/km)	T _{in} (K)	T _{out} (K)	Total He Flow Rate (g/sec.)	Refrigeration Cost*	
							Install. (\$1,000)	Operat. \$1,000 Year
1	14	69	262	10	14	56.2	353	45.4
2	14	69	262	11	14	75.4	345	44.0
3	14	69	262	12	14	114	390	52.2
4	152	207	676	10	14	145	551	85.7
5	152	207	676	11	14	195	535	82.2
6	152	207	676	12	14	295	628	103
7**	14	69	262	6.75	8.75	70.8	535	82.0

* Refrigeration installed cost per 6 km includes refrigeration plant, installation, and housing, but not land, land preparation, etc.

** LILCO Plan 3A, for Nb₃Sn conductor.

temperature difference. With the 6 K inlet temperature, a ΔT of less than 2 K is possible at the 18 atm pressure level. With the 8 K inlet temperature, the temperature difference is limited by the refrigerator design to about 4.3 K. Inlet temperatures from 10 to 12 K gave compatible results between the cable line and the refrigerator, with a minimum refrigerator requirement at an 11 K inlet at both levels of losses.

Table 2-3 shows the results of these calculations, giving the estimated cost of installation and operation of the refrigerator system which will cool a 6 km length of the line. The data for the previous LILCO study using Nb_3Sn are included for comparison. Comparison of lines 2 and 7 shows that, with identical losses, the higher helium temperatures (11-14 K) permit use of refrigeration with 36% lower installation cost and 46% lower operating cost, a saving of about 4% of the total system cost.⁽⁴⁾ This result corroborates a similar estimate given in Reference 8. With total losses increased by a factor of 2.6 the costs are virtually identical (lines 5 and 7). Hence, achieving low losses in Nb_3Ge at elevated temperatures is mandatory in order to derive economic benefits from the higher temperature of operation. A further comparison of lines 5 and 7 of Table 2-3 shows that, for identical refrigeration costs, the higher operating temperature permits removal of 676 W/km instead of 262 W/km. If the losses in the conductor remain the same, then the heat in-leak through the enclosure can be increased from the assumed 55 W/km to 469 W/km, a factor of 8.5. The BNL enclosure design with no heat shields, as described in Reference 3, has about this level of heat in-leak. Reference 4 indicates that absence of

a heat shield could reduce the cost of an enclosure by about 20%. Since the enclosure represents 40% of the total installed and operating costs of the cable system (Plan 3A⁽¹⁾), a saving of 8% of the total system cost is possible. A detailed analysis of the costs of various enclosures is necessary to determine this value more closely, but since the enclosure represents such a large portion of the system cost there is a significant potential for savings in this area. These savings are tentatively estimated to be at the level of 10% of the total system cost.

2.5 Discussion

The results given in preceding sections demonstrate that the direct substitution of Nb_3Ge for the Nb_3Sn superconductor in the existing cable design (Plan 3A) results in a cable having a similar electrical performance.

Several alternative benefits can be derived from the substitution. However, they all represent trade-offs and cannot be obtained simultaneously. Most significant are the alternatives derived from the two potential advantages of Nb_3Ge with respect to Nb_3Sn :

1. The higher operating temperature.
2. The higher critical current capability.

1. A higher operating temperature is the most straightforward consequence of introducing a higher T_c superconductor. We found that for losses at 14 K equal to losses in Nb_3Sn at 8 K, a saving of about 4% of the total system cost is possible as a result of the reduced cost of refrigeration. This is a minimum saving that could be increased by optimum design of

the refrigerator. In this study, a refrigerator identical to the one used previously was assumed. Simplification of this plant should be possible as a result of the higher outlet temperature. An alternate potential saving, achieved by simplifying the cryogenic enclosure was estimated at 8-10% of the total cost.

The total installed cost for Plan 3A is 208 million dollars (M\$) (Table 2-10, Reference 4) in 1973 prices so that the saving of 8% amounts to a cost reduction of M\$16.7. However, the increase in the conductor cost (M\$13, Section 3, Table 3-3) offsets most of it, and in fact, all the alternative savings on refrigeration. Hence, to derive economic benefits from the higher operating temperature one should first improve the economics of Nb_3Ge fabrication which appears possible.

2. A higher critical current capability of the superconductor. Assume that $J_c = 10^7$ amps/cm² can be obtained in the cable operating at the temperature of 6-8 K, so that pure aluminum backing is no longer necessary. The resulting material cost reduction is M\$7, but the net material cost is still by M\$6 higher than for Nb_3Sn . The benefit is essentially technical in that the cable conductor structure and fabrication is simplified. This may be appealing, again if the economics of Nb_3Ge fabrication is improved to the point that no net cost increase or some moderate savings be feasible.

An alternative possibility resulting from higher J_c 's is a possible reduction in Nb_3Ge thickness. A reduction by a factor of two decreases consumption sufficiently to wipe out the materials cost increase (even without improving the fabrication economics). The net benefit

is technical in that the mechanical handling capability is enhanced due to lesser effective brittleness of the superconducting layer. This possibility may, in fact, be the most appealing of all, since mechanical handling problems are severe in case of Nb_3Sn tapes. Preliminary Nb_3Ge bend test data given in Section 6 indicate that brittleness of Nb_3Ge should be comparable to that of Nb_3Sn of the same thickness.

The above two alternatives of exploiting moderately improved J_c of Nb_3Ge are both realistic enough. If, however, one makes a speculative assumption that very high critical current densities of the order of 10^7 amps/cm² will be obtained at temperatures around 14 K, then it might be advantageous to operate the cable at even higher temperatures than 11-14 K since a smaller temperature margin below T_c will be required for faults. As discussed previously, however, this would produce electrical insulation problems with relation to the helium density required to provide adequate electrical breakdown strength in the insulation. At temperatures greater than 14 K, pressures higher than 20 atmospheres would be required to increase the helium density and breakdown strength to a level adequate for operation of the cable at 100 kV/cm as in the Plan 3A design. These pressures are undesirable from the safety standards and equipment requirements points of view. There are two options available when considering higher temperature operation: 1) Decreasing the electric stress in the cable insulation, and; 2) Considering another refrigerating and electrical insulating fluid. The first alternative will alter the SIL and impedance of the cable for similar surface current densities. This may require that

compensating equipment be added at the cable terminations to force rated current through the cable. The advantages of this option are not clear but deserve some investigation. The second alternative would call for the investigation of hydrogen as a coolant and insulating medium. Its high dielectric strength can make feasible very high voltage ratings thus offering an additional degree of freedom for the cable design.⁽⁹⁾

The liquid hydrogen synergistic energy transport capabilities should also be examined since they may shed new light on the cable economics. The key to progress clearly lays in the improved Nb_3Ge conductor development, and the most desirable improvement is that of $J_c(T)$, followed by the reduction of ac losses.

2.6 Conclusions

The following conclusions have been derived from the study of direct substitution of Nb_3Ge for the Nb_3Sn conductor in the BNL cable design, Plan 3A:

1. Operation at higher temperatures, 11-14 K, will result in economic benefits of the order of 10% of the total cost, most likely as a result of the cryogenic enclosure simplification. Economic competitiveness of Nb_3Ge fabrication with that of Nb_3Sn is a necessary prerequisite.
2. Potentially higher critical current density of Nb_3Ge , as compared to Nb_3Sn , should reduce the amount of backing material needed to handle

fault currents, and/or reduce the conductor tape brittleness thus easing the mechanical handling problems.

3. The conformance to utility systems should be investigated without constraints imposed by Plan 3A, i.e. by designing a cable specifically oriented towards utilization of Nb_3Ge . The possibility of achieving the conformance through terminal equipment should be examined.
4. Alternate insulating/cooling fluid (H_2) should be examined for high temperature operation based on Nb_3Ge critical current density and ac losses significantly improved over the present state-of-the-art.
5. The Nb_3Ge material improvement effort should concentrate on increasing the critical current density, and, to lesser extent, on reducing the ac losses.

2.7 References

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3. ECONOMIC ANALYSIS OF THE Nb₃Ge FABRICATION

3.1 Purpose

The purpose of this analysis is to estimate the changes in the cable conductor cost resulting from the direct replacement of Nb₃Sn by Nb₃Ge in the LILCO cable, plan 3A. Changes in the conductor technical design and specification which might result from the properties of Nb₃Ge being different than those of Nb₃Sn are not taken into account. The total length of the conductor is that defined by plan 3A. Modifications in the tape conductor consumption due to the introduction of new cable design concepts such as the double helix geometry,⁽¹⁾ for example, are not considered.

3.2 Conductor and Cable

A composite tape conductor analogous to that of Figure 1-1, Reference 2, is assumed for the analysis. The composite is $w = 0.32$ cm wide, and consists of the following conducting layers:

1. High purity aluminum to carry fault currents, either alone (a) or by current sharing with the superconductor (b).
2. Nb₃Ge to carry fault currents (b) and operating current; the layer thickness is 20 μm .
3. Nb₃Ge to carry the operating current only (a); the layer thickness is 2 μm .

4. Copper to stabilize the superconductor against flux jumps.
5. Stainless steel to adjust the neutral axis and provide mechanical strength.

Thickness, technical properties, and the corresponding cost components of all the normal layers, and all cable materials in general are assumed to be identical as in Reference 2.

The cable conductor radii are (plan 3A):

$$\begin{aligned}\text{inner radius} &= r_1 = 3.01 \text{ cm} \\ \text{outer radius} &= r_2 = 5.83 \text{ cm}.\end{aligned}$$

To estimate the tape consumption, it is assumed that each conductor is composed of tape strands which are helically wound with a filling factor of ~100% so that the tape area, a , per unit cable length (each phase) is:

$$a = a_1 + a_2 = 2\pi(r_1 + r_2).$$

The tape area in each 68 km long 3-phase circuit is $A = 113,300 \text{ m}^2$, and the tape length is $A/w = 35,409 \text{ km}$. Since two circuits are employed in plan 3A the total figures are double of the above.

3.3 Process Parameters

The CVD process assumed is a straightforward, and conservative extension of the laboratory method presently employed by Westinghouse, as discussed in Section 4. Continuous coating of the copper or

copper/stainless steel tape substrate is employed in contrast to the present stationary arrangement. However, no other potentially feasible improvements are a priori introduced, and the presently established process parameters are used. This preserves several margins for improvement of the process economics. Specific margins are noted below.

A simplified block diagram of the process is shown in Figure 3-1. The input, raw materials are listed in Table 3-1. In Step I the active metals, Nb and Ge, are chlorinated at high temperatures using the chlorine gas, Cl_2 , in presence of diluting, inert gas He or Ar. The efficiency of this step is $\eta_I = 100\%$.

In Step II the metal chlorides are mixed with the hydrogen gas, also with $\eta_{II} = 100\%$ efficiency.

In Step III the substrate is coated with Nb_3Ge synthesized by reducing the chlorides with hydrogen in presence of a diluting inert carrier gas, He or Ar. The efficiency or yield (Y) of this step is $\eta_{III} = Y = 40\%$ with respect to active components (in present experiments $\eta_{III} = 30-50\%$). The Nb_3Ge growth rate in the coating chamber is $h_c = 100 \mu\text{m}/\text{hour}$. This value represents the presently verified upper limit for Nb_3Ge . However, it is lower by a factor of at least five than growth rates used in some industrial CVD processes⁽³⁾. The output consists of the manufactured Nb_3Ge tape, the condensates of unused metal chlorides and hydrogen chloride, and the exhaust gas: H_2 highly diluted by the carrier (He or Ar). It is assumed for simplicity that the condensates are not recycled in the process. Recycling is, however, possible in principle, and it could reduce the Nb and Ge

Fig. 3-1—Block diagram of the Nb₃Ge tape fabrication by CVD

Table 3-1. Materials Consumption and Cost (Nb_3Ge only) for Case (b)*

Material (Presently Used Grade)	Form (as Delivered)	Unit	Unit Mat'l Cost (\$, 1975)	Unit Consumption per 1 m^2 of tape	Mat'l Cost per 1 m^2 of tape \$	Total Consumption Metric tons or 10^3 m^3	Total Cost M\$
Niobium, 3N (metallurgical grade)	ingot/chips	kg	100	0.383 kg	38.3	86.8	8.68
Germanium, 4N	ingot/chips	kg	250 ⁽⁴⁾	0.100 kg	25.0	22.7	5.66
Chlorine, UHP 99.9%	compressed gas	kg	14.3 [†]	0.341 kg	4.9	77.3	1.1
Hydrogen, HP	compressed gas	m^3 , 1 Atm	2.6 [†]	2.14 m^3	5.6	485	1.27
Helium/Argon, HP	compressed gas	m^3 , 1 Atm	4.3 [†]	7.14 m^3	30.7	1618	7.00
					104.5		23.71

Total Nb_3Ge tape area $A = 226,600 \text{ m}^2$

* 10% wastage included

[†] Matheson Gas Products, specialty gases. Unit cost of commercial Ar (99.997) by Air Products is \$.42-1.25 per m^3 , depending on quantity

consumption by a factor of two (best guesses). Recycling of the carrier gas is also possible, and can reduce its consumption by an order of magnitude. Table 3-2 lists all the process parameters assumed, and allows the comparison with the experimental results of Section 4 and Appendix 4-1.

The hypothetical production unit is an industrial CVD reactor designed to operate at atmospheric pressures, and to coat the continuously running substrate tape on either one or both sides. The total thickness of coatings on both sides is the same as that of a single coating deposited on one side only. The width of the running tape is 1 m, and the length of the coating zone is only 0.2 m to preserve the coating uniformity. The productivity of a single reactor is $4800 \text{ m}^2/\text{year}$ in case (b) and $48000 \text{ m}^2/\text{year}$ in case (a), assuming the 4800 hrs/year operating time. Resistive electric heating is employed. The coated tape is slit to form tape strands of desired width. Other operations necessary to form the final composite conductor are identical as in Plan 3A.

3.4 Materials Consumption and Cost

The materials consumption and cost per 1 m^2 of tape, as well as the total consumption and cost per Plan 3A, are given in Table 3-1. In Table 3-3 this total cost is compared with the component materials cost of the Nb_3Sn conductor which is deduced from Table 2-7, Reference 5 by scaling from the cost of Plan 2 based on the relative areas of the conductors.

Table 3-2. CVD Parameters Assumed
(Hypothetical Design Basis)

Metal chlorination temperature	T_{Cl}	=	900°C
Deposition temperature	T_d	=	900°C
Efficiency of coating* (moles of Nb_3Ge /moles chloride)	Y	=	40%
Molar ratio hydrogen/chlorides	r	=	10
Molar ratio $NbCl_4/GeCl_2$ delivered	s	=	3
Molar ratio of carrier, He or Ar, to active components (dilution)			10
Gas pressure			1 Atm
Thickness growth rate	h_t	=	100 μm /hour
Thickness grown: (a)	h	=	2 μm
(b)	h	=	20 μm
Moles of Nb_3Ge per 1 m^2 of substrate† (a)			0.050 (.017 kg)
(b)			0.495 (.174 kg)
Coating area/production unit			0.2 m^2
Coating rate/production unit (throughput) (a)			10 m^2 /hour
(b)			1 m^2 /hour
Wastage coefficient			10%

* Effective conversion includes the coefficient of utilization (Nb_3Ge on tape/ Nb_3Ge formed)

† Nb_3Ge molecular weight $m = 351.3$ g,
density $d_x \approx 8.6$ g/cm³

Table 3-3. Cost Comparison of Nb₃Sn and Nb₃Ge Cases
Plan 3A*

<u>Material</u>	Nb ₃ Sn ⁽⁵⁾	Nb ₃ Ge
	<u>M\$</u>	<u>M\$</u>
Niobium	9.59	8.68
Tin	0.15	--
Germanium	--	5.66
Gases	<u>--</u>	<u>9.37</u>
Subtotals:	9.74	23.71
Normal Conductor Components ⁽⁵⁾	<u>8.98</u>	<u>8.98[†]</u>
<u>Total Materials</u>	<u>18.72</u>	<u>32.69</u>
<u>Fabrication Cost</u>	4.60	3.60
		(+ fabrication of composite Cu/stainless steel + Al cladding)
<u>Total Cost</u>	23.32	36.29
		(+ fabrication of composite and Al cladding)
<u>Pricing Year</u>	1973	1975

* 10% Wastage Included

[†] 1973 price

The cost of niobium and tin components of the Nb_3Sn conductor represents the fraction of the total to be substituted by the materials cost of Nb_3Ge . The substitution increases the total materials cost by 70%, approximately.

The comparison of Table 3-3 is somewhat biased in favor of Nb_3Sn since it neglects some cost affecting circumstances. For example, no auxiliary materials used in Nb_3Sn fabrication are costed. Also, the cost of gases used in fabricating Nb_3Ge is based on fixed retail prices of specialty gases as opposed to negotiable wholesale prices of commercial gases.

It is clear, nonetheless, that the use of Nb_3Ge to replace Nb_3Sn , case (b), can lead to a substantial materials cost increase. The increase should be offset by economic gains derived from some other cable cost components and by the reduced materials consumption.

This can be achieved by an improved process effectiveness due to recycling of condensates and gases, the use of lower grade gases and/or by the more effective use of the superconductor having superior technical performance.

With respect to the availability of raw materials it is important to note that the anticipated massive use of germanium significantly exceeds the present demand. Hence, a lead-time of about two years would be required to open or re-open additional primary Ge sources.⁽⁴⁾ Such primary sources are, however, available, and the new demand created by the Nb_3Ge fabrication can be met.

3.5 Fabrication Cost, Utility Requirements, and Total Cost

Reference (5) estimates the Nb_3Sn composite conductor fabrication cost for Plan 3A to be ~4.7 M\$. The breakdown into specific cost components is not provided which makes a detailed comparison with the Nb_3Ge case rather difficult. In Appendix 3-1 we provide a rough estimate of the CVD facility operating cost and related utility requirements. The Nb_3Ge fabrication cost of ~3.6 M\$ (Table 3-3) does not include the composite fabrication (Cu/stainless steel, and Al cladding) but indicates that the most expensive part of the total fabrication process is in the proper ballpark. The utilities requirements are reasonable, with 4.8 MW installed power, and 23.2 MKWH yearly demand.

The estimate indicates that the CVD process of fabricating Nb_3Ge can be economically feasible, and may withstand the comparison with the liquid tin diffusion process used to fabricate Nb_3Sn . However, we would like to state emphatically, that the data presented are not aimed at demonstrating the economic advantages or superiority of CVD over some other possible methods of depositing Nb_3Ge such as electron beam evaporation/ion plating or high rate sputtering. For example, E-beam evaporation may offer the advantage of higher coating rate, in excess of 1000 $\mu\text{m}/\text{hour}$.⁽⁷⁾ Detailed comparison of all vapor deposition alternatives is, however, beyond the scope of this study.

The total cost of Nb_3Ge conductor for Plan 3A is in excess of M\$36.3. The unit cost is $\$160.2/\text{m}^2$. This cost is substantially higher than that of Nb_3Sn , and primarily due to higher materials cost. Suggestions

for possible cost reduction are given in the previous section. In particular, recycling of the CVD process by-products reduces the primary materials cost to the level anticipated for Nb_3Sn .⁽⁵⁾

Significant cost reduction can also be obtained by the use of commercial grade gases (Table 3-1).

3.6 Conclusion

The rough, but conservative economic analysis of Nb_3Ge conductor fabricated by CVD indicates that this manufacturing process is economically viable. Cost increase by, approximately, 50% over that of Nb_3Sn reflects higher cost of raw materials. That cost can, however, be reduced by efficient materials management, by process improvements and by reduced consumption. Production of Nb_3Ge by CVD can be competitive with the production of Nb_3Sn by the liquid tin diffusion process.

3.7 References

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4. MATERIAL PREPARATION

4.1 Scope

Within this program (Phase I) our objective was limited to the determination of the necessary physical parameters of state-of-the-art Nb_3Ge prepared by CVD. The materials research was not included. The assumed "state-of-the-art" was that achieved at Westinghouse and LASL⁽¹⁾ during the first half of 1975, since no other significant information became available. The earlier choice of CVD as a preparation technique resulted from the simple fact that to date no other technically feasible preparation method demonstrated a comparable success.

The systematic investigation of Nb_3Ge synthesis at Westinghouse was supported in part by the Air Force Office for Scientific Research, Contract No. F44620-74-C-0042. The materials preparation under the present program was limited to an effort aimed at obtaining samples in form of tape sections on metallic substrates up to 30 cm (12") long, or cylinders. Such sample form and size was deemed necessary for the transmission-line oriented characterization. Prior to the program only small (0.3 x 1.2 cm) Nb_3Ge film samples on ceramic substrates had been made at Westinghouse⁽²⁾ while LASL coated the inside of copper tubes for the purpose of dc power transmission studies⁽³⁾. Our tape preparation was successful, while cylinder coating has been difficult due to the limitations of the Westinghouse CVD reactor. In consequence, the preparation of cylinders has not been pursued.

4.2 The CVD Reactor

The CVD reactor was built under a Westinghouse sponsored part of Nb₃Ge related programs. The reactor design incorporates preferred features of two earlier approaches based on the high temperature (T_d) hydrogen reduction of Nb and Ge chloride mixtures:

1. The chloride generation occurs in situ by chlorinating solid particle metal beds with Cl₂, as in our earlier work. (2)
2. The mixing of chlorides occurs in a lower temperature ($\sim 500^\circ\text{C}$) mixing zone at a low gas velocity. The mixture then passes at a high gas velocity through the deposition zone where $T_d \gg 500^\circ\text{C}$. This design concept is based on that of LASL. (3)

The general view of the reactor is shown in Figure 4-1, and its schematic diagram is discussed in Appendix 4-1, Figure 1. In addition to that discussion we emphasize here the following points:

1. The deposition occurs on a stationary tape substrate. Hence, only limited tape lengths of relative uniformity can be obtained. Some restricted tape displacement during coating is possible but was not yet attempted. We believe that costly investments into a much more sophisticated equipment allowing for continuous tape coating

Fig. 4.1. The CVD reactor furnace system and controls used for Nb_3Ge deposition.

are not warranted at this time. Rather, a definite level of material properties should be demonstrated first, in order to justify substantial expenditures.

2. The Nb_3Ge deposition occurs inside a quartz liner tube. The inner tube wall is more or less uniformly coated, and so is the tape substrate positioned against the wall. Therefore, Nb_3Ge is deposited only on one side of the substrate. Unfortunately, this complicates the ac loss measurements, as discussed in Section 6. Attempts to coat both sides of the tape by suspending it along the tube axis proved unsuccessful. Unavoidable deformation of the substrate resulted in uneven gas flow pattern on each side. In consequence, the distribution, and properties of deposits were different on each side too. We decided not to pursue this approach until the two-side coatings were deemed necessary for the transmission line application. In principle, two side coating can be conveniently achieved in CVD reactors having proper design features.

4.3 Specimens for Testing

The tape specimens are described in Appendix 4-1. The Hastelloy B tape substrates 1.27 cm (1/2") wide, and 50 μm thick, were used exclusively as a temporary compromise solution to meet the requirements of resistance to corrosion in the deposition zone, the thermal expansion match, and low magnetic losses. These requirements are discussed in Section 6. As in Appendix 4-1 we refer in the following to tapes of Type I or II, depending upon the employed coating rate, and the resulting tape thickness: $h = 10\text{--}40\ \mu\text{m}$ for Type I, and $h = 1\text{--}4\ \mu\text{m}$ for Type II. To obtain profiles of the critical temperature, T_c , along the isothermal deposition zone we routinely sectioned the tapes into ~ 5 cm long segments from which 0.3×1.27 cm test samples were cut with major axis perpendicular to the tape axis. While high $T_c > 20$ K over 30 cm length was obtained in several sectioned samples, only a very limited number of unsectioned tapes 23-25 cm long was preserved for further characterization, as discussed in Section 6.

4.4 References

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5. MEASURING EQUIPMENT

5.1 Scope

The characterization methods employed in this program are defined in Section 6 in conjunction with the data on the properties measured. Here we describe briefly the test facilities built with internal support, and representing the Westinghouse contribution to the program.

The two conductor parameters most essential for the transmission line oriented characterization are: the self-field critical current density, J_c , and the self-field ac loss, p . Both should be measured in the whole temperature range of interest, i.e. from 4.2 K up to the superconducting transition temperature, in order to obtain the $J_c(T)$ and $p(T)$ dependences. The equipment implemented to date is described below.

5.2 Shorted Turn Sample Transformer Set-up

In accord with BNL's advice the shorted turn sample iron core transformer set-up was built to allow both, ac critical current and ac loss measurement. The set-up is a close replica of that invented and built at BNL by Forsyth and Morgan^(1,2). The description of the principle and modes of the transformer operation is given in the references, and will not be repeated here. The transformer (yoke) was

obtained on long-term loan from BNL. The variable temperature cryostat to accommodate the transformer was built with only slight modification of the original BNL design.⁽²⁾ We found it convenient to operate "in-flight", i.e. by allowing the temperature to drift slowly upwards while continuously recording both, the temperature, and the measured quantity such as the ac loss at a constant current level. The temperature rate of change was controlled by the heat dissipation in the transformer itself at a constant level of exchange gas (He) flow. The flow was controlled by the control valve, and the heat exchanger heating rate (see Figure 3-8, Reference 2). The temperature at the sample surface was monitored with a Chromel vs Au-0.07% Fe low temperature thermocouple supplied by BNL,⁽³⁾ and referenced to an encapsulated Ge thermometer immersed in liquid He. To date we had no success in the attempts to maintain a constant temperature of the sample while continuously operating the transformer. However, very little effort was expended in this direction.

To measure losses Westinghouse purchased from BNL the low power factor wattmeter, model IH-744, identical with the instruments used at BNL. The wattmeter was calibrated with reference to the BNL instruments.

To measure the ac critical current density without excessive heating effects a simplified version of the BNL gated burst generator was implemented. It consists of an audio oscillator (to allow measurements as function of frequency), a burst gate with full cycle number

controlled in the range of 0 to 1000 (from crossover to crossover[†]) and two ganged in parallel Kepco Model BOP36-5M operational amplifiers/ power supplies jointly delivering to the transformer up to 14 amps of primary current. To date only ac loss measurements were made using the described setup.

5.3 Short Sample Loss Test

The transformer measurement of ac losses has the advantage that only a small fringe flux is present outside the shorted turn formed by the sample.⁽¹⁾ In case of one-side coated tape on a magnetic substrate, such as Hastelloy B, the substrate will not contribute to losses if the superconducting layer is inside of the shorted ring. Unfortunately, tape length of 29-30 cm is required to form the turn. For shorter sections splicing with another section of superconducting tape is necessary, and two soldered joints must be made. To extract enough of loss signal from a saddle coil positioned far enough from these joints, the section under test should not be shorter than 20-25 cm. To date only few samples of that length were made (i.e. left unsectioned, see Section 4.3).

Also, with some material nonuniformity along the tape, the measurement gives the average loss or weakest link critical current value which makes the preparation diagnostics less definite. Hence, advantages of a short sample test allowing to measure a standard 5 cm long tape section are evident. We adopted the short sample loss measure-

[†]The initial phase of firing is not adjustable in contrast to the BNL version.

ment used at BNL by J. Bussiere,⁽⁴⁾ and based on that of Linford and Rhodes.⁽⁵⁾ The sample with a loss voltage pick-up coil wound tightly around both surfaces is submerged in a spatially uniform ac field parallel to the tape surface in order to conform with the Bean's model⁽⁶⁾. The loss is measured electronically using the low power factor wattmeter specified above. Instead of placing a superconducting field solenoid inside the cryostat, as in Bussiere's system, we designed and built a liquid N₂ cooled normal solenoid positioned outside of a vacuum jacketed cryostat. The coil is connected to 250 amps variac, and can produce axial ac fields up to 1700 gauss (peak). The N₂ boil-off is ~0.5l/min at the highest current. This is acceptable for measurements of short duration. The cryostat can be filled with either, liquid He or liquid H₂ (pumped) so that the temperature range of 13.8-20.2 K can be covered in addition to the fixed 4.2 K. The system was used for the preliminary measurement of p(T) described in Section 6.

5.4 References

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6. PROPERTIES OF Nb₃Ge

6.1 Scope

Of importance for the intended cable application are mechanical, thermal, and electrical properties of Nb₃Ge material itself, and of the Nb₃Ge composite tape conductor. The objective of this study is to summarize, at least in a preliminary way, those properties which could be determined on "state-of-the-art" samples prepared at © and/or LASL. The preliminary nature of these determinations stems from the fact that the properties of presently available Nb₃Ge samples do not necessarily represent the ultimate properties of the material, and of the conductors made thereof. Rather, they constitute a temporary base for projections, and a check for a possible presence of unusual effects which could be basically detrimental for the intended application. Hence, future progress will require continuous re-evaluation of the data presented below. Also, several important properties still remain undetermined. Table 6-1 lists the essential material properties and gives values of those presently known.

6.2 Physical Properties of Nb₃Ge

The composition of the highest-T_c material is believed to be close to the stoichiometric formula Nb₃Ge. Contradicting data such as those of Appendix 4-1 are not yet understood, and are under active

Table 6-1. Physical Properties of high- T_c Nb₃Ge

<u>Property</u>	<u>Unit</u>	<u>Value</u>	<u>Comment</u>
Ge concentration	at. %	25	Possibly a range from 16 to 25 at %
Molecular weight	g/mole	351.3	
Density, d_x	g/cm ³	8.59	For $a_0 = 5.140 \text{ \AA}$
Unit Cell Edge, a_0	$\text{\AA}$	$5.140 \pm .005$	Possibly a range from 5.14 to 5.18 $\text{\AA}$
Thermal expansion coefficient, β	$^{\circ}\text{C}^{-1}$	7.7×10^{-6}	Temp. range 25 $^{\circ}$ -760 $^{\circ}$ C
Linear heat capacity coefficient, γ	mJ/mole K ²	24	Ref. 4, Temp range 4-32 K
Elastic modulus	dyne/cm ²	--	Unknown
Normal State (300 K) electric resistivity, ρ	Ωcm	80-100 180	CVD material Sputtered material

investigation. Nonuniformity of Ge-deficient samples having high- T_c is suspected. It is hoped that a pending determination of the specific heat $c_p(T)$ of such samples will definitely resolve this question.* Surprisingly high oxygen content was found in many high- T_c samples.^(1,2) Its effect is under investigation.

The unit cell edge length (lattice parameter) of nearly stoichiometric Nb_3Ge was determined to be $a_0 = 5.140 \pm .005 \text{ \AA}$ for both @ and LASL samples.^(1,3) A 114.7 Debye-Scherrer powder camera was used in both cases. LASL also used a Picker diffractometer.⁽³⁾ The Ge-deficient samples mentioned above typically have $a_0 = 5.16\text{-}5.18 \text{ \AA}$.

Density of Nb_3Ge calculated from the cell edge of $5.140 \text{ \AA}$ is $d_x = 8.59 \text{ g/cm}^3$. No experimental value is available.

The thermal expansion coefficient, β , was determined only for a pure Al5 @ specimen containing 21.5 at % Ge. We do not believe, however, that β will change substantially for other compositions of the Nb_3Ge solid solution range. The sample was removed from the Hastelloy substrate, and the length of the unit cell edge was measured over the temperature range $25^\circ\text{-}760^\circ\text{C}$ using 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. $MoK\alpha$ 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

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Dept. of Applied Physics.

Fig.6-1—The cell edge length vs temperature for Nb_3Ge compound containing ~21.5% Ge

and the data adjusted using the standard Nelson-Riley extrapolation to $\sin \theta = 1$ ($\theta = 90^\circ$). From the cell size vs T data (Table 6-2, and Figure 6-1) we calculated that the thermal expansion coefficient for Nb_3Ge over the measured temperature range is $7.7 \times 10^{-6}/^\circ\text{C}$.

The heat capacity measurements were performed only on LASL sample containing 85-90% of the A15 phase with the balance of tetragonal phase.⁽⁴⁾ The temperature range was 4-32 K. The value of the linear heat capacity coefficient found is $\gamma = 2.4 \text{ mJ/mole K}^2$. The normal state heat capacity is characterized by a constant Debye temperature, $\theta_d = 280 \text{ K}$ up to 28 K.

Elastic moduli of Nb_3Ge remains unknown, and so are parameters characterizing the material mechanical strength (fracture under tensile load, etc.)

The electric resistivity in the normal state is $\rho = 180 \text{ } \mu\Omega\text{cm}$ at 300 K for sputtered samples having T_c in excess of 22 K, and representing predominantly the A15 phase plus some tetragonal phase. The CVD samples have $\rho = 80\text{-}100 \text{ } \mu\Omega\text{cm}$ depending upon preparation conditions.⁽⁵⁾ On a LASL sample $\rho = 90 \text{ } \mu\Omega\text{cm}$ was determined.⁽⁴⁾ The different resistivities of sputtered and CVD samples relate to their different microstructure. The sputtered samples have grain sizes of $1000 \text{ } \text{\AA}$ and less. In CVD samples coarse microstructure is observed with grain sizes from a few thousands angstroms up to several microns.

6.3 Superconductive Properties of Nb_3Ge

The critical temperature record value for Nb_3Ge is still $T_c = 23.2 \text{ K}$ for a resistive onset determined by Testardi.⁽⁶⁾ The highest measured superconductive onset of a CVD layer on Hastelloy was $T_c = 22.5 \pm 0.05 \text{ K}$, as determined by extrapolation of critical field $H_{c2}(T)$ data to $H = 0$.

Table 6-2. Unit Cell Edge of Nb₃Ge As A Function
of Temperature in the Temperature Range 25°-760°C

<u>Temperature, °C</u>	<u>Cell Edge, Å (± 0.002 Å)</u>
25°	5.160
185°	5.164
457°	5.175
610°	5.180
760°	5.190

Typically, the superconductive to normal transition occurs in the range of 20-22 K with a transition width of $\Delta T = 1-2$ K (Appendix 4-1 and Reference 3).

The critical field extrapolated to 0 K is $H_{c_2}^*(0) = 384$ kilogauss, the highest value found to date for sputtered samples. The highest value for a CVD sample was $H_{c_2}^*(0) = 346$ kilogauss.⁽⁵⁾ Both values refer to the 99% ρ_n point, where ρ_n is the normal state resistivity. The temperature dependence $H_{c_2}(T)$ is analogous for CVD and sputtered samples.⁽⁵⁾

The structure dependent properties such as the critical current density and ac losses are discussed in Sections 6.6 and 6.7.

6.4 The Nb₃Ge Tape Substrates

The compatibility of Nb₃Ge with the metallic substrate is of crucial importance for the tape preparation and its performance in a transmission cable. The properties to be considered, in order of importance, are:

1. Adhesion of Nb₃Ge to the substrate which is promoted by the formation of a diffusion boundary layer.
2. Thermal expansion of the substrate which should match that of Nb₃Ge. A substantial mismatch would produce high levels of strain in both Nb₃Ge and the substrate, upon cooling after the deposition. As a result, severe tape deformation and deposit cracking is likely to occur.

3. The electric resistivity, and magnetic properties of the substrate, if subject to an ac field. The substrate should have, therefore, a high electric resistivity at cryogenic temperatures to minimize eddy current losses. The substrate should be dia- or antiferromagnetic to avoid hysteretic losses.
4. Resistance to corrosion in the CVD process atmosphere.
5. Mechanical strength.
6. Cost.

The candidate substrates are listed in Table 6-4.

Adhesion of Nb_3Ge is best to copper, due to the presumed formation of one or more of the Ge-Cu phases⁽⁷⁾ in the diffusion layer between Nb_3Ge and the substrate. Good adhesion to Hastelloy B is also related to the formation of a diffusion layer, clearly visible in scanning electron microscope (SEM) pictures of fractured Nb_3Ge deposits (Figure 6-2). To prepare the fractured specimen the Hastelloy tape was dissolved in diluted nitric acid. The undissolved diffusion layer had high Ni content, as indicated by the energy dispersion X-ray analysis. The X-ray powder analysis gave a tentative indication of the presence of the Ni_3Nb and $NiNb$ phases.⁽⁸⁾

The least acceptable adhesion so far was observed when depositing on the 21-6-9 ("Nitronic 40") austenitic stainless steel.

The comparative deposition experiments were performed after the conclusion of this phase of the program, and will be reported in detail at a later date.

Thermal expansion coefficients of Nb_3Ge , Nb_3Sn and the selected substrate materials are given in Table 6-3. The thermal expansion of Nb_3Ge is similar to that of Nb_3Sn . The only truly matching substrate is niobium, while copper, and austenitic stainless steel present the problem of enormous mismatch. In experiments to be reported separately substrates of 25-50 μm thickness are completely curled around the tape axis when Nb_3Ge is deposited on one side only. Thermal mismatch with Hastelloy B and martensitic steels is less severe but sufficient to also cause tape deformation when the Nb_3Ge deposit thickness exceeds a few microns (Appendix 4-1). The calculated values of mechanical strain and stress in one-side-coated tape are given in Table 6-4.⁽¹⁵⁾ Nb_3Ge thickness of $h = 10 \mu m$, and a 50 μm thick substrate are assumed in the calculation.

Since Young's modulus of Nb_3Ge is unknown we assumed that estimated for a Nb_3Sn/Nb composite.⁽¹⁵⁾ Clearly, the level of compressive stress in Nb_3Ge is extremely high, and explains the tape deformations observed. Uniform coating of both sides of the substrate can eliminate or greatly reduce the deformation. Hence, two-side coating appears very desirable although the strain and stress levels remain comparably high.

Electric resistivity of stainless steel is the highest while Cu and Nb are least desirable from this point of view (Table 6-4).

Table 6-3. Mean Linear Thermal Expansion Coefficients, β

<u>Material</u>	<u>$\beta, \times 10^{-6}/^{\circ}\text{C}$</u>	<u>Temperature, $^{\circ}\text{C}$</u>	<u>Ref.</u>
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°	9
Nb ₃ Sn (diffusion grown on Nb sheet)	8.7	27°-899°	10
Nb ₃ Sn (single crystals prepared at 925°C)	8.0	15°-774°	10
Nb	7.8	27°-900°	11
Cu	20.0	0°-1000°	12
Hastelloy B	13.0	21°-871°	13
Typical Austenitic Stainless Steel (for Type 303)	20.0	-32°-816°	14
Typical Martensitic Stainless Steel (for Type 410)	12.6	-32°-816°	14

Table 6-4. Characteristics of Substrate-Nb₃Ge Couples

Substrate Material	Thermal Expansion Coefficient α $\times 10^{-6}/^{\circ}\text{C}$	Thermal Expansion Mismatch with Nb ₃ Ge $\Delta\alpha \times 10^{-6}/^{\circ}\text{C}$	Strain in Nb ₃ Ge (undeformed) $\epsilon \times 10^{-3}$	Strain in Substrate (undeformed) $\epsilon \times 10^{-3}$	Compressive Stress in Nb ₃ Ge $\times 10^9$ dyne/cm ²	Tensile Stress in Substrate $\times 10^9$ dyne/cm ²	Young's Modulus $E, \times 10^{12}$ dyne/cm ²	Resistivity or Normal State Resistivity of Substrate (4.2-21 K) $\rho, \times 10^{-6}$ Ωcm	Magnetic Properties of Substrate	Corrosion Resistance	Relative Cost
Nb	7.8	0.1	~ 0.1	~ 0.01	~ 0.1	~ 0.01	1.05 ⁽¹⁷⁾	1-2 ⁽¹⁹⁾	diamagnetic	fair	high
Cu	20.0	12.3	12	1.49	12	1.9	1.29 ⁽¹⁷⁾	.015-.020 ⁽¹⁸⁾	diamagnetic	low	low
Hastelloy B	13.0	5.3	5.1	.48	5.3	.86	1.82 ⁽¹³⁾	40-60 (estimated)	weakly ferromagnetic	very high	moderate
Austenitic Stainless Steel (Type 303)	20.0	12.3	12	.95	12	2.0	2.15 ⁽¹⁷⁾	50-100 ⁽¹⁶⁾	antiferromagnetic	high	low
Martensitic Stainless Steel (Type 410)	12.6	4.9	4.7	.38	4.8	.81	2.15 ⁽¹⁷⁾ (Assumed 1.03 for Nb ₃ Ge)	~ 50 (estimated)	ferromagnetic	high	low

Magnetic properties eliminate the possibility of using martensitic stainless steel in presence of ac fields, and make Hastelloy undesirable (Table 6-4) although losses in this material may not be prohibitive (Section 6.7).

Corrosion resistance is clearly low only in case of copper. In typical $\odot$ deposition conditions a copper layer of $\sim 8-10$ μm thickness is removed before the protective Nb_3Ge layer prevents further attack.

Mechanical strength of Nb and Cu is inadequate, while excellent for the remaining materials.

Cost presents a problem in case of niobium. A 50 μm thick Nb substrate would add additional M\$9.6 to the Nb_3Ge material cost in Plan 3A (Table 3-1).

This brief review clearly indicates that no good solution for a Nb_3Ge -substrate couple exists at this moment, and that Hastelloy B substrate appears as a reasonable compromise choice for application in presence of magnetic fields. If the magnetic field is excluded from the substrate, as in the case when the superconductor coating is continuous around the tape (including edges), then martensitic stainless steel is the preferred choice.

6.5 Deposit Microstructure

The Nb_3Ge deposits prepared in the temperature range of $750^\circ\text{--}900^\circ\text{C}$ have usually a well developed columnar or fiber texture with the fiber axis normal to the substrate. The columnar growth was observed in sputtered,⁽²⁰⁾ as well as in CVD layers. Kawamura and Tachikawa found

Fig. 6-2. Fractured section of 14 μm
thick film of Nb_3Ge . X5300.

the (100) texture in CVD samples grown on niobium substrate⁽²¹⁾, and Newkirk determined the same orientation in deposits on copper.⁽²²⁾ The columnar texture of our deposits on Hastelloy B is clearly visible in SEM photographs of fractured sections. An example is shown in Figure 6-2, where the Hastelloy was removed by etching. The light bottom band represents the diffusion boundary which contains Ni and also Fe. The correlation of columnar growth with the surface topography such as shown in Appendix 4-1, Figure 6, is evident. The texture of our samples was, however, not indexed to date. The extent to which the columnar texture develops in a pure material depends upon the deposition temperature, second phase presence and the growth rate.

The deposit grain size is defined as the smallest grain dimension, perpendicular to the column axis. In sputtered films the grain size is of the order of 1000 Å or less,⁽²¹⁾ while in CVD samples it may range from several thousand angstroms up to several microns (Reference 3 and Appendix 4-1). In our thick tapes (Type I) the grains size reaches 1 µm, while in thin tapes (Type II), deposited at much lower rate, the upper limit is 3000 Å, approximately. The correlation between the microstructure and the critical current density of Nb₃Ge samples is discussed in Section 6.8.

6.6 Critical Current Density

Before discussing the results obtained on CVD deposits we review the information on sputtered Nb₃Ge. This is useful since the properties of the sputtered, fine grained material, can be assumed as a

reference base to be compared with the characteristics of CVD prepared material.

Very fragmentary and incomplete data on the critical current density of thin, sputtered Nb_3Ge have been collected to date. Because of the small sample dimensions, contact heating is a severe problem in the direct current, four-point measurements. Most of the measurements were, therefore, performed in high fields transverse to the film plane, and in the liquid hydrogen temperature range where critical currents are reasonably low. At 4.2 K and 210 kilogauss our early sputtered samples had $J_c \approx 1 \times 10^5$ amps/cm².

For a low- J_c sputtered film, additionally degraded by a narrowing process, we were able to establish the shape of the $J_c(H)$ curve down to 10 kilogauss. Assuming arbitrarily the same shape for higher- J_c specimens (1×10^5 amps/cm² at 210 kilogauss) we find $J_c \approx 1.3 \times 10^6$ amps/cm² at 10 kilogauss (level of fault current equal ~ 25 times of the normal operating current in the LILCO cable discussed in Section 2). In the following we assume the critical current densities at 10 kilogauss as a standard basis for comparisons, although the difference between the self-field J_c and the value at 10 kilogauss is not always negligible, due, for example, to the self-field J_c dependence upon the film thickness. Where appropriate, we indicate the $J_c(H)$ dependence in low fields.

Testardi determined self-field J_c of his sputtered samples using pulse currents in an attempts to avoid contact heating.⁽²³⁾ However, some measurement problems apparently persisted, since his normalized temperature dependence $J_c(T)/J_c(4.2)$ vs. T/T_c is flat up to $T/T_c \approx 0.5$, i.e., to 11 K.

The plateau corresponds to $J_c \approx 2.8 \times 10^6$ amps/cm². If we disregard this plateau and extrapolate the Testardi's $J_c(T)$ curve from the 14-22 K range down to 4.2 K, then the extrapolated value is $J_c \approx 4.4 \pm .2 \times 10^6$ amps/cm². This compares favorably with our estimated value of $J_c = 1.3 \times 10^6$ amps/cm² at 10 kilogauss, and is close to the value of $4-5 \times 10^6$ amps/cm² obtained by Tarutani et al. for an evaporated sample.⁽³³⁾ Such critical current densities are comparable to that of state-of-the-art Nb₃Sn synthesized by bronze or liquid tin diffusion. At present, Testardi's $J_c(T)$ represents the only transport current data to cover the whole temperature range, from 4.2 K up to the resistive transition onset. Unfortunately, the suspect plateau prevents a meaningful discussion of the $J_c(T)$ dependence, at least below 14 K. We assume 14 K as a reference temperature since relatively extensive measurements have been performed in the liquid hydrogen range, from 13.8 K up. Also, 14 K is the preferred upper temperature limit of the LILCO cable operation discussed in Section 2. Testardi found $J_c(14 \text{ K}) \approx 2.1 \times 10^6$ amps/cm².

Critical current densities of CVD samples were determined by the direct transport current four point method, for small samples, a few $\otimes$ tapes and several LASL Nb₃Ge-Cu tube sections.^(27,5) Measurements were usually confined to the liquid hydrogen range, and/or high magnetic fields. Indirectly, approximate values of J_c have been deduced from the field dependence of hysteretic losses at 4.2 K in samples approximately

conforming to the Bean's model,⁽²⁶⁾ and discussed in Section 6.7. In addition, J_c was deduced from the magnetization measurements using the Fietz formula.^(24,25) Magnetization in transverse fields up to 70 kilogauss could be measured on small film discs, ~ 3 mm in diameter, using a Foner magnetometer (PAR Model 151). The whole temperature range from 4.2 K up to the resistive transition could easily be covered thus providing adequate data on the $J_c(T)$ dependence.

Small sample transport measurements by Kawamura and Tachikawa were performed at 4.2 K, 65 kilogauss, and gave $J_c \approx .25 \times 10^6$ amps/cm².⁽²¹⁾ Using our typical $J_c(H)$ dependence mentioned above this corresponds to $J_c \approx 0.7 \times 10^6$ amps/cm² at 10 kilogauss. Our representative small CVD samples J_c could not be measured at 4.2 K due to contact heating. At 14 K our best result to date was $J_c \approx 1 \times 10^6$ amps/cm² (extrapolated to 10 kilogauss).

A small LASL sample was measured at 4.2 K by J. Woollam (NASA-Lewis) who obtained a self-field $J_c \approx 2 \times 10^6$ amps/cm².⁽²³⁾ Self-field critical current density of one $\odot$ tape of Type II (#47), $h \approx 1.5$ μ m thick, 20 cm long, and stabilized on each side with ~ 100 μ m of electroplated copper was measured by R. Bartlett at LASL, both in the LH₂ range and at 4.2 K, using the four-point method. A voltage drop of 0.2 μ V/cm was used as a criterion of normality. Bartlett's data are shown in Fig. 6-3 which also includes best LH₂ range data obtained on a LASL tube section.⁽²⁷⁾ Lack of measurements between 4.2 and 13.8 K makes rather impractical the curve fitting in order to determine the functional dependence of J_c upon T/T_c . The $\odot$ sample J_c exhibits a pronounced tail when approaching

Fig. 6-3—Critical current densities of samples measured at LASL

the resistive transition which starts at ~ 18.5 K, and is complete at 19.7 K. This tail is an indication of possible Al₅ phase nonuniformity discussed below, and not the true property of homogeneous Nb₃Ge. Indeed, the LASL sample has a lesser tail, and in the LH₂ range the $J_c(T)$ curve is fairly linear. A linear extrapolation to 4.2 K gives $J_c \sim 5.2 \times 10^6$ amps/cm² ($T_c^* = 18.9$ K was used for J_c extrapolation, the star denoting a value extrapolated from the steep portion of the $J_c(T)$ curve) which compares favorably with the measurement on the (W) tape:

$J_c \sim 1.5 \times 10^6$ amps/cm². Two 10 to 11 cm long Cu-stabilized tape sections (#45) measured by us at 4.2 K had an even lower J_c , so that the extrapolated LASL value is actually the highest deduced from transport measurements on a CVD material, and close to that of evaporated and sputtered samples. At 14 K the record high $J_c \sim 1.8 \times 10^6$ amps/cm² is again close to that of Testardi's sputtered films.

The shorted turn transformer measurement of ac losses vs. field at 4.2 K (Section 6.7) was performed on (W) tape #47 before it was subject to four-point transport current measurement by Bartlett. From the ac loss measurement a J_c value of $\sim 1.3 \times 10^6$ amps/cm² was calculated in a very satisfactory agreement with the direct current result. Loss measurement on short tape sections, again at 4.2 K and in low fields, gave $J_c \sim 4 \times 10^6$ amps/cm² for Type I and up to $J_c \sim 6 \times 10^6$ amps/cm² for Type II tapes (Section 6-7). However, these high values were obtained in very low field of 1-2 kilogauss, and decreased rapidly with increasing field intensity. A summary of J_c data obtained by various methods is given in Table 6-5, and examples of field dependence in Table 6-6.

Table 6-5

HIGHEST REPORTED CRITICAL CURRENT DENSITIES OF HIGH- T_c Nb_3Ge

Sample Type	J_c $\times 10^6$ A/cm ²		Measuring Method*	Magnetic Field Intensity, Kilogauss	Reference	Comment
	4.2K	14K				
<u>Sputtered & Evap.</u>						
Small	2.8(4.4)	2.1	T	self	23	Values in parentheses obtained by extrapolation, or estimated, see text.
Small	4-5		T	10	33	
<u>CVD</u>						
Small	(0.7)	-	T	10	21	a LASL sample
Small	2.8		T	self	23	
Small	-	~ 1	T	10	(W)	
Tube Section	(5.2)	1.8	T	self	27	Bartlett's measurement
Tape, Type II	{ 1.5	0.5	T	self	(W)	
	{ 1.35	-	L	self		
Short Tape, Type I	~ 4	-	L	1-2	(W)	
Short Tape, Type II	~ 6	-	L	1-2	(W)	
Disc, Type I	{ 0.35	-	M	10	(W)	
	{ 0.85			1		
Disc, Type II	{ 0.30	-	M	10	(W)	
	{ ~ 1.6			1		

* T -- direct transport current, four-point
 L -- deduced from loss vs. field dependence
 M -- magnetization

The magnetization measurements produced the information on the temperature dependence of J_c . First, we verified that numerical J_c results agree to within 20-30% with measurements on small samples. While we use the absolute J_c values from magnetization measurements with caution (demagnetizing effects are ignored), the data should faithfully represent the relative changes in $J_c(T)$. We thus measured $J_c(T)$ of $\odot$ samples of Type I and II. A LASL sample #128M8, and also a Nb_3Sn sample was used as a reference. Figure 6-4 compares the normalized temperature dependences where T_c^* denotes the normalization temperature.

Samples 25-14 (Type I, $h = 7 \mu m$) and 128M8 show temperature dependences virtually identical to that of Nb_3Sn except for the high temperature tail, somewhat less pronounced in the latter Nb_3Ge sample. When neglecting this tail, the data fit reasonably well the $1 - (T/T_c^*)^2$ dependence, as shown in Fig. 6-5. Both Nb_3Ge samples are nearly stoichiometric, i.e., contain ~ 25 at. % Ge, and the x-ray phase analysis indicates the presence of some tetragonal phase.⁽²⁸⁾ In contrast, Sample 23-8 (Type I, $h = 14 \mu m$) shows an abrupt drop in $J_c(T)$, and a very long tail up to T_c . This sample is Ge-deficient (~ 19 at. % Ge) and we strongly suspect that it represents a range of A15 solid solutions, the bulk of them having rather low T_c 's. This interpretation is contradicted, however, by very sharp x-ray powder patterns of the sample. With additional evidence pending, we assume that the tail is not representative for pure Nb_3Ge properties, and that samples 25-14 and 128M8 represent an acceptable approximation of the material characteristics to be used in the cable analysis.

Fig. 6-4 — Reduced current density versus reduced temperature for 3 CVD produced Nb_3Ge films and 1 diffusion produced Nb_3Sn film

Fig. 6-5—Normalized critical current vs temperature

The magnetometer measurements are also conveniently used for the determination of the $J_c(H)$ dependence at low field intensities. The shape of $J_c(H)$ varies widely from sample to sample and depends strongly upon the preparation conditions. Table 6-6 shows examples of normalized $J_c(H)/J_c(10)$ vs. H data, where $J_c(10)$ is the value at 10 kilogauss. LASL sample #128M8 has a less pronounced dependence of J_c upon H .

Table 6-6
LOW FIELD DEPENDENCE OF J_c vs. H
 $T = 4.2$ K

Sample	Thickness $h, \mu m$	$J_c(H)/J_c(10)$				
		1	2	5	10	20
25-14 (Type I)	7	2.33	1.86	1.33	1	.69
39-6 (Type II)	0.6	5.9	3.7	1.85	1	.52
$H, \text{ kilogauss}$		1	2	5	10	20

The example shown suggests some caution when comparing the self-field J_c data with those obtained at 10 kilogauss. In many cases the self-field values will be substantially higher, as can also be inferred from Table 6-5.

The critical current density susceptibility to mechanical deformation was tested by subjecting two low grade tapes of Type II ($T_c \approx 13-14$ K, pure Al5, $h = 1.7$ and $2.9 \mu m$, $10 \mu m$ copper coat) to a bending test at 4.2 K. The test was performed by C. Klamut at BNL. To

Fig. 6-6 — Results of bending test

reduce the current through the tape a field of 30 kilogauss was applied parallel to the test sample axis. The starting critical current density was $J_c \approx 4.4 \times 10^4$ amps/cm² for the tape $h = 1.7$ μ m thick. The critical current was degraded at a bending radius of less than 0.3 cm, with the layer subject to compression. For a radius r_0 the mechanical strain is $\epsilon = y/r_0$, where y is the distance from the neutral axis of bending, i.e., from the plane of zero strain. For the 50 μ m thick substrate $y \approx 25.9 \times 10^{-4}$ cm. Hence, $\epsilon = 25.9 \times 10^{-4}/0.3 \approx 8.6 \times 10^{-3}$, almost double of the strain due to thermal expansion mismatch. The value of $r_0 = 0.3$ cm is very satisfactory. The thicker tape, of inferior $J_c \approx 2.1 \times 10^4$ amps/cm² degraded at $r_0 \leq 0.6-0.8$ cm (estimated). This corresponds to a strain of $\epsilon = 4.4 \times 10^{-3}$. Testing of thicker, Type I tapes is necessary to obtain a fuller picture of the Nb₃Ge layer susceptibility to mechanical deformation. However, the above preliminary results are encouraging.

6.7 The AC Losses

The only ac loss data determined for Nb_3Ge are those of ② Type I and II tapes on Hastelloy substrates and of one LASL sample. The results should still be considered as preliminary. Since the Nb_3Ge layer is present only on one side of the normal metal (Hastelloy B or Cu) the substrate contributes to losses when subject to the ac magnetic field. The shorted turn transformer measurement method is therefore preferred for tapes, as already stated in Section 5.3. Three tapes of Type II were subject to transformer measurements at 4.2 K, 60 Hz: #45, 47 and 48. The first developed soldering problems at two joints with the Nb_3Sn splice, and was not measured to date. The #48 had negligible J_c (in spite of high $T_c \approx 21$ K), so that only #47 was measured, both at BNL (with M. Garber) and ②. At higher surface currents $\sigma > 800$ A/cm (rms) the loss vs field dependence had the $n = 3$ exponent, and thus conformed approximately to Bean's model with $J_c \approx 1.3 \times 10^6$ amps/cm². However, at low σ the losses were very high with $n < 1$, and the $p(H)$ curve was similar to those of Nb_3Sn with PbSn solder.⁽³⁰⁾ At $\sigma = 426$ A/cm (rms) the loss was $p = 150$ $\mu\text{W}/\text{cm}^2$. We don't understand this result, and defer interpretations to the time when additional tapes of sufficient length (~ 30 cm) will be available for testing.

To liberate ourselves from the tape length restriction, we used the short sample test method (Section 5.3), and measured several 4-5 cm long tape specimens at BNL (with the participation of M. Suenaga and J. Bussiere). Figure 6-7 compares the 4.2 K, 60 Hz data for Type I tape 23-9, and Type II tape 39-7 with results for two

Fig. 6-7—The 60 Hz losses of Nb_3Ge and Nb_3Sn tapes at 4.2 K (Nb_3Sn data from BNL measurements)

commercial Nb_3Sn tapes measured earlier at BNL by the same method, (31)

The coarse-grained, rough-surfaced 23-9 has very high losses at low σ , with $n < 3$. At higher fields, however, $n = 3$, and $J_c = 4 \times 10^6 \text{ amps/cm}^2$.

The much smoother 39-7 (and other Type I and II smooth samples) has losses comparable to the Nb_3Sn IGC tape with $J_c = 6 \times 10^6 \text{ amp/cm}^2$. The surface topographies of both types are shown in Figure 6, Appendix 4-1 and seem to have a significant effect on losses, as observed for Nb_3Sn by J. Bussiere at BNL. However, even losses of the smooth tapes are considerably higher than those of optimized, low loss Nb_3Sn such as KB15 or Airco. No significant surface barrier field, $\Delta H > 100 \text{ gauss}$, was observed in any Nb_3Ge tape on Hastelloy B. Table 6-7 gives 4.2 K loss data at the normal and continuous contingency σ level (Plan 3A), and at $\sigma = 1000 \text{ A/cm (rms)}$, for typical samples measured to date. All the samples have T_c in the 20-22.5 K range.

The Nb_3Ge losses include the contribution of Hastelloy B substrate. Measurements of bare substrate sections indicated that the loss in Hastelloy is by itself comparable or higher than losses in best Nb_3Sn tapes, but contributes only 20-25% or less, to the losses of most Nb_3Ge samples (Table 6-7). The effective contribution is probably somewhat less significant because of the current sharing between the superconducting layer and normal substrate. On the other hand, however, the low field loss in Hastelloy is predominantly hysteretic, and therefore, independent of the induced current. The loss in Hastelloy itself, while highly undesirable, does not appear prohibitive for the cable application. The contribution of the Ni_3Nb and NiNb -- containing diffusion layer

Table 6-7. The AC Losses of Nb₃Ge Short Tape Samples and Selected Nb₃Sn Tapes

Electronic wattmeter measurement, T = 4.2 K, f = 60 Hz

Surface Current, σ A/cm (rms)	Loss			Comment
	~ 215	426	$p(\sigma), \mu W/cm^2$ 1000	
<u>Sample Type</u>				
Nb ₃ Ge on Hastelloy				
23-9	33	75	350	Rough Surface
23-11	18	55	700	Rough Surface
25-14	4.0	80	-	Rough Surface and Premature Penetration
27-10 Type I	2.5	10	400	Smooth Surface
28-14	3.5	-	-	Premature Penetration
31-11	7.0	30	250	Smooth Surface
39-7 Type II	4.8	25	~ 200	
43-8	4.0	18	-	Premature Penetration
Hastelloy B	1.3	3-5	15	
<u>Nb₃Sn</u>				
IGC 1 (samples 3,4,6) (30)	1-2	~ 30	800	
KB15	<1	8	280	
AIRCO (BCA 2843-45)	<<1	~ 1	130	

at the $\text{Nb}_3\text{Ge}/\text{Hastalloy}$ interface cannot be estimated without measuring Nb_3Ge tapes deposited on alternate substrates. This was not yet attempted.

In several samples we observe premature flux penetration: above a certain σ level the slope of the $p(\sigma)$ curve decreases towards $n \leq 1$. This is shown in Figure 6-8, and marked in Table 6-7. The occurrence of this premature penetration is also confirmed by the hysteretic loss measurements using the Foner magnetometer (discussed below). We tend to associate this effect with strong dependence of J_c upon H (Table 6-6) but do not yet have any correlation between the effect and the sample preparation conditions, uniformity, etc. Since it occurs only sporadically it is certainly not representative for the Nb_3Ge material as such.

To assess the Nb_3Ge behavior in a cable operating at higher temperatures, 14 K for example (Section 2), it is essential to determine the dependence of ac losses upon temperature. The shorted turn, "in flight" transformer measurement of tape #47 (Section 5.2) at $\sigma \approx 500$ A/cm (rms) indicated that loss decreases continuously with increasing temperature up to the vicinity of the resistive transition. This is a completely unexpected behavior. Since losses are inversely proportional to J_c they should increase as $J_c(T)$ decreases. For Nb_3Sn this is shown in Reference 31 and we obtained the same result by our "in flight" shorted turn $p(T)$ measurement on a KB15 tape. Hence, we initially felt that for Nb_3Ge we observed an artifact of the experiment due, for example, to the solder at the joints with the Nb_3Sn splice. In effect, we did not analyze it further. Rather, we performed the short sample loss measurements in the liquid hydrogen range and in He (Section 5.3). Sample 27-10 showing low

Fig. 6-8—Comparison of AC loss data measured electronically, and using the Foner magnetometer

loss, and no premature penetration was used for the purpose. Again, losses at 14 K were lower than at 4.2 K in the range of $\sigma = 160-540$ A/cm (rms). Above 14 K losses increased up to the transition. The Nb₃Sn reference sample (Airco BCA-2843-45) exhibited the normal dramatic increase of losses with temperature. Hence, the anomalous p(T) behavior appears to be characteristic of at least some of our Nb₃Ge tapes on Hastelloy.

To gather further evidence on the Nb₃Ge p(T) dependence we employed the Foner magnetometer. The hysteretic loss per cycle is simply the area of the M-H loop where M is the magnetic moment. The samples are used in form of sandwiches made of several small Nb₃Ge film sections separated by the substrate and a cement. The spacing is at least 3-5 times larger than the film thickness. The number of layers is 10 to 30 in order to obtain a sufficiently large M-signal. The sandwich plane is aligned parallel to the magnetic field to conform with Bean's model geometry. Figure 6-8 compares the p(σ), 4.2 K curve for sample 28-14 with the electronic wattmeter result. The agreement is satisfactory in the surface current range of interest, $\sigma \leq 500$ A/cm. The discrepancy at higher σ (i.e. field) may be due to a slight misalignment of the sample with respect to the field, while at very low σ the sensitivity is insufficient.

The temperature dependences of the losses of the two samples measured to date are shown in Figure 6-9. A very gradual increase is observed in very low fields (H = 450 gauss, equivalent to $\sigma = 255$ A/cm, rms) and a gradual slight decrease at the level of 1 kilogauss ($\sigma = 562$ A/cm, rms). At the last moment, when completing this report, a comparison with LASL

Fig. 6-9—Normalized AC loss (60Hz) vs temperature at low surface current levels

sample #128M8 was made. In this sample losses increase moderately with temperature up to 12-14 K but very dramatically when approaching T_c .

It appears that the behavior of our Nb_3Ge /Hastelloy is somewhat different from sample to sample but probably does not represent the typical characteristic of Nb_3Ge . Possibly a loss component associated e.g. with the presence of the Nb_3Ge /Hastelloy diffusion boundary has a negative $p(T)$ slope. Of course, this is only a speculation, and the problem clearly requires a further investigation. For the purpose of the cable analysis it is sufficient to state that in no case, including the LASL sample, are losses at 14 K much higher than at 4.2 K.

6.8 Discussion

The preceding review of Nb_3Ge properties indicates that much remains to be learned about the Nb_3Ge characteristics, and their correlation with preparation parameters. The phase and uniformity control leaves much to be desired, as suggested in particular by the $J_c(T)$ data of Figure 6.4. The critical current densities of @ tapes on Hastelloy B are significantly inferior to the best results published for sputtered films, and for a CVD sample prepared at LASL.⁽²⁷⁾ It is interesting to note that contrary to our earlier speculations the J_c level in best sputtered, evaporated, and CVD films is nearly the same, in spite of a significantly different microstructure or, more specifically, grain size. This suggests that in Nb_3Ge the flux pinning may not predominantly occur on grain boundaries, in contrast to Nb_3Sn tapes.⁽³⁴⁾ While more evidence

must be gathered it seems that a further significant increase in J_c should be pursued not only through the control of microstructure, but also by experimenting with flux pinning impurities and/or second phase precipitates. The theoretical upper limit for J_c is estimated to be in the range of $10^8 - 10^9$ amps/cm² at 4.2 K if determined by spin depairing when the kinetic energy of electrons approaches the condensation energy. Alternatively, a similar J_c limit can be deduced from mechanical strength of pinning centers subject to enormous Lorentz forces.⁽³²⁾ In any case, there should exist a significant margin for J_c improvement up to $(1-2) \times 10^7$ amps/cm², still below the theoretical limit.

To achieve Nb₃Ge performance at 14 K equal to that of best Nb₃Sn at 8 K, ($J_c \leq 4 \times 10^6$ amps/cm²), a moderate improvement of J_c by a factor of two could be sufficient. Since this is highly probable Nb₃Ge clearly emerges as a conductor candidate superior to Nb₃Sn.

The present data on ac losses, and their understanding are very fragmentary. A closer look into the effect of Hastelloy substrate and the diffusion layer is mandatory for @ samples. However, no evidence is found of high loss levels at temperatures up to 14 K. Loss reduction to the low level represented by the best Nb₃Sn tapes is an important objective and calls for technological efforts. But it seems secondary in importance when compared to the high- J_c goal.

To conclude this discussion we compare in Table 6-8 the best reported properties of Nb₃Sn and Nb₃Ge. In both cases we quote mostly laboratory results obtained for specimens synthesized by any of the alternative techniques (diffusion, physical evaporation, sputtering or

Table 6-8
Comparison of Relevant Properties
of Nb₃Ge and Nb₃Sn
(Best data)

Property	Notation & Unit	Nb ₃ Sn	Nb ₃ Ge	Comment
Critical Temperature	T _c , K	18.2 ⁽³⁵⁾	23.2 ⁽⁶⁾	Superconductive Onsets
Critical Field, 4.2 K	H _{c2} , kOe	~225 ⁽³⁶⁾	~380 ⁽³⁷⁾	
Self-Field Critical Current, 4.2 K 14 K	J _c , A/cm ²	5-7 x 10 ⁶ (38,39) ~1.2 x 10 ⁶ (27)	~5 x 10 ⁶ ~2 x 10 ⁶	
Low Field Losses 60 Hz, 4.2 K σ = 215 A/cm(rms) 426 1000	p, μW/cm ²	<<1 ~1 130	2.5 10 400	Nb ₃ Ge data from Table 6-5 Data from Table 6-7
Thermal Expansion Coefficient	β, °C ⁻¹	8 x 10 ⁻⁶	7.7 x 10 ⁻⁶	
Brittleness	--	high	high	From Table 6-3

CVD). We do not show ac losses at higher temperatures, above 4.2 K, since the data for Nb_3Ge are too fragmentary, as discussed above. The comparison indicates that after more than a decade of Nb_3Sn development its critical current capability is on the same level as in Nb_3Ge samples obtained during the first year of study. The ac losses in Nb_3Sn are at the moment much lower than in Nb_3Ge . However, this progress in Nb_3Sn occurred only most recently (as a result of BNL studies) and can most likely be duplicated for Nb_3Ge . The overall improvement potential of Nb_3Ge properties is thus high, in particular with respect to higher temperatures, 14 K and perhaps above, where Nb_3Sn simply cannot perform.

6.9 Conclusions

1. The determination of Nb_3Ge "state-of-the-art" properties did not reveal any characteristics basically detrimental to the intended cable application.
2. The temperature dependences of the critical current density and ac loss do allow for Nb_3Ge utilization at temperatures up to, at least, 14 K.
3. The most essential conductor improvement needed is to increase the critical current density by a factor of at least two, and possibly more. This appears to be feasible.
4. Second in importance is Nb_3Ge loss reduction. The present loss level is not prohibitive.
5. For transmission line application Nb_3Ge emerges as a superconducting material potentially superior to the Nb_3Sn .

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7. GENERAL CONCLUSIONS

Based on the specific conclusions formulated in Sections 2.6, 3.6 and 6.9 we present here the general conclusions drawn from Phase I of this program, which used the BNL design of LILCO ac superconducting transmission line, Plan 3A, as an exhibit.

1. The cost benefit analysis comparing existing cable conductors based upon Nb_3Sn to potential Nb_3Ge conductor shows that the use of Nb_3Ge leads to savings in refrigeration or cryogenic enclosure cost. The maximum saving can be 4 to 10% of the total plan cost. The savings are contingent upon the economic competitiveness of Nb_3Ge manufacture with that of Nb_3Sn . The analysis of the CVD fabrication process shows that this is feasible.
2. The Nb_3Ge conductors can be successfully substituted for Nb_3Sn if the critical current density, J_c , of Nb_3Ge is substantially improved over the present state-of-the-art. Depending upon the extent of the improvement either economic, or technical benefits, or both, can be derived. Substantial increase of J_c is technically feasible. Coupled with the increase

in J_c a reduction of ac losses is desirable.

Other properties of Nb_3Ge are generally acceptable.

No Nb_3Ge properties basically detrimental to the utilization in transmission cables have been discovered.

8. RECOMMENDATIONS

The implementation of Nb_3Ge in superconducting ac transmission cables should be preceded by several investigations and development efforts recommended below in descending order of priority.

1. Develop a reproducibly improved Nb_3Ge tape conductor aiming at $J_c \geq 10^7$ amps/cm² and low loss in the broadest possible temperature range.
2. Investigate the design of Nb_3Ge superconducting cable optimized to the conductor rather than to the power system, with possible use of compensating terminal equipment.
3. Develop an economic process of Nb_3Ge tape fabrication from vapor phase.
4. Investigate hydrogen as a coolant and insulating fluid.

9. ACKNOWLEDGEMENTS

We express our gratitude to the Brookhaven National Laboratory, Power Transmission Project, represented by E. B. Forsyth and D. H. Gurinsky. Without their cooperation and generous advice this program would not have been possible. We are also very indebted to W. E. Keller and L. R. Newkirk of the Los Alamos Scientific Laboratory for their most helpful and cooperative attitude.

We express our sincere thanks to all the contributors listed in Section 1.4. Also, we acknowledge the valuable technical help and expertize offered by M. T. Miller, P. A. Piotrowski, H. C. Pohl, E. P. A. Metz, R. P. Storrick, A. L. Foley, and S. Pollack (BNL). Finally, we thank C. W. Hughes for the scanning electron microscopy work. Careful typing of this document was performed by Joyce McQuiston with help of Cathie Kowalczyk.

APPENDIX 3-1. ROUGH ESTIMATE OF FABRICATION COST

A CVD facility capable of producing in one year the amount of Nb_3Ge , corresponding to Plan 3A is assumed (case (b), $h = 20 \mu\text{m}$ thick coating). Hence, the basis is $226,600 \text{ m}^2/\text{year}$ with 4800 operating hours/year. The plant consists of $226,600/4800 \approx 50$ semi-automatic standard production units or a lesser number of correspondingly larger reactors. The capital cost of a standard unit is assumed to be 0.1 M\$. The Nb_3Ge superconductor deposition is the only process estimated. Table 1 summarizes the components of a yearly operating cost.

The direct labor cost is based on the present @ costing rates for skilled nonprofessional personnel. A crew of one operator and three assistant operators is maintaining 10 units in continuous operation. The labor operating time is 6000 hrs/year.

The electric energy demand is estimated by assuming that for the anticipated operating conditions (with resistive electric heating used) radiation is the prime source of heat loss. We assume the heating and cooling power requirements to be roughly equal and estimate the heat loss, Q , per m^2 from the Stefan-Boltzmann law:

$$Q \approx 10^4 \epsilon \sigma T_d^4$$

where:

$\epsilon = 0.15$ is the total radiant emittance for a smooth metal such as the copper/stainless steel composite,⁽⁶⁾

$\sigma = 5.673 \times 10^{-12}$ watt/cm²°K⁴, is the Boltzmann radiation constant,

$T_d = 1173$ K is the deposition temperature

$$Q = 10^4 \times 0.15 \times 5.673 \times 10^{-12} (1173)^4 = 16.1 \text{ kW/m}^2$$

The total heat requirement per tape side is assumed to be $2Q + 25\%$ for chlorination and miscellaneous uses, and additional 25% for losses and contingencies

$$Q_{TOT} = 48.3 \text{ kW/m}^2$$

One CVD unit energy demand is 96.6 kWh/hour (two sides).

The total yearly electric energy demand (50 reactors) is:

$$96.6 \times 50 \times 4800 = 23,200,000 \text{ kWh/year}$$

and the installed power is 4.8 MW.

The use of water for cooling of equipment, and output is assumed. The cooling water temperature is raised in the process from 16°C to ~100°C, and the unit energy removal is 0.05 kWh/l. The quantity of water required is

$$V = \frac{23,200,000}{3 \times 0.05} \times 155 \times 10^6 \text{ l/year} \\ (\sim 41 \times 10^6 \text{ gal/year}).$$

Other components contributing to cost, and listed in Table 1 are standard.

Table 1. CVD Yearly Operating Cost

<u>Direct Labor</u>	\$
Operator (5/shift) @ \$12/hr	360,000
Assistant operator (15/shift) @ \$10/hr	900,000
Supervisor (1/shift) @ \$15/hr	90,000
Quality controller (2/shift) @ \$12/hr	<u>144,000</u>
	1,494,000
<u>Utilities</u>	
Electric energy 23.2 MkwH @ \$0.03/kwH	696,000
Cooling water 155 Ml/year @ \$85/Ml	<u>~13,000</u>
	709,000
<u>Maintenance</u>	
8% fixed capital	400,000
<u>Depreciation</u>	
20% fixed capital	1,000,000
<u>Grand Total</u>	3,603,000
<u>Cost per m² of tape</u>	15.90

APPENDIX 4-1

CHEMICAL VAPOR DEPOSITION OF Nb_3Ge *

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ABSTRACT

Chemical vapor deposition (CVD) was used to prepare high critical temperature superconducting films of Nb_3Ge on metallic tape substrates. A CVD system was developed to produce uniform tape sections up to 25 cm in length. The evaluation of conductor parameters such as self-field critical currents and AC losses indicated that at 4.2K the first Nb_3Ge tapes have properties comparable to commercial Nb_3Sn . Comparison with sputtered samples indicated that a significant margin exists for further improvements, particularly of the critical current density.

*The research on Nb_3Ge synthesis and properties was supported in part by AFOSR under the Contract No. F44620-74-C-0042. The preparation and evaluation of samples with regard to transmission line applications was supported by ERDA under the Contract No. E(11-1)-2522.

CHEMICAL VAPOR DEPOSITION OF Nb_3Ge

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INTRODUCTION

The discovery by Cavalier⁽¹⁾ that sputtered thin films of the A-15 compound Nb_3Ge have a superconducting transition temperature, T_c , in excess of 22K, as well as attractive high-field properties, led us to examine the available methods for the synthesis of high- T_c Nb_3Ge by a process more adapted to fabrication in useful form, e.g., as a metallic tape. The difficulties in obtaining high- T_c Nb_3Ge are compounded relative to, for example, Nb_3Sn , because of the occurrence of competing tetragonal phases in the Nb-Ge system. Moreover, it is believed that the highest- T_c material is only stable at temperatures below 1000°C, so that a synthesis technique that can be used at reasonably low temperatures is required. The choices available to us were the chemical vapor deposition (CVD), the physical evaporation, or a diffusion process, and of these we chose the CVD process as offering the most immediate promise of success. The choice was based on the earlier successes in using CVD for synthesis of Nb_3Sn ⁽²⁾ and Nb_3Ga ,⁽³⁾ and the previous CVD synthesis of Nb_3Ge with T_c values up to 19K.⁽⁴⁾ We reported

the results of our initial experiments in two earlier papers.^(5,6) The results of parallel, independent efforts were reported by Newkirk et al.,⁽⁷⁾ Kawamura and Tachikawa,⁽⁸⁾ and Vieland and Wicklund.⁽⁹⁾ High T_c material was obtained in all cases, thus confirming the potential of CVD. The purpose of this paper is to report on progress of our Nb_3Ge synthesis effort and on the superconducting properties obtained.

THE CVD PROCESS

The CVD process we use involves direct chlorination of Nb and Ge to NbCl_4 and GeCl_2 with subsequent reduction of the chloride gas mixture by H_2 to form metallic deposits. The CVD sum reaction can be written as

for which the equilibrium constant, written in terms of partial pressures, p , is

$$K_p = \frac{[p_{\text{HCl}}]^{14}}{[p_{\text{NbCl}_4}]^3 [p_{\text{GeCl}_2}] [p_{\text{H}_2}]^7} \quad (2)$$

In our gas flow system equilibrium is not attained because the process is controlled also by kinetic factors such as the residence time. However, Eqs. 1 and 2 still provide useful guidelines; for example, it is clear that by varying the amount of HCl present in the deposition zone, we could modify the rate of Nb_3Ge deposition. This technique was used in previous CVD deposition of Nb_3Sn and Nb_3Ga ,^(2,3) but we opted to control the deposition with other variables, such as the residence time and dilution. Since K_p is so dramatically dependent upon p_{HCl} , we would expect a gradual growth rate change along the tube as HCl is produced by Reaction 1. In fact, we observe such a growth-rate change in our experiments (see below).

The CVD flow reactor is constructed of quartz glass heated with resistance furnaces and operates at atmospheric pressure. A schematic diagram is shown in Fig. 1. The first stages of the reactor are chlorination chambers for generation of the metal chlorides. We have studied in detail the chlorination reactions of the elements to ensure that reproducible Nb/Ge ratios are delivered to the deposition zone of the CVD reactor, and that all delivered Cl_2 is consumed during chlorination. In the case of Nb, chlorination proceeds stoichiometrically to NbCl_4 above about 700°C . Below that temperature the reaction is complicated by the formation of nonvolatile NbCl_3 . For Ge, chlorination proceeds stoichiometrically to GeCl_2 above about 650°C .

As in all CVD processes, a complete mixing of the gas phase components is mandatory to ensure uniform film deposition. Mixing is achieved by allowing the GeCl_2 gas obtained by chlorinating Ge at a temperature $> 650^\circ\text{C}$ to flow through the Nb chlorination bed which in turn is chlorinated with an independent flow of Cl_2 .

Following chlorination, the third active component of the gas phase (H_2) and the carrier gas are mixed with the chloride gases in a mixing chamber operating at 500°C , a feature of the reactor which follows the design concept of Newkirk et al.⁽⁷⁾ Mixing is accomplished by passing the gas through a series of baffles and jets shown in Fig. 1. The mixing temperature is critical; mixing H_2 with the chloride gases at $T_{\text{mix}} > 550^\circ\text{C}$ results in significant reduction to metal, while at $T_{\text{mix}} < 500^\circ\text{C}$ lower chlorides of Nb, e.g., NbCl_3 , condense from the vapor phase.

After mixing, the gas mixture passes into the deposition zone, which is specifically designed to provide a uniform temperature region ($\pm 5^\circ\text{C}$) over a 30-50 cm length, where deposition occurs on the walls of the quartz tube and on any desired substrate material. An inert component in the gas phase, He or Ar, allows us to dilute the vapor reactants and to control the velocity of the gas phase through the deposition zone and thus the residence time. This modifies the deposition profile while maintaining the molar ratios of $s = \text{NbCl}_4/\text{GeCl}_2$ and $r = \text{H}_2/(\text{NbCl}_4 + \text{GeCl}_2)$ constant.

DEPOSITION RESULTS

Single Elements

In the deposition temperature range of $T_d = 700^\circ$ to 900°C , the Gibbs free energy changes, $\Delta G(T_d)$, in the NbCl_4 and GeCl_2 reduction with molecular hydrogen differ substantially. For example, at 900°C $\Delta G \approx +6$ kcal/mole for niobium while for germanium $\Delta G \approx -17$ kcal/mole. (2,10) It is not surprising, therefore, that we observe Ge to deposit at a much higher rate than Nb, and that the atomic ratio of metals in the solid Nb-Ge deposition differs from that of the gas phase. In such a case, there are different depletion rates for each constituent in the gas phase and solid phase segregation is likely to occur along the deposition tube. In the present study we tried to attain phase, composition and thickness uniformity along the constant temperature zone of substantial length, and the first step was to investigate the deposition of single elements. The experimental variables included the molar ratio of hydrogen to metal chloride, r , the delivery rate of reacting species in moles/hour, the dilution of reaction components by the inert carrier gas, the gas mixture velocity in the deposition zone, v , and the deposition temperature, T_d . We measured the rate of reduction of chloride to metal expressed as total reaction yield, Y , the longitudinal distribution of growth rate and the film thickness, h .

A brief summary of the results accumulated using quartz substrate tubes of ~ 2.5 cm ID and various lengths is given below.

1. The reaction yield is relatively independent of delivery rate in the range of 10^{-2} to 1 mole/hour, other variables held constant. This means that yield is not much affected by dilution, and hence the $Y(r, T_d, v)$ data provide directly usable information for scaling and predicting growth rates.

2. Yield increases nearly linearly with r at low r values, and gradually saturates at $r > 5$ to 10. Hence, there is no substantial benefit to be gained by using large hydrogen excess, $r \gg 10$.

3. Yield is higher for germanium than for niobium in the temperature range $T_d = 700^\circ$ to 950°C , as expected from ΔG values.

4. For both Ge and Nb, yield increases with temperature. The temperature dependences of Y are, however, different.

5. The longitudinal uniformity of growth rate improves with decreasing yield due to reduced gas-phase depletion and lesser concentration of HCl generated (Reaction 1). Low yields can be obtained by lowering either r or T_d , or increasing v to reduce the species residence time in the deposition zone. Gas velocities in the 400-500 cm/sec are sufficient to obtain relatively uniform deposits of Ge or Nb over 50 cm of tube length, even at the high $r = 10$.

Deposition of Nb-Ge

The two sets of deposition parameters given in Table I were selected on the basis of single element data. The first set was intended to produce a substantially larger deposit growth rate and thickness than the second set. The Nb/Ge ratio in the chloride vapor mixture, s , was the only independent variable.

The deposited phases were identified by the x-ray Debye-Scherrer powder method. The phases found at a specific position, $z \approx 15$ cm, in the isothermal deposition zone (Fig. 1) are listed in Table II as function of s .

The expected progression from Nb to the A15 phase occurred as s decreased from 10 to 7, and A15 was the only phase observed between $s = 7$ and 4.5. The A15 cell size was $a_0 = 5.170 \pm 0.001 \text{ \AA}$ at $s = 5.6$ and decreased with s until a tetragonal second phase appeared along with A15 at $s = 4.2$. The A15 cell size then stabilized at the level of $a_0 = 5.150 \pm 0.005 \text{ \AA}$, close to that obtained by Newkirk *et al.*⁽⁷⁾ for A15 samples containing second phase. The tetragonal phase does not have the usually reported T1 structure ($a = 10.148 \text{ \AA}$, $c = 5.152 \text{ \AA}$) for the phase of composition $\text{NbGe}_{0.54 \pm 0.06}$ ^(11,12). The powder diffraction data are essentially the same as those reported for the Nb_5Si_3 phase (T2 structure) found in the Nb-Si system.⁽¹³⁾ A similar T2 structure is also

Table I
STANDARD DEPOSITION CONDITIONS USED

	<u>Set 1</u>	<u>Set 2</u>
Temperature, T_d , °C	900	900
Helium Carrier Flow Rate, l/min	20	20
Gas Mixture Velocity at 900°C, v , cm/sec	~ 500	~ 500
Molar Ratio Hydrogen/Chlorides, r	10	10
Molar Ratio $NbCl_4/GeCl_2$ Delivered, s	12.5-2.6	5-4.2
Chloride Delivery Level, mole/hour	0.150	0.03
Molar Ratio of He to Active Components (Dilution)	30	150
Typical Observed Thickness Growth Rate, h_t , $\mu m/hour$	20-50	4-10
Deposition Time, min	30-60	15-30

Table II

Nb-Ge PHASES PRESENT AS A FUNCTION OF GAS PHASE Nb/Ge RATIO, s^{*}
(Set 1 of Deposition Conditions)

<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	T1 + T2 Tetragonal Phases

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

known for α -TaGe_{0.5}⁽¹¹⁾. The cell size of our T2 structure is $a = 6.63 \text{ \AA}$, $c = 11.96 \text{ \AA}$. Further decrease of the Nb/Ge ratio resulted in the appearance of the T1 structure together with T2.

We observed that the growth-rate profiles along the isothermal deposition zone, $h_c(l)$, depended upon s . While both single elements showed satisfactory uniformity of h_c , a substantially heavier deposit accumulated near the zone inlet as Nb-Ge phases formed. This suggested that these phases have a low free energy of formation. The shift towards the inlet deteriorated the growth rate uniformity, as shown in Fig. 2 for $s = 4.5$. The ratio Nb/Ge in the solid deposit increased with l , i.e., along the deposition zone, as indicated by the increasing cell size $a_0(l)$ shown in Fig. 2. At $s = 4.5$, a pure Al5 phase extended over 30 cm of the isothermal zone while the growth rate varied by a factor of less than 2. The superconductivity onset, determined by resistive measurements, showed a broad maximum of $T_c = 22.5 \pm 0.05 \text{ K}$ with $\sim 24 \text{ cm}$ of the tape substrate having $T_c \geq 20 \text{ K}$. The $T_c(l)$ profiles for several values of s are shown in Fig. 3. With s decreasing from about 7 the peak value of T_c increased while the peak shifted downstream, towards higher l . At $s = 3.3$, in presence of the tetragonal T2 phase $T_c(l)$ showed a monotonic increase. The reason for this is not understood since one would expect Al5 coexisting with T2 phase to have a constant T_c . We would, however, expect a peak in T_c to occur at still higher l , where only Al5 would exist. Figure 3 also illustrates the degree of the process control one

could achieve in the system. With automatic Cl_2 flow controllers* used, s could be reset within $\pm 2\%$, for example, $s = 4.5 \pm 0.1$, while the s range in which pure Al5 deposits were obtained with T_c in excess of 20K extended from 4.2 to 5. These s values were characteristic of our experimental conditions, and have limited general significance.

Inductive measurements of T_c were performed on powdered (grains $< 100 \mu\text{m}$) samples obtained by dissolving the Hastelloy substrate, and grinding the deposit. The measuring frequency was $f = 17 \text{ Hz}$. Good agreement was found between inductive and resistive data thus indicating that the deposited layers were uniform. Hence, the resistive data such as shown in Fig. 3 were assumed to be representative of bulk sample T_c 's. The uniformity of high- T_c Al5 deposits was corroborated by micrographic and electron microprobe examination. Figure 4 shows a microphotograph of anodized section of a tape having $T_c \approx 22.5\text{K}$. No second phase could be detected. Figure 5 shows the composition profile of the same film section indicating the absence of any noticeable compositional gradient. A surprising finding is that pure Al5, high T_c samples with inductively measured superconducting transitions above 20K had cubic cell edges at large as $a_0 = 5.160 - 5.170 \text{ \AA}$. The electron microprobe analysis of such samples indicated 19-16 at.% Ge. In contrast, high T_c samples containing only slight traces of T2 had $a_0 \approx 5.15 \text{ \AA}$ and overall Ge content of $\sim 25\%$ Ge, thus corresponding to a nearly stoichiometric Nb_3Ge .

*Hastings, Model FC-1P.

PROPERTIES OF Nb_3Ge TAPE SECTIONS

Two types of tape sections, I and II, were fabricated in conditions of Set 1 and Set 2 of Table I, respectively. Their characteristics are summarized in Table III, and the Nb_3Ge surface topography is shown in Fig. 6. Tapes I were relatively thick, and had rough surface due to the columnar grain microstructure of the deposit,⁽⁶⁾ while the second type had thinner and smoother Nb_3Ge coating. The deposits were under severe compressive stress due to thermal expansion mismatch between Hastelloy B and Nb_3Ge . As a result of this mismatch, Tapes I were slightly bent around the longitudinal axis. The adhesion to Hastelloy was only fair and the brittle thick coatings (Type I) occasionally cracked and chipped away when bent over a radius less than 1 cm.

We discussed the critical temperatures in the previous section. We point out, however, that the resistive and inductive transition widths were relatively narrow and comparable, and the high- T_c tape sections were up to 25 cm long.

The tape critical fields were comparable to those of small samples previously reported.⁽⁶⁾ The DC critical current densities at high fields $J_c(H,T)$ were substantially lower than those of sputtered

Table III
PROPERTIES OF Nb₃Ge TAPE SECTIONS

Parameter	Type I	Type II
Substrate	Hastelloy B, 50 μ m thick, 1.27 cm wide	
Deposit Thickness, h, μ m	10-40	1-4
Nb-Ge Phase Composition	Pure A15 and A15 + T2	
Grain Size (Shortest Dimension from Scanning Electron Microscopy of Fractures), μ m	0.5-1	0.1-0.3
Surface Topography	see Fig. 6	
Critical Temperature Onset, T _c , K	22.5	21.6
Transition Width, Δ T, K	1-2	$\sim$ 2
Maximum Length of Coating having T _c > 20K, cm	$\sim$ 25	
Critical Field H _{c2} , T; at 16K	14	11
OK*	34	30
Critical Current Density ⁽¹⁴⁾ (DC, Transport Current, J _c , A/cm ² J _c $\perp$ H) at 4.2K, 14T	$>> 1 \times 10^4$ [†]	1×10^3
15K, 7T	6×10^3	4×10^3
Low Field AC Loss, 60 Hz, 4.2K ⁽¹⁵⁾		
p, μ W/cm ² , at a Surface Current Density (rms): $\sigma = 300$ A/cm	15-50	8-10
500 A/cm	$\sim$ 100	$\sim$ 30
Self-Field Critical Current Density at 4.2K, from Bean's Relation ^(15,16) J _c , A/cm ²	$2-4 \times 10^6$	$4-6 \times 10^6$

$$* H_{c2}(0) = 0.69 T_c \times \Delta H_{c2} / \Delta T$$

$\Delta H_{c2} / \Delta T$ determined in the 15-22K range.

[†] Estimated value.

samples,⁽¹⁷⁾ and at 4.2K also somewhat lower than in stabilized commercial Nb₃Sn tapes fabricated by the diffusion technique.⁽¹⁸⁾

The self-field AC losses at 60 Hz, p, were determined by the electronic wattmeter methods of Bussiere et al.,⁽¹⁹⁾ and Forsyth et al.⁽²⁰⁾ in the configuration of Bean's model.⁽¹⁶⁾ At low surface current densities, $\sigma \sim 500$ A/cm, the losses were comparable to those of commercial Nb₃Sn tapes.⁽²¹⁾

We regard the J_c and p data as only preliminary but very encouraging. The first samples made show properties comparable to "state-of-the-art" Nb₃Sn while the comparison with sputtered samples indicates a significant potential for improvement through metallurgical treatment and control of microstructure.

CONCLUDING REMARKS

The purpose of this paper is to report the status of a study of Nb_3Ge as a practical superconductor. The results obtained to date should still be regarded as preliminary, and we abstain, therefore, from a detailed analysis of our findings. We formulate, however, two conclusions of general nature.

1. The CVD process has already proven its capability to prepare the Nb_3Ge superconductor in a practical configuration. Relatively uniform tape sections have dimensions adequate for extensive, application-oriented characterization. Much longer sections of Nb_3Ge tape could be obtained by continuous coating of a moving tape.

2. The high-field DC critical currents and low-field AC losses of the first tape sections approach those of commercial Nb_3Sn tapes. Further, substantial improvements in these properties could be achieved through metallurgical control of the Nb_3Ge microstructure.

ACKNOWLEDGMENTS

We acknowledge the valuable technical assistance of M. T. Miller, P. A. Piotrowski, H. C. Pohl, R. P. Storrick and A. L. Foley. The microprobe analysis was performed by R. W. Palmquist and the scanning electron microscopy by C. W. Hughes.

NOTATION

- a, c = tetragonal unit cell edge lengths
- a_0 = cubic unit cell edge length
- f = frequency
- ΔG = reaction free energy change
- H = magnetic field
- H_{c2} = critical field
- h = film thickness
- h_t = film thickness growth rate
- J_c = critical current density
- K_p = equilibrium constant at constant pressure
- t = specimen position in deposition zone
- p = self-field AC loss
- $p_{\text{gas } i}$ = partial pressure of gas i
- r = ratio $H_2/(NbCl_4 + GeCl_2)$ in gas phase
- s = ratio $NbCl_4/GeCl_2$ in gas phase
- T = temperature
- ΔT = width of superconducting transition
- T_c = temperature of superconducting transition onset
- T_d = deposition temperature
- v = gas velocity
- Y = total reaction yield

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FIGURE CAPTIONS

Fig. 1 -- Schematic diagram of CVD reactor.

Fig. 2 -- Profile of the growth rate, superconductive onset, and lattice parameter along the deposition zone.

Fig. 3 -- Critical temperature profiles for different values of $s = \text{Nb/Ge}$ in the gas phase.

Fig. 4 -- Photomicrograph of an anodized cross-section of single phase (A15) Nb_3Ge deposit, X500. Dark spots indicate electron microprobe traces; $T_c = 22.5\text{K}$.

Fig. 5 -- Electron microprobe traces of a single phase Nb_3Ge deposit. Analyzed composition: 81 at.% Nb, 19 at.% Ge; $T_c \approx 22.5\text{K}$.

Fig. 6 -- Surface topography of Nb_3Ge deposits, Type I and II, X10,000.

Fig. 1. Schematic diagram of CVD reactor.

Fig. 2. Profile of the growth rate, superconductive onset, and lattice parameter along the deposition zone.

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Fig. 3. Critical temperature profiles for different values of $s = \text{Nb/Ge}$ in the gas phase.

Fig. 4. Photomicrograph of an anodized cross-section of single phase (Al5) Nb_3Ge deposit, X500. Dark spots indicate electron microprobe traces; $T_c = 22.5\text{K}$.

Fig. 5. Electron microprobe traces of a single phase Nb₃Ge deposit. Analyzed composition: 81 at.% Nb, 19 at.% Ge; $T_c \approx 22.5K$.

I

II

Fig. 6. Surface topography of Nb_3Ge deposits, Type I and II, X10,000.