PHYSICAL REVIEW B VOLUME 21, NUMBER 11 1 JUNE 1980

Impurity stabilized *A* 15 Nb_3Nb—a new superconductor

G. R. Stewart, L. R. Newkirk, and F. A. Valencia
University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87545

(Received 18 October 1979)

We have succeeded in preparing by chemical vapor deposition essentially single-phase, *A* 15 Nb_3Nb with the addition of small amounts of Ge or Si. The compositions and lattice parameters of the five samples reported on here are as follows: $Nb_3(Nb_{0.92}Ge_{0.08})$, 5.239 Å; $Nb_3(Nb_{0.82}Ge_{0.18})$, 5.230 Å; $Nb_3(Nb_{0.71}Ge_{0.29})$, 5.219 Å; $Nb_3(Nb_{0.61}Si_{0.39})$, 5.213 Å; $Nb_3(Nb_{0.46}Si_{0.54})$, 5.192 Å. Using these compositions and lattice parameters, the lattice parameter for pure *A* 15 Nb_3Nb is found to be 5.250 ± 0.005 Å. The low-temperature specific heat of all five samples was measured from 1.4 to 11 K, showing bulk superconduting transitions in all cases, with T_c midpoint and $\Delta C/\gamma T_c$ values as follows: $Nb_3(Nb_{0.92}Ge_{0.08})$, 5.2 K and 1.24; $Nb_3(Nb_{0.82}Ge_{0.18})$, 4.15 K and 1.16; $Nb_3(Nb_{0.71}Ge_{0.29})$, 3.6 K and 1.27; $Nb_3(Nb_{0.61}Si_{0.39})$, 5.4 K and 0.78; $Nb_3(Nb_{0.46}Si_{0.54})$ 3.4 K and 1.16. Transition widths were in general quite narrow, less than 0.5 K, and for $Nb_3(Nb_{0.71}Ge_{0.29})$, the transition width was 0.15 K. From the specific-heat measurements *A* 15 Nb_3Nb has a T_c of ~6 K, a Θ_D of 270 ± 10 K, equivalent to that of bcc elemental Nb, and a density of states of 1.22 ±0.1 states/eV atom. Microprobe analysis of the *A* 15 Nb_3Nb samples shows no detectable oxygen, i.e., < 0.2 at.%. In addition to the essentially single-phase samples, a predominantly *A* 15 sample with $a_0 = 5.246$ Å and 50% bcc Nb second phase has been prepared, with less than 3% of the *B*-site atoms occupied by Ge, showing that *A* 15 Nb may be stabilized by less than 1% second-atom additions.

I. INTRODUCTION

Up to this time, only one element, W, has been known to be stabilized in the *A* 15 structure by small amounts[1] (~5%) of second-atom additions. Vieland and Wicklund,[2] in 1974 while preparing Nb_3Ga and Nb_3Ge by chemical vapor deposition (CVD) anticipated the present work by accidentially preparing nonsuperconducting (above 4.2 K), multiphase samples which contained high-lattice-parameter, 5.23–5.25-Å *A* 15 material with 12–20% *B*-atom site occupation by Ge. The present work deals with 80–100% single-phase samples of high-lattice-parameter *A* 15 Nb-Ge and Nb-Si, and uses small sample specific-heat measurements both to characterize the samples and to show conclusively that the observed superconductivity is associated with the majority, *A* 15 phase and not with very small amounts of bcc Nb which may be present and which could confuse inductive or resistive measurements. By having a range of compositions that approaches closely pure *A* 15 Nb_3Nb, extrapolation of its properties may be convincingly carried out. These properties, in particular the density of states, $N(0)$, may be compared to the recent band-structure calculation for *A* 15 Nb_3Nb by Pickett, Ho, and Cohen.[3]

II. EXPERIMENTAL

The samples were prepared by the hydrogen coreduction of chlorides of niobium and germanium and of chlorides of niobium and silicon in a manner similar to that described in the literature.[4] Deposition temperatures ranged from 730 to 900°C for the samples containing Ge and from 875 to 925°C for samples containing Si. Prior to the deposition of samples containing Si, the copper substrate was clad with a thin layer of pure Nb to prevent attack of the Cu by $SiCl_4$ vapor.

Gas-flow conditions necessary to stabilize *A* 15 Nb_3Nb with Ge or Si are substantially different than those described in Ref. 4 for producing high-T_c Nb_3Ge. The ratio of H_2:($NbCl_5 + GeCl_4$) or H_2:($NbCl_5 + SiCl_4$) must be kept relatively low in contrast to the very large ratios required to produce high-T_c Nb_3Ge. It seems very likely that the *A* 15 Nb_3Ge phase boundaries in the 4-component Nb-Ge-Cl-H system are extremely dependent on the H_2:HCl ratio. As this ratio is increased, the phase boundaries move in the direction of Nb_3Ge, and as it is decreased they move toward Nb_3Nb. Deposition temperature also seems to affect this movement, with the lower deposition temperatues favoring the Nb_3Nb

direction.

After preparation, samples were removed from the copper substrate tubes by cutting $\frac{1}{2}$- to 1-in. sections and immersed in a one to one HNO_3:H_2O copper etch solution. For the Nb-Si samples, a further etch of the back side of the coat was performed in HF:$5HNO_3$ to remove the Nb backing. This etch was performed by coating the front of the coat with black Apiezon wax and controlling the etch by measuring the weight loss of the sample plus wax combination. Enough of the back side of the material was etched off (33-50 wt.% of the total coat weight) to insure total removal of the Nb backing. Total removal was also apparent upon grinding the coat to a powder, which was the next step for both the Nb-Si and the Nb-Ge systems.

Lattice spacings were determined using a 114.6-mm Debye-Scherrer power camera. Also, diffractometer traces were taken on the $Nb_3(Nb_{0.92}Ge_{0.08})$ and the $Nb_3(Nb_{0.82}Ge_{0.18})$ samples and are shown in Figs. 1 and 2. As may be seen qualitatively only a small amount of bcc Nb exists in the $Nb_3(Nb_{0.92}Ge_{0.08})$, $a_0 = 5.239$ Å, sample and almost no detectable bcc Nb exists in the diffractometer trace for $Nb_3(Nb_{0.82}Ge_{0.18})$. In order to quantify the amount of bcc Nb evidenced by these diffractometer traces, two calibration samples were prepared by grinding lightly together measured amounts of fine bcc Nb powder and powder from the $Nb_3(Nb_{0.71}Ge_{0.29})$ sample, which contained no detectable bcc Nb. Figure 3 is a diffractometer trace of a 10 wt.% bcc Nb, 90 wt.% *A* 15 calibration sample prepared in this way; Fig. 4 is similarly for a 30 wt.% bcc Nb, 70 wt.% *A* 15 Nb calibration sample, where for the samples discussed in this work, wt.% is essentially equivalent to at.%. The intensity of the (200) bcc Nb and the (211) bcc Nb peaks compared to the intensity of the (321) *A* 15 Nb peak in each of the four figures was determined. Comparing these relative intensities [bcc (200) to *A* 15 (321) and bcc (211) to *A* 15 (321)] for Fig. 1 with those in Fig. 3 implies that the sample shown in Fig. 1, $Nb_3(Nb_{0.92}Ge_{0.08})$, has 18 wt.% bcc Nb; comparison with Fig. 4 implies 20 wt.% bcc Nb. Similar comparisons for Fig. 2, $Nb_3(Nb_{0.82}Ge_{0.18})$, imply less than 3 wt.% bcc Nb in this sample. These estimates of second phase content for the $Nb_3(Nb_{0.92}Ge_{0.08})$ and $Nb_3(Nb_{0.82}Ge_{0.18})$ samples and estimates based on Debye-Scherrer results for the other samples are shown in Table I, along with lattice spacings and other parameters for all the samples.

Figures 1 and 2 show the complete absence of the (110) peak, as did in fact traces using much higher sensitivity. Using a computer code, ANIFAC,[5] to calculate relative intensities, this lack of (110) peak indicates that fewer than 10% vacancies exist on the *B*-atom sites in these samples; i.e., these samples are indeed essentially Nb_3Nb. This is identical to the result for β-W stabilized by a few atomic percent of

TABLE I. Parameters for impurity stabilized *A* 15 Nb_3Nb and bcc Nb.

Sample	Midpoint T_c (K)	Lattice (Å) parameter ±0.001 Å	bcc Nb second phase (%)	Composition [Ge or Si (at.%)]	γ (mJ/mole K^2)[b]	Θ_D (K)	λ	$N(0)$ (states/eV atom)	$\Delta C/\gamma T_c$
$Nb_3(Nb_{0.92}Ge_{0.08})$	5.2	5.239	15–25		18.6 ± 0.5	260 ± 5	0.61	1.22	1.24
$Nb_3(Nb_{0.82}Ge_{0.18})$	4.15	5.230	< 3	4.6 ± 0.2	18.9 ± 0.5	271 ± 5	0.56	1.28	1.16
$Nb_3(Nb_{0.71}Ge_{0.29})$	3.6	5.219	< 3	7.3 ± 0.4	17.5 ± 0.4	305 ± 5	0.52	1.22	1.27
$Nb_3(Nb_{0.61}Si_{0.39})$[a]	5.4	5.213	10–20	8.7 ± 0.4	22.0 ± 1.0	283 ± 8	0.60	1.46	0.78
$Nb_3(Nb_{0.46}Si_{0.54})$	3.4	5.192	< 3	13.5 ± 0.7	15.8 ± 0.5	269 ± 5	0.53	1.09	1.16
bcc Nb	9.2	3.3006			31.2	277	0.82	1.82	1.96

[a] Composition corrected for presence of 2nd phase.

[b] Where a mole contains 4 atoms.

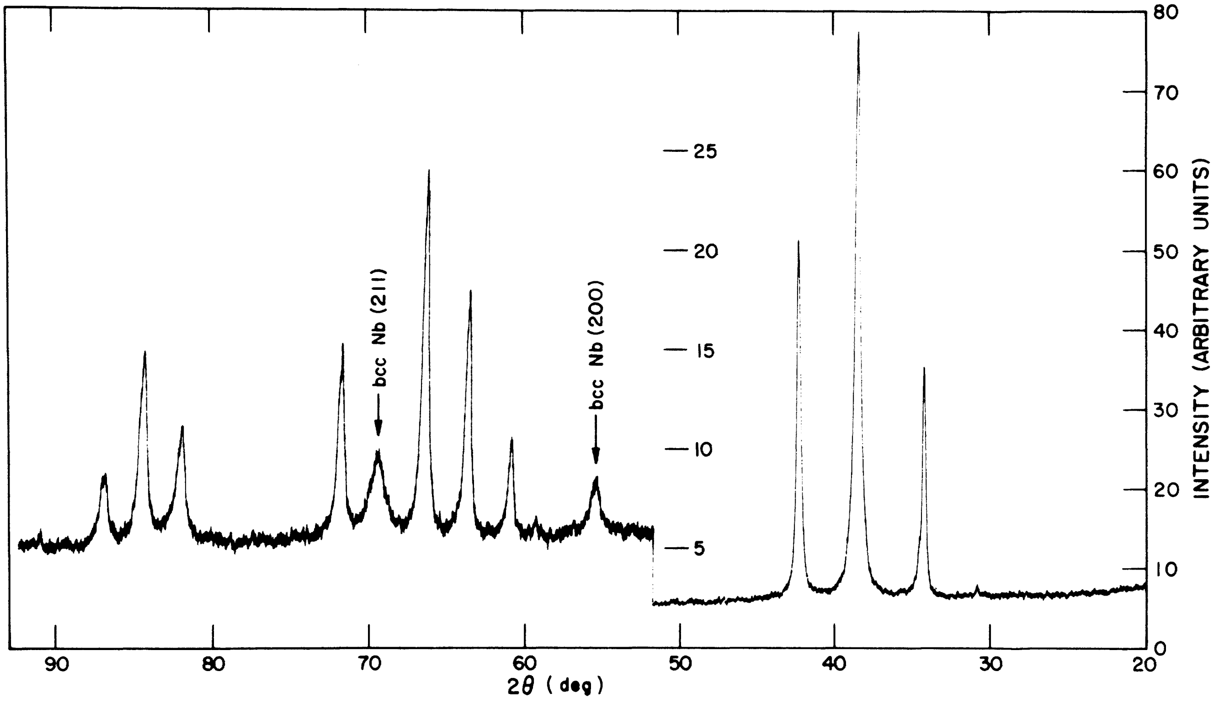

FIG. 1. Diffraction trace of powdered $Nb_3(Nb_{0.92}Ge_{0.08})$, using copper *K*α radiation. Note the presence of bcc Nb lines at 55.7 and 69.7 degrees 2θ.

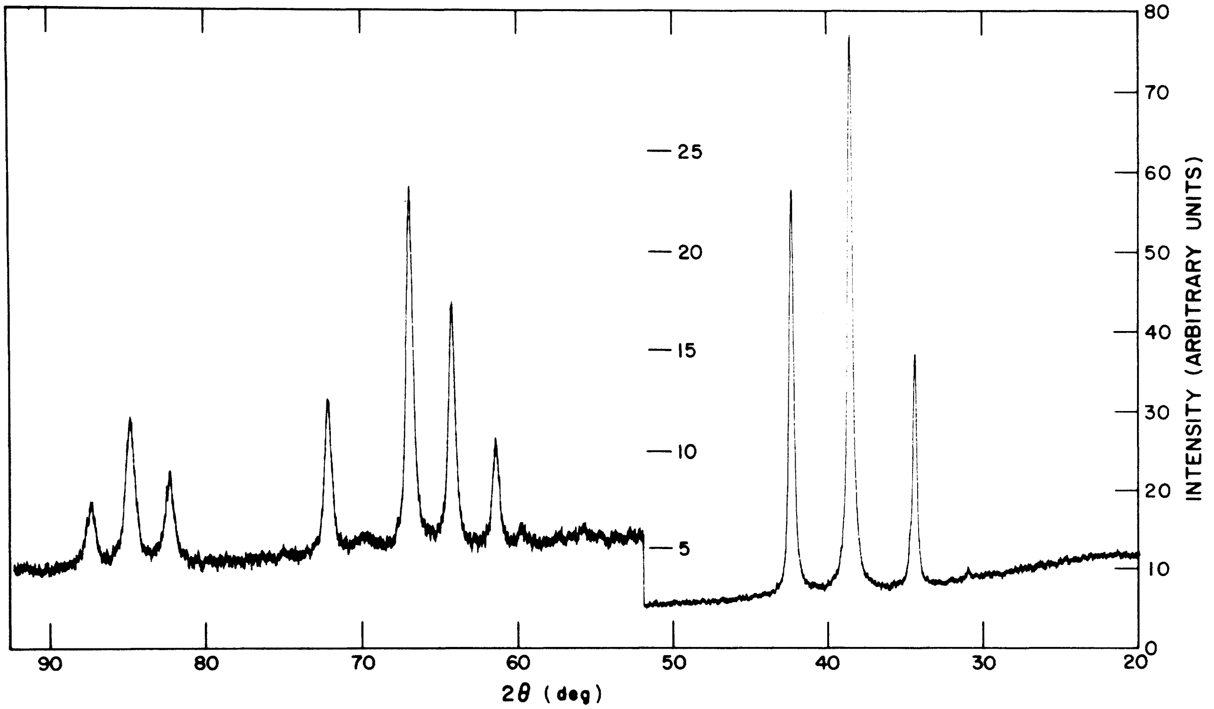

FIG. 2. Diffraction trace of powdered $Nb_3(Nb_{0.82}Ge_{0.18})$. Note the lack of bcc Nb lines at 55.7 and 69.7 degrees 2θ.

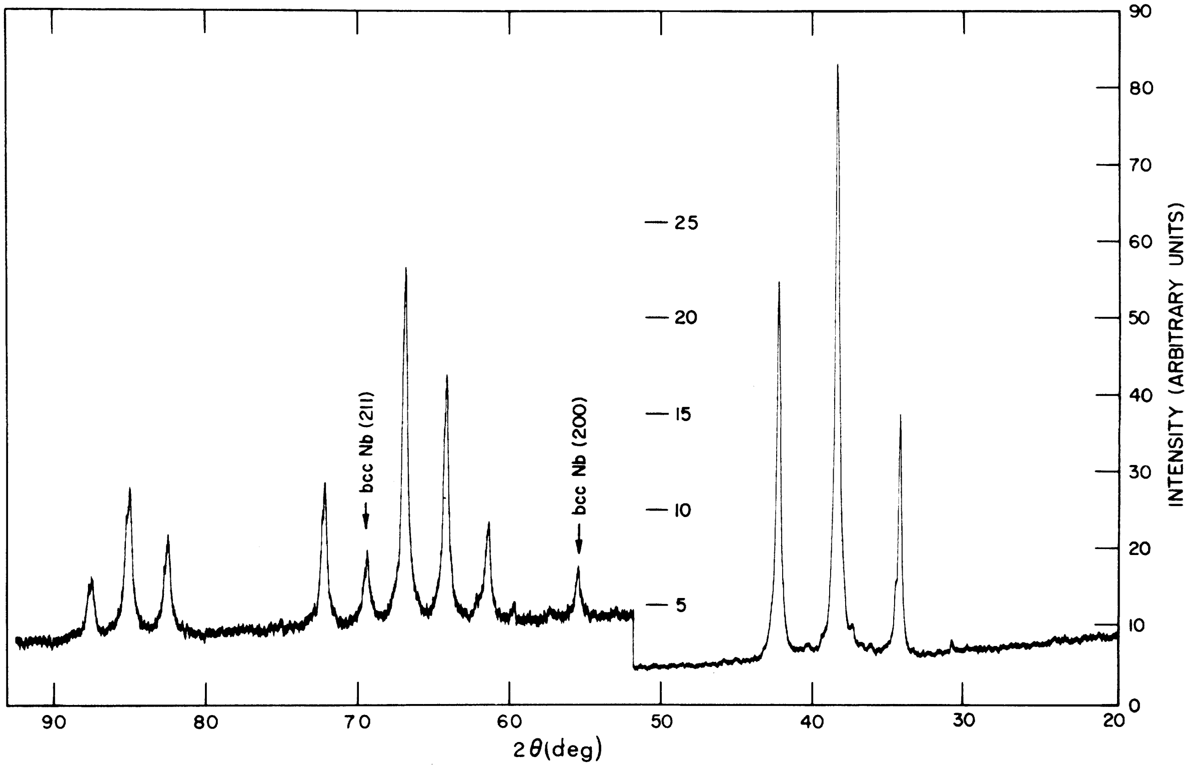

FIG. 3. Diffraction trace of a 10 wt.% bcc Nb, 90 wt.% *A*15 Nb calibration sample prepared as discussed in the text.

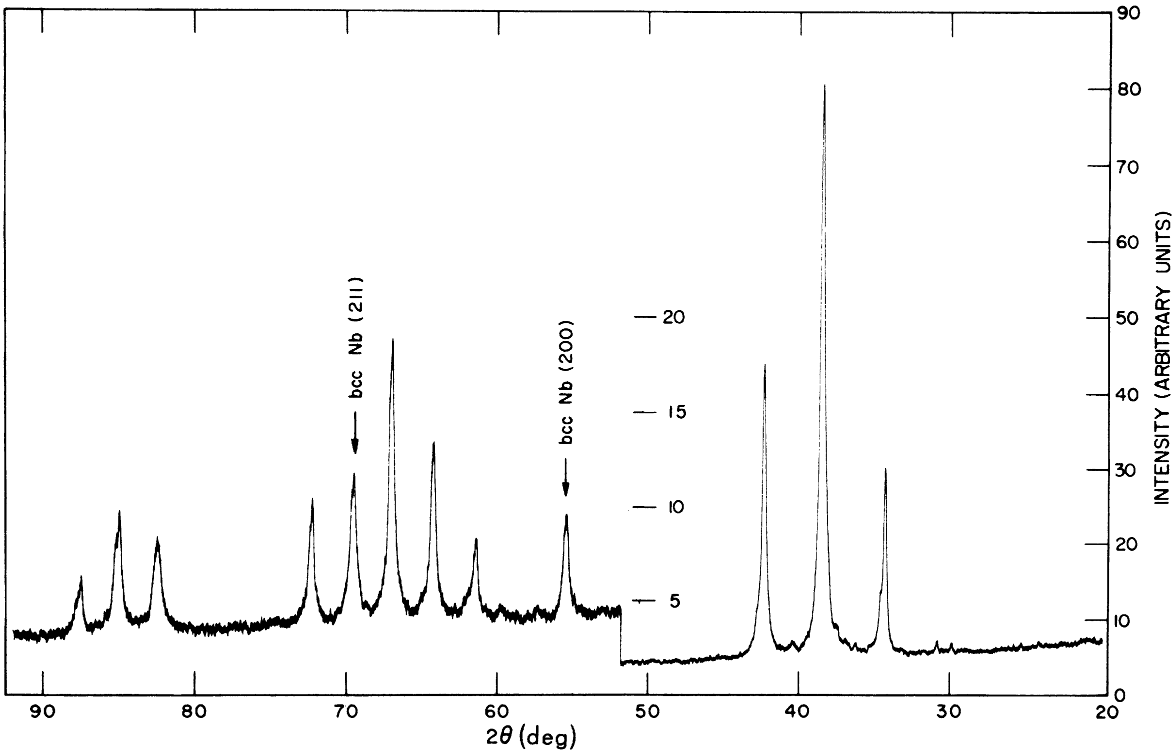

FIG. 4. Diffraction trace of a 30 wt.% bcc Nb, 70 wt.% *A*15 calibration sample prepared as discussed in the text.

O, where the *B*-atom site also appears to be fully occupied. It should be noted that the observed intensity ratios for the *A* 15 peaks in the diffractometer traces agree well quantitatively with the ANIFAC calculations.

Compositions for the $Nb_3(Nb_{0.82}Ge_{0.18})$, $Nb_3(Nb_{0.71}Ge_{0.29})$, $Nb_3(Nb_{0.61}Si_{0.39})$, and $Nb_3(Nb_{0.46}Si_{0.54})$ samples were determined by microprobe and in the case of $Nb_3(Nb_{0.61}Si_{0.39})$ was corrected for the presence of the second phase bcc Nb-Si of approximate composition $Nb_{0.97}Si_{0.03}$. For the other three samples, the presence of second phase was small enough that the composition of the entire sample could be taken as that of the *A* 15 phase. The microprobe data, see Table I, were taken at both 10- and 15-keV incident electron energies at a detection angle of 38.5° on 0.32-cm ($\frac{1}{8}$-in.)-diameter pellets pressed from the powder at 1 400 000 kPa (200 000 psi). Closure (the nearness of the summation of the measured amounts of the components to 100%) was quite good for something as porous as pressed powders and ranged from 96.9 wt.% to 99.1 wt.%. The weight percent figures are converted to atom percent by dividing by the respective molar weights. The two atom percent numbers are added together and defined as 100%, thus normalizing the two components. Accuracy of the microprobe results, based on data from at least five selected areas on each pellet, is ± a few tenths of a percent, see Table I. At first, the microprobe data indicated approximately 1 at.% C, which was found to be an adsorbed film from the pellet press, as this signal disappeared when the surface of the pellet was scraped away. No O or Cl (i.e., less than 0.2 at.%) was detected on the scraped surfaces either.

The compositions of the *A* 15 Nb-Ge samples are shown in Fig. 5 plotted against lattice parameter and are seen to agree well with the extrapolation from the Ge-rich side of the *A* 15 phase, where lattice parameter and composition data are well established. The composition for *A* 15 $Nb_3(Nb_{0.92}Ge_{0.08})$ is derived from Fig. 5, rather than from microprobe work.

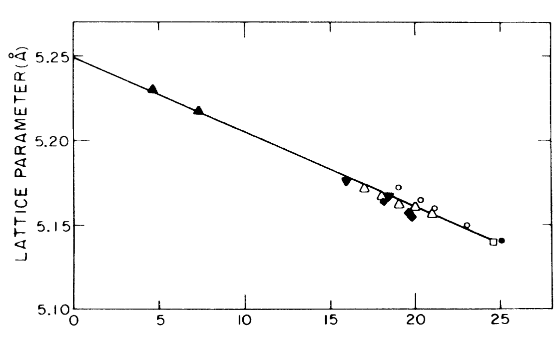

FIG. 5. Lattice parameter vs composition for the *A* 15 Nb-Ge phase. *A* 15 Nb_3Nb is seen to have a lattice parameter of 5.250 Å. ▲: present work; ▼: Ref. 17; Δ: Ref. 13; ◆: Ref. 15; □: Ref. 16; ●: Ref. 18; ○: Ref. 14 .

Assuming *A* 15 Nb_3Nb has $a_0 = 5.25$ Å, as shown in Fig. 5, and that[6] *A* 15 Nb_3Si has an $a_0 = 5.08$ Å, then the composition versus lattice parameter data for the *A* 15 Nb-Si samples deviates substantially from Vegard's law. This has also been seen by the Stanford group[6] in their low-lattice-parameter Si-rich Nb-Si work. This apparent deviation from Vegard's law may be a result of site switching, i.e., Si atoms on the *A*-atom chain sites. Site switching has been observed in radiation-damage studies to increase lattice parameters.[7] This possibility of altered ordering in the Nb-Si samples will be discussed further below.

The small sample calorimeter used has been described eleswhere.[8] The pressed pellets were of sufficient mass (30–50 mg) such that the addenda correction (known[8] to ±5%) to the total measured specific heat of four of the samples was only 10% at 1.4 K and rose to approximately 30% at 11 K. For the fifth sample, $Nb_3(Nb_{0.46}Si_{0.54})$, only 14 mg was available and the addenda contributions were 13% at 1.4 K and 60% at 11 K, resulting in larger uncertainty in the data for this sample. All of the pressed powder pellets had imperfect thermal contact between the constitutive grains, leading to a second decay constant in the decay constant method[9] used to measure specific heat. This problem, known as the "τ_2 problem", was not of a serious nature in the temperature range of measurement and could be accurately corrected for following techniques described in the literature.[9]

Since the possibility existed that hydrogen from the CVD process was present in the samples, all samples were dehydrided by annealing at 750°C in 10^{-6} torr vacuum for 30 min. Evolution of a gas presumed[10] to be hydrogen was observed only for the $Nb_3(Nb_{0.82}Ge_{0.18})$ sample. The lattice parameter for the unannealed sample was noticeably higher (5.236 Å) than for the annealed sample (5.230 Å). The lattice parameters and specific-heat data reported here are for the dehydrided samples. In addition, the specific heat of unannealed $Nb_3(Nb_{0.82}Ge_{0.18})$ was measured for comparison.

III. RESULTS AND DISCUSSION

The specific heats of the five dehydrided samples are shown in Figs. 6–10. Figure 11 contains the specific-heat data for both annealed and unannealed $Nb_3(Nb_{0.82}Ge_{0.18})$. The transition heights ΔC, are seen to be uniformly bulk in appearance and in some cases, the transitions are quite narrow in width. The normal-state specific heat C_n is given by

$$C_n = \gamma T + \beta T^3 \ . \tag{1}$$

The data shown in Figs. 6 to 10 have been fit to this equation by the method of least squares. The thermodynamic constraint shown in Eq. (2) provides an independent method for checking the accuracy of the fit obtained from Eq. (1).

$$\int_0^{T_c} \frac{C_s}{T}\,dT = S_s(T_c) = S_n(T_c) = \int_0^{T_c} \frac{C_n}{T}\,dT \ . \tag{2}$$

The superconducting and normal-state entropies $S(T_c)$, calculated from the superconducting and normal-state heat capacities C_s and C_n, must be equal. Agreement between the two entropies, using the fitted parameters from Eq. (1) to calculate C_n below T_c, is better than 3% for all five samples. The results for γ and β are shown in Table I.

The transition discontinuity $\Delta C = C_s(T_c) - C_n(T_c)$, may be quantified as $\Delta C/\gamma T_c$ and is also shown in Table I. It is evident from the values that the samples studied definitely exhibit bulk superconducting transitions, with values comparable to the BCS prediction for $\Delta C/\gamma T_c$ of 1.43.

Of special interest in these samples is the extrapolated T_c and $N(0)$ for no second-atom additions. Figure 12 shows a plot of T_c midpoint versus composition for both the Nb-Ge and Nb-Si samples. As may be seen, the T_c for $A15$ Nb_3Nb is dependent

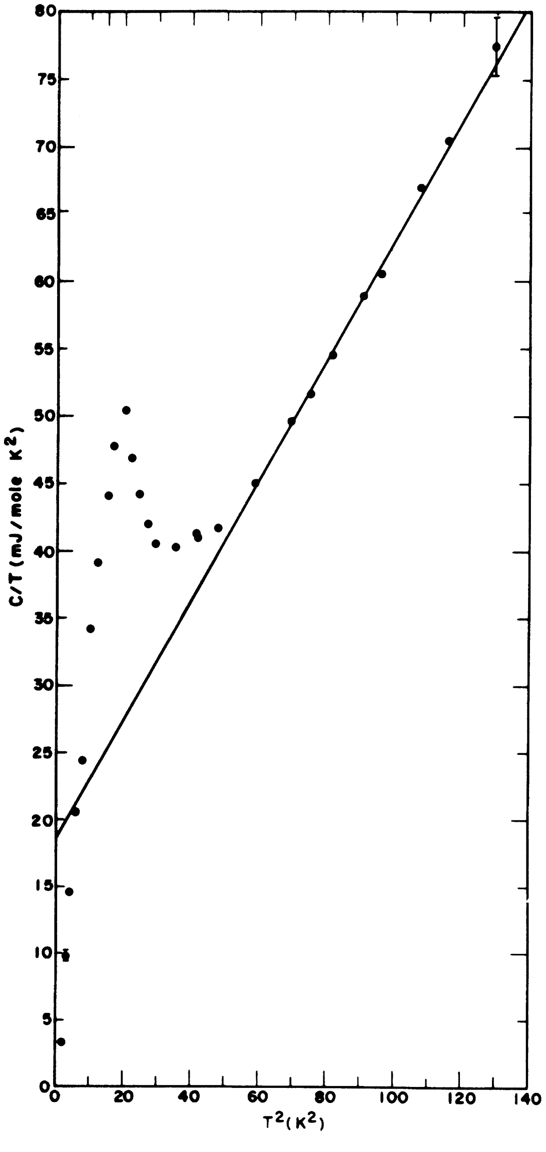

FIG. 6. Specific heat of $A15$ $Nb_3(Nb_{0.92}Ge_{0.08})$.

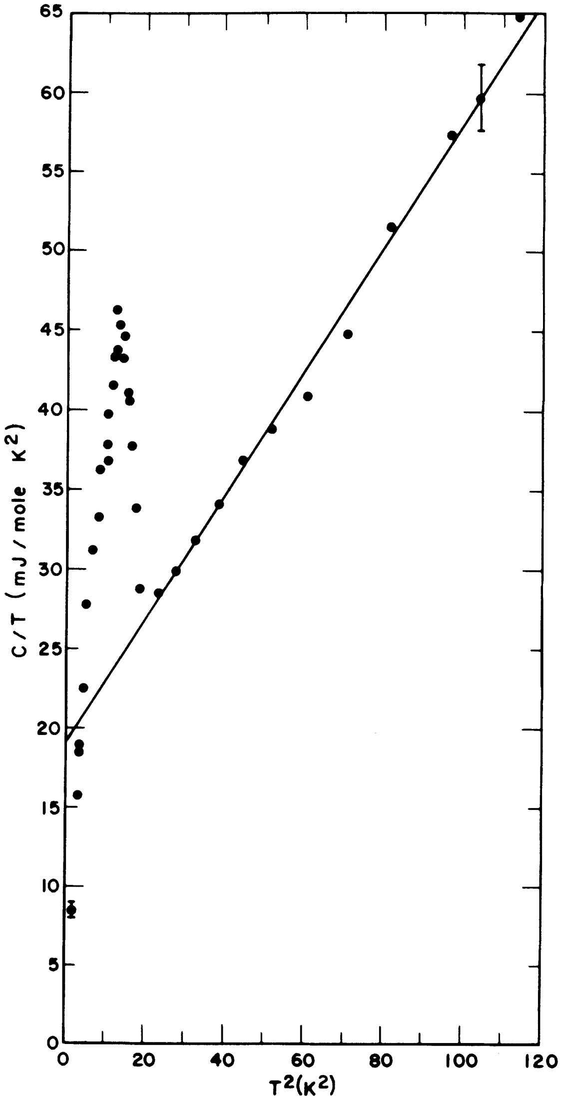

FIG. 7. Specific heat of $A15$ $Nb_3(Nb_{0.82}Ge_{0.18})$.

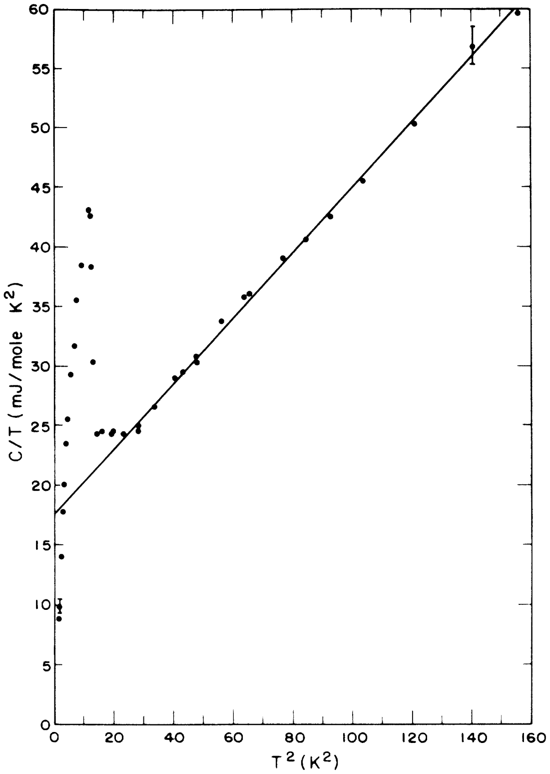

FIG. 8. Specific heat of $A15$ $Nb_3(Nb_{0.71}Ge_{0.29})$. Note the narrowness (0.15 K) of the transition and the flat region in the data just above T_c.

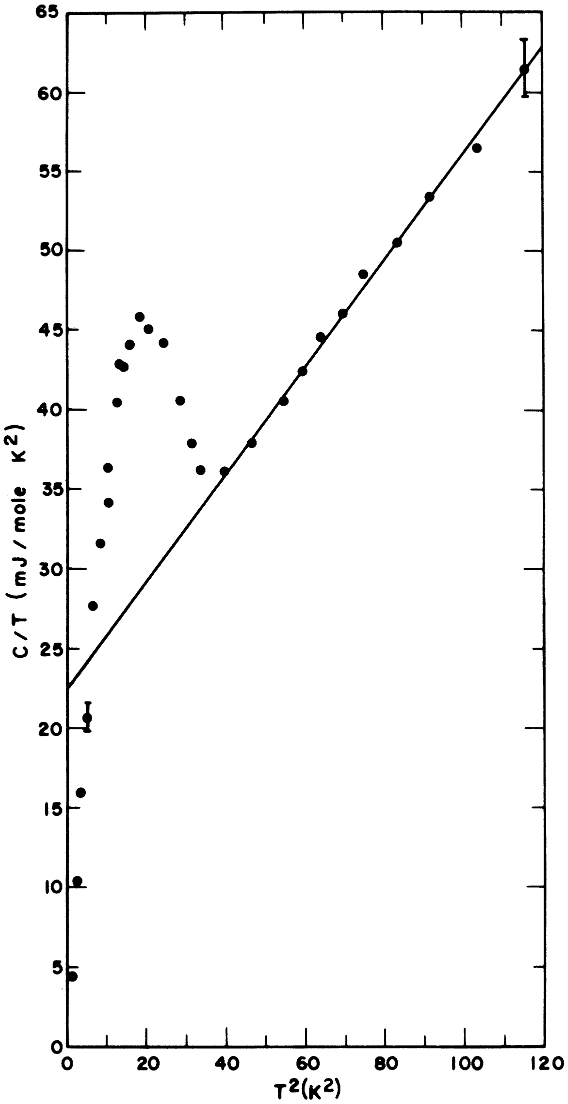

FIG. 9. Specific heat of $A15$ $Nb_3(Nb_{0.61}Si_{0.39})$.

on the second atom used to stabilize the $A15$ structure. This is probably due to a difference in ordering for the two systems; i.e., the occupation factors for Ge and Si on B sites in the $A15$ A_3B structure are not the same. The variation of lattice spacing with Ge composition shown in Fig. 5 is consistent with most or all of the Ge atoms residing on B sites. If this were not the case, the agreement with data in the range of 15–25 at.% Ge, where the Ge atoms are known to reside mostly on B sites, would be much poorer. Radiation-damage work[7] has shown that site switching in the $A15$ structure usually increases the lattice parameter. The absence of any positive deviation from Vegard behavior in Fig. 5 therefore effectively eliminates the possibility of significant site switching.

In the Si stabilized $A15$ Nb_3Nb system, as discussed above, the lattice parameters measured show a substantial positive deviation from the behavior expected based on lattice spacings of 5.25 and 5.08 Å for Nb_3Nb and Nb_3Si, respectively. This suggests that the degree of ordering may be changing with Si content; i.e., the fraction of the Si atoms present in the alloy residing on B sites changes with composition. This apparent variation with composition of the degree of ordering on A and B sites results in substantial uncertainty in attempting to extrapolate to pure $A15$ Nb_3Nb from the Si data. It is well established in $A15$ materials that A-B site switching has a significant effect on T_c as well as lattice spacing; hence, for a system in which the ordering is changing with composition in an unknown manner, no basis exists for extrapolation. Because of this problem and also because of the large gap between the lowest composition Si data and pure Nb_3Nb, it is therefore inadvisable to use the Si data to predict the T_c of pure $A15$ Nb_3Nb.

The density of states, $N(0)$, for $A15$ Nb_3Nb may

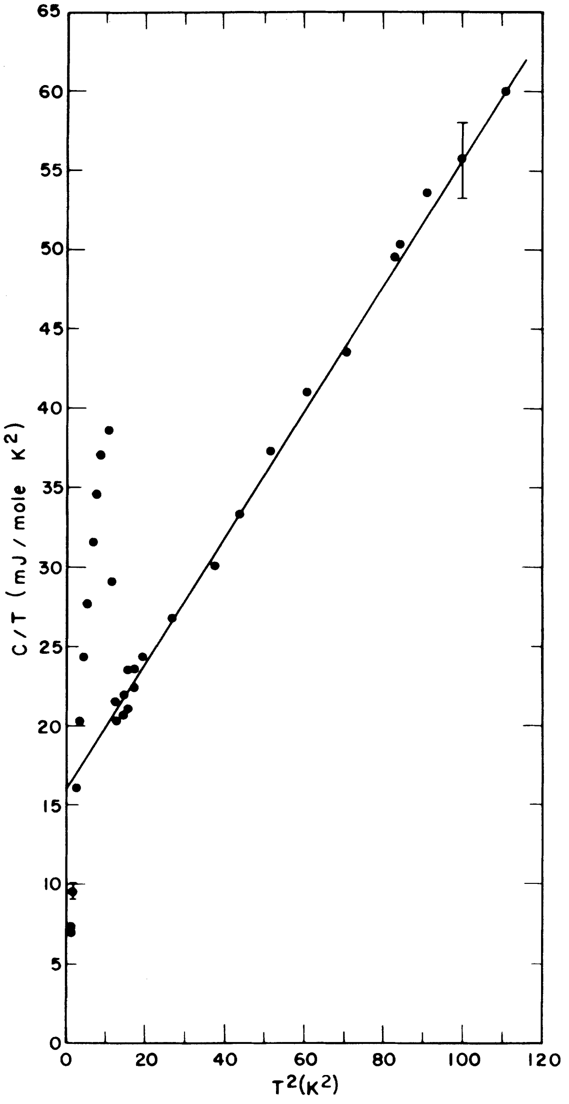

FIG. 10. Specific heat of $A15$ $Nb_3(Nb_{0.46}Si_{0.54})$.

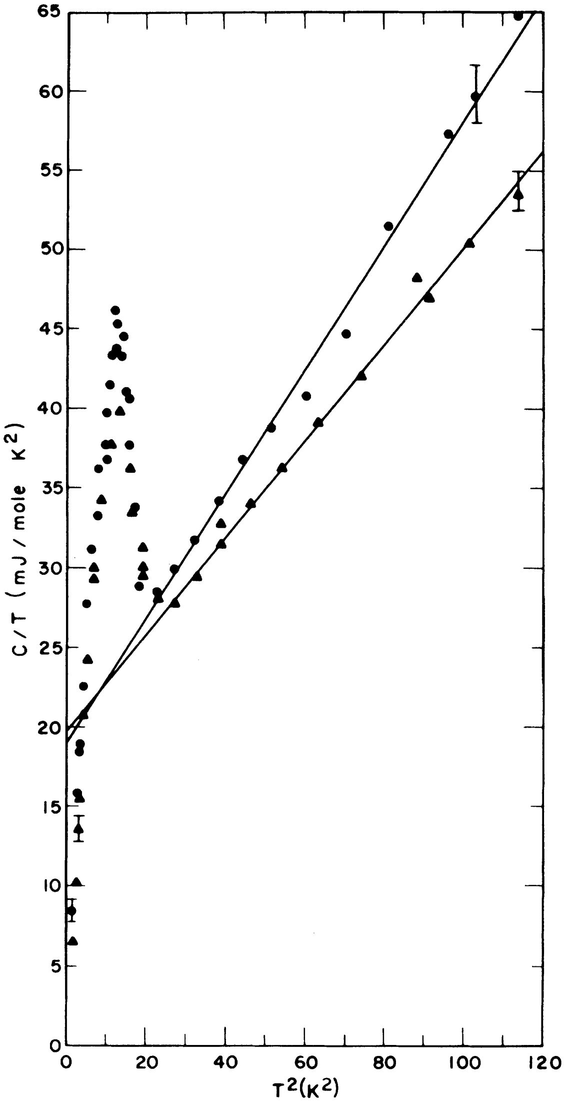

FIG. 11. Specific heat of $A15$ $Nb_3(Nb_{0.82}Ge_{0.18})$ (circles) and $A15$ $Nb_3(Nb_{0.82}Ge_{0.18})H_x$ (triangles). Note the larger discontinuity for the dehydrided sample.

be derived from the measured γ's by

$$\gamma = (\tfrac{1}{3})\pi^2 k^2 N(0)(1+\lambda) \ , \tag{3}$$

where the electron-phonon coupling constant λ may be derived via McMillan's formula[11]

$$\lambda = \frac{1.04 + \mu^* \ln(\Theta_D/1.45T_c)}{(1-0.62\mu^*)\ln(\Theta_D/1.45T_c) - 1.04} \ . \tag{4}$$

The parameter Θ_D, the Debye temperature, is a measure of lattice stiffness and may be derived from the normal-state data, Eq. (1), via

$$\Theta_D = [(1944)4/\beta]^{1/3} \ .$$

See Table I. The parameter μ^* is taken as 0.1. Using a T_c of 6 K and a Θ_D of 270 K for $A15$ Nb_3Nb, λ is 0.63. From Table I, there is an average γ value for the five samples of 18.8 mJ/mole K^2. This agrees well with the γ for the sample with the smallest amount of second-atom additions, $Nb_3(Nb_{0.92}Ge_{0.08})$. Thus, using $\gamma = 18.8$ mJ/mole K^2 and $\lambda = 0.63$, $N(0)$ for $A15$ Nb_3Nb is found to be 1.22 states/eV atom. A recent band-structure calculation by Pickett, Ho, and Cohen[3] for $A15$ Nb_3Nb, $a_0 = 5.26$ Å, predicted $N(0) = 1.03$ states/eV atom. This agreement, better than 20%, is remarkable, since their calculation showed the Fermi energy to be between two peaks in

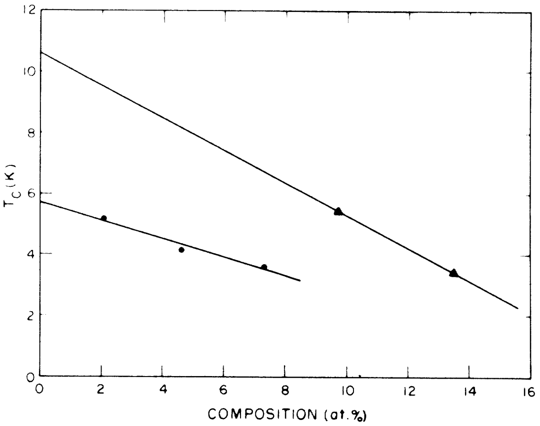

FIG. 12. T_c vs composition for the Nb-Ge system (dots) and the Nb-Si system (triangles). As discussed in the text, the T_c extrapolated for pure *A* 15 Nb_3Nb ($T_c = 6$ K) from the Nb-Ge system is thought to be the correct value. This would be the first case of an *A* 15, bcc allotropic pair where the T_c of the *A* 15 structure was less than that of the bcc.

the density of states. One further result of their work is worth noting here: they found that putting Nb atoms on the *B*-sites weakened the interaction between *A*-atom chains. This would be expected to lower the transition temperature and is perhaps one explanation of the low (6 K) T_c predicted for *A* 15 Nb_3Nb from the present work.

One further parameter may de deduced from the data in Figs. 6–10 the energy gap, Δ. This technique is discussed fully in the literature.[12] The energy gap normalized as $2\Delta/kT_c$ is predicted to be 3.52 by BCS and serves as an indicator, along with $\Delta C/\gamma T_c$, of whether a material is strong coupling (larger values) or not. Values derived from the C_s data indicate a range of from 2.6 to 3.4 for $2\Delta/kT_c$ for these samples which, coupled with the $\Delta C/\gamma T_c$ values given in Table I, indicate relatively weak coupling for *A* 15 Nb_3Nb.

Figure 11, which shows specific-heat data for both as-deposited and dehydrided $Nb_3(Nb_{0.82}Ge_{0.18})$, shows the effect of the hydrogen to be minor in terms of density of states, but significant for $\Delta C/\gamma T_c$ and for Θ_D. The Debye temperature for $Nb_3(Nb_{0.82}Ge_{0.18})H_x$ is 295 K, indicative of a harder lattice than for the dehydrided sample, $\Theta_D = 271$ K. The transition discontinuity is increased by dehydriding by about 45%, accompanied by a slight narrowing of the transition, while the actual transition temperature is apparently unaffected by this amount of hydriding.

One further speculative comment should be made, regarding Fig. 8, the specific-heat data for $Nb_3(Nb_{0.71}Ge_{0.29})$. This sample has a very sharp transition, with a width of 0.15 K, and is single phase with a very sharp Debye-Scherrer x-ray pattern, with high-angle doublets resolved down to the (520) line. The flat region in Fig. 8 just above T_c, which is really based on only three data points, is puzzling for a sample with such a sharply defined transition. Even more puzzling is that this flat feature does not show up in inductive measurements of the pressed powder, whereas the transition at 3.6 K gives quite a large inductive signal. Considering the sharpness of the x-ray pattern, one could speculate that this feature in the data may be a martensitic transformation. Measurements in a magnetic field will be undertaken to resolve this issue.

IV. CONCLUSIONS

It is possible to stabilize *A* 15 Nb_3Nb by addition of less than 1 at.% Ge to the matrix. The resulting material is a bulk superconductor with a T_c of approximately 6 K and a denstiy of states of 1.2 states/eV atom. Similar stabilization of *A* 15 Nb_3Nb by Si results also in a bulk superconductor, with a higher T_c that extrapolates to 10.5 K for no Si additions and with apparently some important degree of site switching. The possibility is raised by the present success in preparing *A* 15 Nb_3Nb with slight second-atom additions that other elements may be prepared in their *A* 15 allotropes, e.g., Ta, V, and Mo, by low-temperature preparative techniques such as sputtering, *e*-beam evaporation, or CVD.

ACKNOWLEDGMENNTS

The authors gratefully acknowledge the microprobe work performed by Mr. Chris Zercher, Stanford University. The authors also wish to gratefully acknowledge helpful discussions with Dr. Bernd Matthias and Dr. A. L. Giorgi, who also preformed the ANIFAC calculations. This work was completed under the auspices of the U.S. DOE and the Electric Power Research Institute.

[1] W. R. Morcom, W. L. Worrell, H. G. Sell, and H. I. Kaplan, Metall. Trans. 5, 155 (1974).

[2] L. J. Vieland and A. W. Wicklund, Phys. Lett. A 49, 407 (1974).

[3] W. E. Pickett, K. M. Ho, and M. L. Cohen, Phys. Rev. B 19, 1734 (1979).

[4] L. R. Newkirk, F. A. Valencia, and T. C. Wallace, J. Electrochem. Soc. 123, 425 (1976).

[5] A. C. Larson, R. B. Roof, Jr., and D. T. Cromer, Los Alamos Scientific Laboratory Report LA-3335 (1965).

[6] R. D. Feldman, R. H. Hammond, K. E. Kihlstrom, J. Kwo, and T. H. Geballe, Bull. Am. Phys. Soc. 24, 455 (1979).

[7] A. R. Sweedler, D. E. Cox, and S. Moehlecke, J. Nucl. Mater. 72, 50 (1978).

[8] G. R. Stewart, L. R. Newkirk, and F. A. Valencia, Phys. Rev. B 20, 3647 (1979).

[9] R. Bachmann, F. J. DiSalvo, T. H. Geballe, R. L. Greene, R. E. Howard, C. N. King, H. C. Kirsch, K. N. Lee, R. E. Schwall, H.-U. Thomas, and R. B. Zubeck, Rev. Sci. Instrum. 43, 205 (1972).

[10] This presumption is based on the temperature at which the gas evolved from the sample, ~600°C, which is the usual temperature for hydrogen to evolve from Nb in high vacuum.

[11] W. L. McMillan, Phys. Rev. 167, 331 (1968).

[12] G. R. Stewart and A. L. Giorgi, Phys. Rev. B 19, 5704 (1979).

[13] J. L. Jorda, R. Flükiger, and J. Muller, The Phase Diagram of the Niobium-Germanium System (unpublished).

[14] D. A. Rogowski and R. Roy, J. Appl. Phys. 47, 4635 (1976).

[15] A. B. Hallak, R. H. Hammond, and T. H. Geballe, Appl. Phys. Lett. 29, 314 (1976).

[16] A. R. Sweedler, D. E. Cox, S. Moehlecke, R. H. Jones, and F. A. Valencia, J. Low Temp. Phys. 24, 645 (1976).

[17] A. Müller, Z. Naturforsch. Teil A 25, 1659 (1970).

[18] A. I. Braginski, G. W. Roland, and M. R. Daniel, Appl. Polymer Symp. 29, 93 (1976).