A STUDY OF Nb$_3$(Al$_{17.5}$Ge$_{25}$) AND V$_3$Au SUPERCONDUCTING TUNNEL JUNCTIONS

by

JAMES ALLEN GREGORY

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A STUDY OF HT(AM) AND VH SUPERCONDUCTING TUNNEL JUNCTIONS

JANE SCOTT

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ABSTRACT

A STUDY OF Nb₃(Al₇₅Ge₂₅) AND V₃Au SUPERCONDUCTING TUNNEL JUNCTIONS

by

JAMES ALLEN GREGORY

Nb₃(Al₇₅Ge₂₅) - Pb₇Bi₃ and V₃Au-In superconducting tunnel junctions have been fabricated. Various methods of surface preparation, oxidation, and junction fabrication have been investigated. The tunneling data obtained from the Nb₃(Al₇₅Ge₂₅) junctions indicate a superconducting energy gap, 2Δ, of the order of 8.8 mV or 5.4 kTc.

Thesis Supervisors: Robert M. Rose
Professor of Metallurgy and Materials Science
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Assistant Professor of Physics
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"And if it all blows up, and goes to hell,
We'll say we did it for the stories we could tell."
I. INTRODUCTION

Since the first superconductor was discovered in 1911 by Kamerlingh Onnes with a transition temperature ($T_c$) of 4.15 K, superconductivity has been found in many elements, alloys, and compounds. The superconductor with the highest $T_c$ and critical magnetic field ($H_c$) is Nb$_3$(Al$_{75}$Ge$_{25}$) with a $T_c$ of 20.5 K and a critical field at 0 K of about $5 \times 10^5$ Oe. By trial and error it has been found that only special compounds of given crystallographic classes, e.g. the A-15 and rock salt structures, have relatively high $T_c$'s ($> 10$ K). But aside from the rule proposed by Matthias, that the number of valence electrons divided by the number of atoms in a compound should average 4-3/4 or between 6-1/2 and 6-3/4$^2$, there are no tested guidelines for obtaining a maximum $T_c$. It is not known how superconductivity is related to the material and its structure on a microscopic level. Although there do exist various microscopic theories of superconductivity this approach is not able to maximize or predict $T_c$ for real materials. Despite extensive experimental investigation concerning the variation of $T_c$ with changes in compound composition, methods of fabrication, and times and temperatures of annealing$^{3,4}$, it has not been possible to relate these parameters to the theoretically important variables: the electronic density of states, the phonon spectrum, the electron phonon coupling constant ($\lambda$), and the Coulomb coupling constant ($\mu^*$).

The relation between these theoretical and experimental aspects of superconductivity can, in principle, be established by application of the techniques of electron tunneling. Briefly, electron tunneling occurs when
one conductor is separated from another by a thin insulator and a current flows between them. If the two materials are superconductors, then observing changes in the current as the bias voltage across the insulator is varied enables us to measure the electronic density of states. Further analysis of the current versus voltage characteristic reveals the phonon spectra of the electrode materials. This information can be used to obtain $\lambda$ and $\mu^*(5)$. The different values of the parameters in one alloy system can be attributed to differences in composition, atomic ordering and microstructure since it is assumed that the form of the insulating barrier does not influence the tunneling mechanism. This is not to say that the metal-insulator interface does not affect the current since the electrons clearly do sample the bulk material at the interface, but that this effect can be made minimal and its influence on the tunneling current is recognizable(6).

Hence, by using electron tunneling we can, in principle, relate changes in the microstructure and $T_c$ to the density of states and phonon spectrum of a material. In this way a great deal can be learned about their superconducting and normal state properties and we expect more refined mathematical models of these materials can be developed for use in theory.

Towards this end, we attempted to tunnel into $V_3Au$ and $Nb_3(Al_{1.75}Ge_{2.5})$, both of which have the $Al_5$ crystal structure as shown in Figure 1. The stoichiometric composition of these alloys is $A_3B$ where the B atoms assume the BCC positions as depicted by the white balls in the figure, and the A atoms form three mutually orthogonal chains on the faces of the cube. The precise structure of stoichiometric, well ordered $Nb_3(Al_{1.75}Ge_{2.5})$ has not been determined yet, but it is believed that the Al and Ge atoms share the B
Figure 1: Crystallographic structure of the $A_3B$ compounds. The B atoms form a body centered cubic matrix in which three mutually orthogonal linear A chains are embedded.
sites\(^{(7)}\). The A15 system is important in superconductivity because almost all materials with transition temperatures above 15 K have this structure\(^{(8)}\) and it is relatively easy to correlate the changes in \(T_c\) with variations in composition and long range order in these alloys since these changes can be very large.

In the next section we describe at greater length A15 materials and why we chose \(\text{Nb}_3(\text{Al}_{75}\text{Ge}_{25})\) and \(\text{V}_3\text{Au}\), in particular, to experiment on. In the remainder of this thesis, we describe the theory and techniques of our experiments and results of others' as well as our own tunneling experiments on A15 compounds.
II. A15 MATERIALS

Superconductors possessing the A15 structure are of considerable interest even aside from their high transition temperatures and large critical magnetic fields. Many do not form at the stoichiometric composition of 25 atomic percent of element B, and their ranges of composition as a single phase are very narrow(9). The atomic radius of an A atom, taken as one quarter of the length of the A15 unit cell, is considerably smaller than the atomic radius in the elemental state(10). This strained state may be related to the martensitic phase transformation some undergo at temperatures slightly above their superconducting transition temperature. The $T_c$ and electronic specific heat of certain A15 materials depend markedly on crystalline imperfections and the percentage of A sites occupied by A atoms, which is a measure of atomic order. In addition, A15 crystals are very hard and brittle and difficult to deform plastically once the elements have been reacted. Considering these properties, it is clear that producing good, useable A15's for industrial use or experimental work is a difficult matter.

For this reason we decided to tunnel into A15 compounds that already have well established procedures for both fabrication and optimization of superconducting properties. We wanted to be certain that the processing steps were foolproof and would yield A15 materials. The materials also had to be processed so that the surface region, which is not representative of the bulk material, is thin compared to the coherence length, $\xi_0$, of the superconductor: in general the energy gaps sampled by the junction will
be representative of the region within \( S_0 \) of the surface. If true bulk values for the energy gap and other parameters are to be obtained, then only a small portion of the sampled region may be permitted to be non-characteristic of the bulk.

We should note at this point that the insulating barrier, usually a thermally grown oxide, can be considered to enlarge the effective surface region after a period of time, due to diffusion of the oxide. So as time progresses, tunnel junctions tend to give erroneous gap values when the effective surface region grows. This does not disprove our earlier statement that the shape of the barrier does not influence the current, but reinforces the point that interference from the barrier-electrode interface can be minimized, in this case by testing samples before diffusion becomes appreciable.

The optimal procedure for junction fabrication is to begin with a clean flat surface of the material to be tested and do as little to it as possible. This is because the specific effects of cleaning, polishing, and etching the surface of a material are not known but are generally presumed to increase the effective surface depth. The reason we undertook tunneling into \( \text{Nb}_3(\text{Al}_{1.75}\text{Ge}_{2.25}) \) was because a new method of fabrication\(^{11}\) allowed us to prepare surfaces which we believe are representative of the bulk and require little cleaning or polishing. We feel this method of fabrication produces bulk \( \text{Nb}_3(\text{Al}_{1.75}\text{Ge}_{2.25}) \) which is most suitable for tunneling work. Consideration of \( T_c \) and critical current, \( J_c \), versus applied magnetic field of codeposited or sputtered \( \text{Nb}_3(\text{Al}_x\text{Ge}_{1-x}) \) films leave room for doubt that they reflect the properties of the bulk pseudo-binary\(^{12}\),
while the $J_c$ versus $H$ curves of the samples used in this work are in good agreement with the arc-melted values. In addition, since $\text{Nb}_3(\text{Al}_{0.75}\text{Ge}_{0.25})$ is the record holder for $T_C$ we believe that density of states and phonon spectrum measurements of this material could tell us a good deal about high temperature superconductivity. Combining this information with that obtained from lower $T_C$ systems we might be able to observe a trend that could be exploited to increase $T_C$ above the present maximum.

Unfortunately, $\text{Nb}_3(\text{Al}_{0.75}\text{Ge}_{0.25})$ is believed to have nearly the same coherence length as other high $T_C$ superconductors. This is determined by $H_{c1}$ and $H_{c2}$ measurements and estimates range from 20-80 angstroms\(^{(13)}\). This distance is only four to fifteen unit cells deep and leads us to speculate that true gap values may never be able to be obtained since the surface region certainly extends over this same distance. As $\xi_0$ scales as $1/T_C$\(^{(14)}\), we would also like to study $\text{V}_3\text{Au}$ which has a $T_C$ of less than 3.5 K but could have a coherence length up to ten times larger than $\text{Nb}_3(\text{Al}_{0.75}\text{Ge}_{0.25})$. Thus, $\text{V}_3\text{Au}$ would presumably show less surface interference in its tunneling characteristics. This material is also of interest to us because it should have the most rapid change in $T_C$ of all A15's as complete ordering along the $A$ chains is approached\(^{(3)}\). This is shown in Figure 2 where $S$ refers to the Bragg-Williams order parameter defined by

$$S = \frac{\text{(fraction of } A \text{ atoms on } A \text{ sites} - \text{fraction of } A \text{ sites})}{(1 - \text{fraction of } A \text{ sites})}$$

Labbé and VanReuth have proposed that the essential feature in the decrease of $T_C$ is the concentration of $B$ atoms on $A$ sites; the decrease in $N(E)$ with an increase of this concentration, $c$, is demonstrated in Figure 3\(^{(15)}\). The decrease of $N(E)$ is then related to $T_C$ by the Bardeen, Cooper, and
Figure 2: The transition temperature of V$_{77}$Au$_{23}$ as a function of Bragg-Williams long range order parameter(3). The solid line indicates the relative change of ordering in the sample as a function of annealing procedures.
TRANSITION TEMPERATURE (°K) vs. LRO PARAMETER(S)

V₃ Au

4.5%  2.0%  0.5%
Figure 3: The density of states as a function of impurity concentration in the A chain sites for the A₃B compounds where the B atom does not essentially perturb any given A atom d-wavefunction (15).
$C = 0$

$C = \epsilon_1$

$C = \epsilon_2 > \epsilon_1$
Schrieffer relation $T_c \approx 1.14 \theta_D \exp(-1/N(E_F)V)$ where $\theta_D$ is the Debye temperature of the solid, $N(E_F)$ is the density of states at the Fermi level and $V$ is the average electron-phonon interaction.

To date, however, we have not determined if the only effect of ordering is the change $N(E)$, and thus $T_c$. This is because we have not been able to prepare good tunnel junctions on $V_3Au$ due to the lack of good, flat surfaces. However, we have been able to prepare samples that are almost entirely (>99%) $V_3Au$ which show the expected dependence of $T_c$ on order parameter and annealing times and temperatures. We feel that further work will result in suitable surfaces and insulating barriers that will allow energy gap and density of states measurements to be obtained.
III. SUPERCONDUCTOR TUNNELING

Electron tunneling, like superconductivity, is a quantum mechanical effect, without a classical analogue. It consists of an electron traversing a potential barrier in excess of the electron's total energy. From classical physics we should expect the electron to be totally reflected, but if quantum mechanical concepts are employed, there is a probability of crossing to the other side of the insulator which decreases exponentially with barrier thickness(16).

If we assume the incremental current from one superconductor to another is proportional to the number of unfilled states on one side of the barrier as well as to the number of filled states on the other then the net current through the junction will be:

\[ I = \int_{-\infty}^{\infty} C_{NN} \rho_1(E) \rho_2(E+eV) \left[ f(E) - f(E+eV) \right] dE \]  

where \( C_{NN} \) is the normal state conductance of the junction, \( f(E) \) is the Fermi function, and \( \rho_i \) is the ratio of the superconducting to the normal density of states of superconductor \( i \)

\[ \rho_i = \frac{N_s(E)}{N_N(E)} = \text{Re} \left\{ \frac{|E-E_F|}{[(E-E_F)^2 - \Delta^2(E)]^{1/2}} \right\} \]

(Taking the real part arises from the modification of the BCS theory for strong coupling superconductors.)

If the conductivity, \( dI/dV \), obtained when one side is normal and the other is superconducting is divided by \( dI/dV \) when both sides of the junction are normal we obtain an expression for \( \rho_i \) of the side that is
superconducting.

An idealized tunneling curve is shown in Figure 4 with the sum peak at $(\Delta_A - \Delta_B)$. Knowing $N_S(E)$, we can build up I versus V from its dependence on $dI/dV$, but it is more instructive to consider the quasiparticle excitation diagram in superconductors to explain the current characteristic\(^{(19)}\). In a normal metal the energy of an electron is $\varepsilon_k = (\hbar^2 k^2 / 2m) - E_F$. We have assumed the nearly free electron theory to be valid and take the Fermi level to be the zero of energy. This dependence is shown in Figure 5A. Actually, electron excitations with $\varepsilon_k < 0$ and $|k| < k_F$ can be described just as well by holes, or the absence of electrons, with $m_h = -m_e$. Thus, holes and electrons under the same electric field move in opposite directions.

In superconductors the energy, $E$, of an excitation above the superconducting ground state is $E = \pm (\varepsilon^2(k) + \Delta^2)^{1/2}$ with the positive branch applying to electrons and the negative branch applying to holes (since negative electron energies are positive hole energies). If $E$ is plotted versus $k$, we have Figure 5B with electrons above $E = 0$ and holes below. Note we can no longer state $|k_{\text{hole}}| < k_F$ nor can we state a hole is characterized by the lack of an electron, as in semiconductors. To determine the character of a quasiparticle excitation injected into a superconductor we must use the excitation amplitudes $u_k$ and $v_k$\(^{(19)}\). The probability that the excitation will be electron-like is the probability that the state is unoccupied by an electron $u_k^2 = 1/2 \left[ 1 + (\varepsilon / |E|) \right]$ and the probability that the excitation will be hole-like is $v_k^2 = 1/2 \left[ 1 - (\varepsilon / |E|) \right]$. It is clear from the way they are defined that $v_k^2 + u_k^2 = 1$ and $u_k^2(\varepsilon) = v_k^2(-\varepsilon)$. As an example, we take $E = 2\Delta$, then $|\varepsilon| = \sqrt{3} \Delta$ so $u_k^2 = .93$ and $v_k^2 = .07$ while
Figure 4: Idealized tunneling curve showing sum and difference peaks in the current (20).
\[ S_a/B/S_b \]
Figure 5: (A) Excitation diagram for a normal metal. Note holes appear below \( k_F \) and electrons above. (B) Excitation diagram for a superconductor. Note that both holes and electrons can exist with \( k \) greater or less than \( k_F \) (19).
\( u_k^2 = 0.07 \) and \( v_k^2 = 0.93 \). Thus a quasiparticle with \( k > k_F \) is mostly electron-like and one with \( k < k_F \) is mostly hole-like. We may note that as \( \Delta \) approaches zero, the energy, \( E \), of excitations becomes more like \( \varepsilon_k \) and excitations with \( |k| < k_F \) become more hole-like. In this limit, the electron-like branch with \( k < k_F \) and the hole-like branch with \( k > k_F \) do not disappear, but the probability that they are occupied disappears and they become irrelevant.

The process occurring at the sum peak is shown for \( k > 0 \) in Figure 6A. A Cooper pair is broken into two quasiparticles; one becomes electron-like in the superconductor on the left and the other tunnels across into the electron-like state of the superconductor on the right. The quasiparticle on the left must have at least energy \( \Delta_L \) above the superconducting ground state; the quasiparticle on the right must have at least energy \( \Delta_R \) above the ground state in the superconductor on the right. These energies can only be supplied by the potential difference, so \( V \geq (\Delta_L + \Delta_R) \). Above this bias the current increases linearly with voltage because the number of filled states on the left hand side of the barrier varies nearly linearly with energy, as does the number of unfilled states on the right. Thus, there is an approximately constant increase in the current for a small change in bias and \( I \propto V^{(17)} \).

The mechanism of the difference peak is shown in Figure 5B. Due to the smaller energy gap there are more thermally excited quasielectrons on the left of the barrier than the right. Consequently, the quasielectrons on the left wish to tunnel to the right side of the barrier. But because of the energy gap and sharp drop in density of states as one moves away
Figure 6: (A) The tunneling process in the excitation diagram representation for the difference peak in the tunneling characteristic. (B) The process in the excitation diagram representation for the sum peak (19).
from $E = \Delta$; the tunneling occurs at a maximum rate when the quasiparticles in the lowest excited states (e.g. $E = \Delta_L$) of both superconductors are at the same energy. This means the difference in the Fermi levels, i.e. the applied bias, must be $V = (\Delta_L - \Delta_R)$. Since this process depends on the temperature being greater than zero in order for the excited states to be populated, there will always be thermal smearing of the structure and the peak will appear as a gradual increase in current on the I-V, followed by a negative resistance region as the number of available final states decreases. The current is an odd function about zero, as can be seen by considering the electron-hole excitation diagrams.

Of course, there are effects that cause the I-V to be less than ideal. Some of the causes for excess current are asymmetric barriers, anisotropy of the superconducting gap, impurity states in the barrier, alternative conduction processes to tunneling, and multiparticle tunneling processes. These effects can give rise to non-zero currents at arbitrary bias voltages, asymmetrical conductance curves, low voltage structure, and broadening of all peaks.\(^{6}\)

The excess currents and the broadening phenomena often make it difficult to determine the position of peaks on the I-V curve. Hence, the $dI/dV$, which measures small changes in slope, is more convenient for determining energy gaps. Our convention for determining sum peak and difference peaks is detailed in the literature\(^{6}\). However, we have not yet been able to produce the high quality Al5 tunnel junctions required by our own stringent rules for data analysis. Consequently, we use the more lax convention that the sum peak is the point of maximum slope and the difference peak is at the midpoint of the dip after the first rise in the conductance curve.
IV. EXPERIMENTAL APPARATUS AND MATERIALS

Sample Preparation

It should be apparent from the preceding sections that sample and junction preparation is the crux of a tunneling experiment. The material itself used in the junction must be representative of the bulk, and the barrier interfaces of both electrodes should exhibit bulk-like properties in so far as is possible. The metal-insulator interface should be sharp, and the insulator should be of a thickness which allows single particle tunneling to dominate the characteristic. The thickness is generally assumed to be 20-50 Å\(^{(20)}\). A major requirement is that effects of the surfaces must be minimized, otherwise analysis of the characteristic becomes difficult and often inaccurate. In this section we describe the processes involved in making samples which we believe show bulk superconducting properties.

In Table I we list the different combinations of steps used to clean and/or form barriers on the surface of the samples, along with the yield for each process. The V\(_3\)Au samples were arc-melted buttons with junctions prepared on fracture surfaces and the Nb\(_3\)(Al\(_{75}\)Ge\(_{25}\)) was fabricated as a ribbon in our laboratory\(^{(11)}\).

Vanadium-Gold Samples

We began our tunneling studies by arc-melting vanadium and gold in an attempt to produce single phase V\(_{75}\)Au\(_{25}\) with the A15 structure. The phase diagram employed at the time indicated this was possible, but that the single phase had a very narrow linewidth of approximately 1 at. %\(^{(21)}\). It
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</tr>
<tr>
<td>$\text{Nb}<em>3(\text{Al}</em>{0.75}\text{Ge}_{0.25})$</td>
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<td></td>
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<tr>
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<td>11</td>
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was not until later that we learned this phase diagram was in error and the range of homogeneity of the A15 phase extends from 19 at. % to 23 at. % Au at room temperature (4). Both the earlier and later phase diagrams are shown in Figure 7.

The vanadium used was in the form of electrolytically refined chips obtained from the Bureau of Mines in Boulder, Colorado, and had less than 100 PPM elemental impurities. The gold was .020 inch wire of 99.97% purity obtained from MIT Laboratory Supplies and was cut into lengths comparable to the vanadium chips. The gold and vanadium were mixed in the proportion 3.00 parts vanadium to 1 part gold (approximately 55 wt. % gold) and compacted in a hardened steel casing with a 5/8 inch inside diameter. The samples were reacted in a copper hearth arc melter using a non-consumable electrode in a half atmosphere of argon gas. These samples were turned and remelted two or more times to achieve homogeneity. It was very difficult to minimize weight losses during the arc melting because the samples would often crack and fly apart, due to residual stresses and the large thermal gradients imposed when the arc was first applied to the material. Also, since the vapor pressure of gold is higher than that of vanadium (22) the losses of Au were presumed to be higher, which would tend to result in samples that differ from the starting composition in an unknown way. This last effect was minimized by lowering the power and hence the temperature of the arc. This was a compromise with the fact that if the temperature was made too low, the vanadium would not melt completely and a single phase material would not be obtained. It was possible to trade off these two effects and still react all of the material with weight losses of less than
Figure 7: On the right the V-Au phase diagram (21) and on the left the correct diagram up to 30 at. % Au (4). Note that 25 at. % Au is not in a single phase region and the temperature scales of the two diagrams are not the same.
2 wt. %. We initially attempted to use 1/8 inch rod vanadium obtained from Materials Research Corporation with a total purity of 99.98%. These rods were unsuitable for use in the arc melter since they sank to the bottom of the molten VAu mixture and did not liquify further. This behavior persisted after melting the sample four or five times and we subsequently switched to vanadium chips which had a larger surface to volume ratio.

After arc melting, the samples were annealed at less than 10^{-5} Torr in a quartz tube for a variety of times and temperatures. The annealing served two purposes: to improve the atomic ordering so only vanadium atoms appeared in the A chains on the faces of the unit cells and bringing the V₃Au into equilibrium with any unreacted gold or vanadium. This would bring the material into agreement with the phase diagram. The atomic ordering effect optimized the T_c of the sample. Susceptibility and four-point resistivity measurements were used for determining T_c, whose values were consistent with those expected for the specific temperatures and durations of anneal used (3). In particular, the samples used for tunneling were annealed at 1000°C for 220 hours or 120 hours at 1000°C, followed by a second anneal of 1 hour at 800°C. The T_c of the samples were 2.3 ± .1K and 1.4 ± .1K, respectively.

During annealing the samples were wrapped in a vanadium foil getter, but oxidation of the sample occurred, despite this precaution and that of cooling the sample under vacuum. To provide new, internal surfaces for tunneling, free of impurities and reflecting the bulk composition, the samples were cooled to liquid nitrogen temperature and split with a hammer and chisel. We felt that the low temperature and high speed of cracking
would make the fracture entirely brittle, with very little plastic deforma-
tion occurring at the new surfaces. These samples were felt to be ideal
for tunneling because the surface region could only extend the small
distance over which there was plastic deformation. However, the cracking
resulted in an irregular surface and the process was not amenable to con-
trol. It was difficult to find a smooth area two or three millimeters by
one millimeter on which to deposit a continuous counter-electrode for the
tunnel junction.

X-ray diffraction analysis showed less than 1 at. % free gold was
present in one of the samples with a $T_c$ of 1.4 K. Metallographic examina-
tion of another sample etched with hydrogen peroxide showed that it had the
most free gold, between 10 and 20 volume %, in a $V_3Au$ matrix. This sample
appears in Figure 8 and it should be noted that it was not possible to
obtain a photograph as sharp as, and with the higher contrast of, the virtual
image, consequently, the volume fraction of gold appears to be higher than
20%. Assuming that the two phases have equal densities and using the Lever
Law, the sample composition was between 61 and 63 wt. % gold, or between
$V_{71}Au_{29}$ and $V_{69}Au_{31}$. That is, the composition of the sample had shifted
between 4 and 6 at. % from $V_{75}Au_{25}$, according to the old phase diagram.
However, using Muller's phase diagram for the A15 boundary and assuming
the gold-rich boundary for the two phase field is correct at 1230 C, the
composition of the sample was between 57 and 59 wt. % Au or $V_{72}Au_{28}$ to
$V_{74}Au_{26}$. Thus the composition had not changed more than 3 at. %. It is
our conclusion that single phase $V_3Au$ can be produced if the proper start-
ing composition is used.
Figure 8: Micrograph of Au (dark phase) in V₃Au matrix (500X).
After fracturing, the samples were oxidized by either exposing the new surface to oxygen or by depositing a very thin layer of aluminum on the junction area, to be subsequently oxidized by backfilling the deposition system (22). Samples were fractured in a closed box containing an oxygen atmosphere or in the laboratory atmosphere. No dependence of junction quality on this aspect of fabrication was observed. Samples whose natural oxide barriers were formed in the closed box were prepared immediately after cracking. The other samples were allowed to oxidize at room temperature in an oxygen atmosphere (approximately 350 Torr) for 24 hours or more before counter-electrode deposition.

The alternative employed to form a barrier was to deposit 20-100 Å of aluminum onto the new internal bulk surface at pressures below 5 x 10^{-5} Torr. The thickness of deposition was measured by a Kronos QM300 Film Thickness Monitor, which measured the change in period of oscillation of a quartz crystal mounted next to the sample, as deposition material accumulated on the quartz. This change in quartz oscillation period with accumulation supposedly gave accurate thickness values to better than 1%. However, films of approximately 1000 Å in thickness agreed with angstrometer measurements only within 10%. Accuracy of the monitor below 100 Å was of secondary importance; rather, the most important problem was achieving uniformity of deposition. Thin films of less than about 1000 Å, due to free energy considerations, tend to form "islands" on the substrate, leaving regions of the substrate bare of deposited material. This process is not detectable by the crystal monitor since it only measures the total mass of deposited material and yields an average thickness of the deposit. To
counteract diffusion of the aluminum atoms on the substrate into aluminum islands, we backfilled the system with oxygen immediately after deposition in an effort to bond oxygen with the aluminum atoms and thus slow their flow.

Again, detailed knowledge of the precise thickness of the aluminum was not crucial because tunnel junction properties are only determined roughly by barrier thickness, but critically by the sharpness of the barrier interface. The kinetics of formation of very thin aluminum oxide films on our substrate is not known. Accordingly, we used the thickness monitor to obtain a reasonable value of the average thickness of the aluminum, and observed the implied change in mass after oxidation took place. This information was used to estimate how much of aluminum had reacted and thus the resultant insulating barrier thickness. Some samples were oxidized in an atmosphere saturated with water vapor under the assumption that the vapor acts as a catalyst to increase the rate of formation of aluminum oxide(23).

In general, neither the natural oxide or aluminum oxide layer was an effective tunneling barrier. Both showed hysteresis and caused shorting in the I-V and more often than not, the junction was too unstable to permit derivative analysis. Both types of samples underwent the same remaining steps of junction fabrication. The samples were masked with formvar to leave open a relatively flat barrier area about one millimeter square. About 3000 Å of Sn or In were deposited on the samples, care being taken to deposit the .010 inch wide stripe of counter-electrode over the unmasked areas. Two leads were then attached to the counter-electrode and two to the bulk to measure the current versus voltage characteristic. The
junction was covered with a protecting layer of formvar and the leads were soldered to the binding posts of a nylon sample holder. The binding posts were wired to a ten prong Winchester plug which was screwed into the nylon holder.

Niobium-Aluminum-Germanium Samples

The Nb$_3$(Al$_{75}$Ge$_{25}$) was prepared in a new way, developed in our laboratory(11). Cupronickel tubes were filled with Nb, Al, and Ge powders in the stoichiometric composition. The Nb powder was 99.7% pure and the aluminum and germanium were 99.98% and 99.999% pure, respectively. The tube was reduced in size by swaging and rolling steps and the cupronickel tube was removed with nitric acid. The resulting ribbon (.1 mm X 2.5 mm cross section) was then heated resistively to 1700°C for 10 seconds in one-half an atmosphere of argon. The T$_c$ of this ribbon was between 17 and 20K as opposed to the 20 to 21K of the best bulk samples(11). The T$_c$ versus H curves of the samples used here were about on order of magnitude higher than those of a bulk sample with T$_c$ of 18.5K(24) (Sputtered and codeposited films of Nb$_3$(Al$_x$Ge$_{1-x}$) have been prepared with T$_c$ an order of magnitude higher than with our ribbons and with T$_c$'s between 15 and 17.5K(12)). X-ray diffraction showed our samples to be almost entirely A15 in structure and metallography revealed about 5% other phases present, along with considerable porosity. We therefore felt the ribbon adequately reflected bulk properties and was especially suitable for tunneling work because of the existence and accessibility of its flat surfaces.

About nine inches of the ribbon was annealed at 725 C for 90 hours, at less than 10$^{-5}$ Torr which raised T$_c$ to 19K from 17.5K. These samples later
showed the largest gap values as obtained from dI/dV. Figure 9 shows one of the annealed ribbons as examined metallographically. The sample is almost entirely A15, with a small amount of niobium solid solution and a third unidentified phase. The majority of the junctions, however, were made on ribbon that was not annealed. Nickel etching solution was used on several of the samples, annealed and unannealed, to remove the oxide layer formed during heat treatment and any nickel that may have remained after the bath in nitric acid.

All but six samples were cleaned by ion bombardment in a glow discharge system (Figure 10). The samples were clamped in position by an aluminum wire about 4 inches above the grounded anode and 6 inches above the metal base plate. They were maintained at a negative potential difference greater than 1000V at 30 x 10^{-3} Torr of argon, using a controlled leak. The Ar was ionized by the potential difference and the ions were attracted to the cathode, striking it hard enough to dislodge atoms on the surface of the sample. In this manner oxidized and cold worked material was removed and asperities were reduced due to preferential attack. The current density was maintained at 3.3 milliamperes per square centimeter of the sample surface; a drop in the voltage necessary to maintain this current indicated that some sputtering was taking place. This drop occurred between 10 and 25 minutes after the discharge was initiated. The total sputtering was continued until a total time of one hour had elapsed. The sample, as expected, appeared shinier after ion bombardment except for the one millimeter of length which had been under the aluminum clamp.

The samples were oxidized in a free flow of oxygen at 150 C for 75
Figure 9: Micrograph of Nb$_3$(Al$_{75}$Ge$_{25}$). The main body (with the highest porosity) is Al5. The darker phase, most visible near the edge of the sample, is believed to be Nb$_2$(Al$_x$Ge$_{1-x}$) and the light phase with lesser porosity than the Al5 is a Nb solid solution.
Figure 10: Schematic of apparatus for glow discharge cleaning and oxidation. Note the sample holder served as the cathode during sputtering and the anode during oxidation.
CATHODE DURING OXIDATION, GROUNDED AT ALL OTHER TIMES

CATHODE DURING GLOW DISCHARGE
ANODE DURING OXIDATION

SAMPLE

ANODE
minutes in a system described elsewhere (25) or they were anodized in the

glow discharge apparatus without exposure to atmosphere. We followed the
work of Miles and Smith (26) and maintained the sample at zero or 3 volts
positive potential while the second cathode, grounded except during anodic
oxidation, was a few hundred volts negative in an atmosphere of 50 X 10^{-3}
Torr of O_2. The current going from the sample to ground was monitored and
when this had decayed to 10% of its initial value (about 20 μA) after 45
minutes or an hour, the discharge was halted. The sample was masked with
formvar after oxidation, leaving two or three one millimeter long uncovered
areas for junctions.

Three thousand angstroms of Pb_7Bi_3 were deposited on the sample at
pressures below 5 X 10^{-5} Torr and scored in appropriate places to make
separate tunnel junctions. Two leads were attached to each segment of the
counter-electrode and two to the sample common. The junctions were then
coated with a layer of formvar and the leads were soldered to the binding
posts of the sample holder.
Cryogenic Apparatus and Electronics

The cryogenic and electronic systems used are the same as detailed elsewhere\(^{(25,27)}\) and are only briefly described here.

Cryogenics

The cryostat used was a conventional double dewar liquid He\(^\text{+}\) system. The lowest temperatures obtained were 1.2 K by mechanical pumping and less than 0.9 K with the assistance of an oil diffusion booster pump.

Inserted into the cryostat were one of two copper and stainless steel headers. One header was connected to the sample mechanically and electrically through a ten-prong Winchester plug. The other header used the Winchester plug for mechanical support, and electrical connections were made by soldering Number 36 varnished copper wires to binding posts on the sample holder with indium solder. This latter header was used for lower temperature and higher sensitivity \(\frac{dI}{dV}\) measurements where the instability and noise of the first header had to be avoided.

In both headers, the copper wires ran up thin wall stainless tubing, through glass-to-metal solder feedthroughs, and then to miniature R-F connectors, all of which was enclosed in a metal can to provide shielding from stray fields.

Electronics

The current versus voltage characteristics of the tunnel junctions were plotted on a Hewlett-Packard 7000A X-Y recorder by measuring the current response to a variable d.c. current source (Figure 11).

The first derivative of the current with respect to voltage was
Figure 11: Circuit diagram of I-V and derivative measuring electronics.
obtained by using an a.c. modulation technique well described in the literature (28). A block diagram of the circuitry is shown in Figure 12. Analysis of the circuit is deferred to an appendix. Briefly, a small a.c. signal (dV), on the order of a few microvolts, was superimposed on the d.c. voltage driving the junction. The a.c. current response (dI) was detected at the input frequency of 5000 Hz by a Princeton Applied Research Lock-In Amplifier (HR-8). The \( \frac{dI}{dV} \) curve was then plotted as a function of voltage. The bias voltage was scanned by a ten turn potentiometer via a variable speed gearbox driven by a synchronous motor. The entire circuit was floated above ground and all the cables were shielded.

The HR-8 rejects signals not at the set frequency through the use of tuned circuit in the first stage with a variable damping factor (Q control). At 5000 Hz and with the Q control set at 25, the power of signals at 4900 Hz and 5100 Hz (noise) were attenuated by 50% compared to signals precisely at 5000 Hz. Signals between this 200 Hz bandwidth were reduced less than 50% while those outside it were attenuated more. Much greater sensitivity is achieved by the phase sensitive detector which follows the front end, with integrating times (typically) of one tenth second to one second. Bandwidths of the order of one cycle per second or less resulted and full scale deflection of the lock-in was commonly at 10\( \mu \)V or better.

When possible, a type C preamplifier was used in conjunction with the HR-8; this allowed the signal to be entered differentially and consequently reduced the noise due to common mode fluctuations. In addition, taking the signal differentially from the measuring circuit to the input of the
Figure 12: Block diagram for I-V characteristic and derivative detection network.
DC BIAS BOX
FROM VOLTAGE OUTPUT
FROM CURRENT OUTPUT

8% OF SIGNAL

UTC LS-33 TRANSFORMER
60% OF SIGNAL
TO REFERENCE

GENERAL RADIO 1309 OSCILLATOR

PAR-HR 8 LOCK-IN AMPLIFIER
TO X-AXIS

TO Y-AXIS

MOSELEY 7000 AR X-Y RECORDER
preamplifier in two coaxial cables provided extra shielding against stray a.c. signals present in the laboratory. However, when the normal state junction resistance was less than fifty ohms, a single-ended type B preamplifier was necessary because of its better noise rejection characteristics at low input impedances.
V. RESULTS

As was stated earlier, we were not able to prepare good tunnel junctions with V₃Au since we did not have appropriate surfaces. We believe, however, we did obtain energy gap values for \( \text{Nb}_3\text{Al}_{75}\text{Ge}_{25} \) which exhibited the strongest coupling encountered in the A15 system until this time \( (2\Delta = 5.8 \ k_B T_c) \). It must be made clear here that only one junction displayed these results explicitly; another showed a vestigial sum peak along with a difference peak at the appropriate biases to yield gap values within 10% of those obtained from the first junction. The sum peak on this second junction was apparent only if we looked for it at the bias where we expected it to appear. Three other junctions have given reasonable values for the energy gap of the counter-electrode, \( \text{Pb}_2\text{Bi}_3 \) and these yielded an energy gap of \( \text{Nb}_3(\text{Al}_{75}\text{Ge}_{25}) \) below 2 millivolts.

The junctions which displayed sum and difference peaks are listed in Table II along with the values obtained for the half gap, \( \Delta \), of \( \text{Pb-Bi} \) and \( \text{Nb-Al-Ge} \). Also included are the date and temperature of the measurement, other peaks in the conductance curves and resistances of the junctions at 4.2K and 77K. Normalized conductances \( \frac{(dI/dV_{NS})}{(dI/dV_{NN})} \) are not available on any junctions at the present time.
Vanadium-Gold Samples

The $dI/dV$ with the most structure is shown in Figure 13. It was taken at .9K using an indium counter-electrode and the insulating barrier was the natural oxide formed when the new surface was exposed to air on fracture. The I-V was not included because it did not contain any information not apparent from $dI/dV$. It had the same form as all $A15$ characteristics have exhibited with two exceptions: junctions $AB$ and $JL$. The I-V is basically ohmic with changes in slope barely discernible to the eye. The average resistance of the junction was 5 ohms. The dips in conductance at 1.6, 4.2, 5.6, and 6.6 mV cannot be related in any way to give gap values for indium near the expected 1.05 mV. All the junctions prepared showed no structure or were too unstable to obtain a derivative. We attribute this lack of structure to failure to obtain a proper insulating barrier. Further consideration is given to this problem in the Discussion section.
Figure 13: \( \frac{dI}{dV} - V \) for \( V_3 \text{Au-In} \) junction.
Niobium-Aluminum-Germanium Samples

Junctions AB and JL were on the same sample, while the three other junctions in Table II were the only ones on their respective pieces of ribbon to give sum and difference peaks. All samples were cleaned in the glow discharge system prior to oxide formation. Junctions AB and JL had been exposed to atmosphere between a week and a month before cleaning in the glow discharge apparatus and were then oxidized as described at 150 C. Sample BF was immersed in nickel etching solution between being removed from the annealing furnace and being placed in the glow discharge system. It, too, was thermally oxidized. Junction CD was on an annealed piece of ribbon and it was oxidized in the glow discharge system after being sputter cleaned. The sample was at +3 V and the cathode was held at roughly 500 V below ground. The discharge was maintained at 1 mA (total current from cathode to ground) for 90 minutes in 50 X 10⁻³ Torr of oxygen. Junction DL was not on annealed ribbon, but it was etched in concentrated nitric acid before sputter cleaning and then oxidized in 50 X 10⁻³ Torr of oxygen for 12 minutes with the sample grounded and the cathode at -500 V.

With this recapitulation of the differences in sample preparation, we proceed to examine the specific results of each junction. Due to unfamiliarity with the glow discharge system at the time junctions AB and JL were made the anode and, consequently, the sample acquired a red tinge from the copper cathode shortly after applying the bias. Occasionally, the glow would become an arc for a fraction of a second due to instabilities in the discharge and consume a great deal more power than the usual five to ten watts. This arcing occurred after the sample had been sputtered onto and
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<th>$\Sigma$ Peak mV</th>
<th>$\delta$ Peak mV</th>
<th>Other Peak mV</th>
<th>$\Delta$Pb$<em>{2}$Bi$</em>{3}$ mV</th>
<th>$\Delta$Nb$<em>{3}$Al$</em>{7.5}$Ge$_{2.5}$ mV</th>
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<th>Resistance 77K $\Omega$</th>
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had a duration of over one second. The sample became red hot and after the arc had stabilized into a glow, the copper on the surface had disappeared, presumably dissolving into the Nb$_3$(Al$_{75}$Ge$_{25}$) or vaporizing due to the heat. It was now possible to reach a higher potential difference than before, and to acquire a measure of the capability of the system and characteristics of the glow, the sample was subjected to another half hour of discharge at various voltages, with the red tinge reappearing. The sample was then oxidized and a counter-electrode deposited.

The I-V and dI/dV of sample AB are shown in Figures 14 and 15, these yielded very small gap values for Nb$_3$(Al$_{75}$Ge$_{25}$) but they also had the least excess current of all samples tested as of this data. Junctions AB and JL were representative of a good proportion of the sample in that they deteriorated at liquid helium temperatures after passing a current for two or three hours. This behavior does not compare very favorably with that of Nb-Pb$_2$Bi$_3$ junctions which allow derivatives to be taken for several hours and go through two or three cycles from room temperature to liquid helium without ill effect. Junction JL, in point of fact, lasted through only one complete derivative trace before the junction deteriorated and further attempts at obtaining a conductance curve resulted in a parabolic trace, without other structure, indicative of normal-normal tunneling. The first conductance curve was rather noisy and was not included for this reason, but the sum and difference peaks agree with those of junction AB. The reason for junction breakdown is not known but it may be caused by the high electric field applied to the junction. This is approximately (10$^{-3}$V)/50 X 10$^{-8}$ cm = 2 X 10$^5$ V/cm. Why the effect is time dependent is not
Figure 14: I-V of junction AB at 4.2 K.
$\text{Nb}_3(\text{Al, Ge})$

Sample AB

$T = 4.2 \, ^\circ\text{K}$
Figure 15: \((dI/dV) - V\) of junction at 4.2 K and at an average temperature of 2.5 K.
Sample AB

\[ \frac{dI}{dV} \text{ vs. } V \]

$T = 4.2^\circ K$

$T = 2.5^\circ K$

C 1973 MIT
understood, nor the fact that junctions occasionally "heal" themselves at room temperature.

The derivative obtained at the lower temperature was approximately 2.5 K since the trace was begun while pumping at 2.85 K and finished at 2.49 K, as determined by the pressure of the helium in the dewar at those times. When a conductance trace was attempted at 1.2 K, it yielded the normal-normal tunneling parabola, indicating the junction had deteriorated. One sum peak was at 2.73 K and the other at 2.58 K and these combined with the difference peaks gave an "average" gap value .22 mV larger than at 4.2 K. Note that the Pb$_7$Bi$_3$ half gap had shifted by .02 mV, only.

None of the junctions tested in this study returned from the normal-normal state once they had "burned out", but BF did improve with age. On its date of fabrication, junction BF displayed a conductance peak at 2.5 mV, but a difference peak or another dI/dV trace were not obtained due to instability of the junction. Twenty-eight days later, the junction was tested again and produced the gap values listed in Table II. As is readily apparent from Figure 16, the structure of the junction is completely obscured on the I-V and we must rely on the derivatives to obtain gap values. The sum peak would exhibit a shoulder immediately preceding it when approached from biases above the sum peak (Figure 17), making it difficult to determine accurately. The shoulder was missing on the other side of the same trace, leading to an asymmetry in dI/dV, but was observed at that voltage when the direction of the trace was reversed. Decreasing the speed of the trace to 1/10 rpm from 1/5 rpm and increasing the dI/dV scale showed the sum peak was symmetric and correctly given by the peak.
Figure 16: I-V and (dI/dV) - V of junction BF at 1.2 K. Note large dip in dI/dV at 7.5 mV.
Figure 17: (dI/dV) - V of junction BF at 1.2 K. The arrows denote the direction of bias scan. (A) The sum peak as scanned at 1/10 rpm and approximately 20 μV a.c. signal. Note the shoulder and that the peak is symmetric about zero bias. (B) The dI/dV as scanned at 1/5 rpm, 20 μV signal size. Note the direction of the scan has been reversed and the sum peak is not symmetric about zero. (C) The dI/dV as scanned at 1/5 rpm and 15 μV a.c. signal size. Note the outward displacement of both the difference and sum peaks and the dip is conductance at -4 mV.
associated with the shoulder. Another discrepancy arose when the a.c. signal size was decreased by about 30%; the sum and difference peaks increased their biases more than .2 mV. We still take the sum peak at the bias obtained from the slower scan because both of these signals are below 25 μV peak to peak, which is much less than the thermal smearing of 100 μM at 1 K and the slower scan allows more time for the HR-8 to integrate the input for a given bias.

A third anomaly apparently related to the method of measurement was a pronounced dip which would occasionally appear on one side of the trace or the other, but not both. This dip appears at -4 mV in Figure 17c.

We have no explanation to offer for this behavior or for the large dips in the conductance curve after the sum peaks and smaller dips after the difference peak. This junction was still producing useable data when the last curve had been taken on this date. However, tests seven and 40 days later yielded parabolic derivatives with a small zero bias anomaly around .5 mV.

At the time of its preparation, a current-voltage characteristic was obtained for junction CD but a conductance measurement was not made. The junction was tested again 43 days later and two dI/dV measurements were made. The I-V and dI/dV at 1.2 K are shown in Figure 18. The conductance curve at 4.2 shows a very small peak superimposed on a rapid rise in conductance trailing into parabolic behavior at 9.2 mV. In niobium-indium tunneling work in our laboratory, this behavior occurred at the sum peak for junctions with resistances less than 1 ohm\(^{29}\). Junction CD, however, had a resistance of 40 Ω. It is more likely that this peak, which does not
Figure 18: I-V and (dI/dV) - V of junction CD at 1.2 K. Note the parabola extrapolated from the high bias behavior and the maximum in difference between the conductance curve and the parabola at 6.3 mV.
appear at the lower temperature, arises from a lead or lead-bismuth phonon. The trace at 1.2 K showed a difference peak at 3.1 mV and what could be construed as a sum peak at 6.3 mV. That is, we observe the onset of the parabolic dependence of the conductance curve at 4 mV and situated on this is an additional conductance which has its greatest difference from the extrapolated parabola at 6.3 mV. These two values give \( \Delta_{\text{Pb,7Bi,3}} = 1.6 \) mV and \( \Delta_{\text{Nb}(\text{Al,75Ge,25}) = 4.7 \) mV, which is within 10% of the values obtained from junction BF. Alternatively taking the conductance peak at 1.9 mV as a lead-bismuth multiparticle peak we obtain \( \Delta_{\text{Nb,3(Al,75Ge,25}) = 4.4 \) mV, the same as sample BF. However, the same conductance peak at 4.2 K was at 1.7 mV and this is too much of a decrease in \( \Delta(T) \) to be accounted for by the empirical relationship for the temperature dependence of the gap:

\[
\Delta(T) = \Delta(0) \left[ \cos \left( \frac{\pi}{2} \left( \frac{T}{T_c} \right)^2 \right) \right]^{1/2} \tag{30}
\]

Junction DJ shows a very broad sum peak at 2.3 mV and a difference peak at 0.58 mV. These determined \( \Delta_{\text{Pb,7Bi,3}} = 1.44 \) mV and \( \Delta_{\text{Nb,3(Al,75Ge,25}) = 0.86 \) mV. The low value for the energy gap of the ribbon was again attributed to surface effects. See Figure 19.

In the next section, we discuss the factors which could affect the size of the gap seen, the similarities exhibited by all junctions yielding gap values, and comparisons of gap values for \( \text{Nb,3(Al,75Ge,25}) \) with those obtained in other A15 alloys.
Figure 19: I-V and (dI/dV) - V of junction DJ at 1.2 K. Note the broaden-
ess of the sum peak.
VI. DISCUSSION

Vanadium-Gold Samples

In the present work we attribute the failure to obtain good tunnel junctions to two major causes: poor insulating barriers and/or insufficiently smooth surfaces. For the $V_3Au$ samples there are strong indications that both of these problems were encountered.

The free gold present in all samples which were examined metallographically or by X-ray was most probably not oxidized when the barriers were fabricated. Such a situation could lead to shorts and hysteresis in the I-V curve since most of the current crossing the junction would see low resistance Au-Sn or Au-In metallic path and joule heating would act to change the resistance of the short.

To avoid having such gold shorts we attempted an alternative means of oxidation: depositing a thin layer of aluminum and exposing it to oxygen. In principle, a uniform insulating layer of $Al_2O_3$ would form, thus placing a barrier between the noble metal and the counter-electrode while not eliminating normal-superconductor tunneling currents from the gold to the conductor. We were unable to form good insulating barriers on the $V_3Au$ samples using this technique. We subsequently investigated the possibility of fabricating such barriers in In-In and Sn-Sn thin film junctions and had little success with these materials either. Hence, the failure for $V_3Au$ junctions may be independent of the $Al_5$ material.

On the other hand, it is quite possible that the thin film of Al could not cover the steps between planes of brittle fracture on the $V_3Au$
surface, since these were certainly more than 100 Å apart in height. Consequently, the 3000 Å of counter-electrode shorted out against the uncovered $V_3Au$.

We believe that reliable tunneling data on $V_3Au$ will not be obtained until we possess single phase $A15$ material and smooth out the sample surfaces to be used for tunnel junctions. Towards this end we are investigating the possibility of having higher speed of fracture or tensile failure produce fracture surfaces smoother than those now available. We shall also attempt to etch or polish away the surface layer of the arc melted buttons.

We feel confident that carrying out such a program will result in good tunnel junctions from which information on the effects of atomic order in superconducting $V_3Au$ can be obtained.

**Niobium-Aluminum-Germanium Samples**

As in $V_3Au$ we had to contend with a gold phase in the sample, so in $Nb_3(Al_{1.75}Ge_{2.25})$ there are $Nb_2(Al_xGe_{1-x})$ and niobium solid solution phases. In this case they are less of a problem to oxidize than the Au was, relative to the $V_3Au$, since these three Nb alloys are believed to oxidize similar to the element itself\(^{(30)}\). The presence of the two additional phases is detrimental to tunnel junction characteristics because they add "excess current" to the tunneling current of interest: that between the $A15$ phase and the lead-bismuth counter-electrode.

The resistances of most of the junctions ($>40$) which showed no structure in $dI/dV$ were less than $10\Omega$ at $77\,K$ and all were less than $100\Omega$. The junctions yielding sum and difference peaks ranged from $10\Omega$ to $500\Omega$ at
At 4.2 K, the resistances were scattered over four orders of magnitude and the grouping of "successful" and "unsuccessful" junctions were less clear cut.

The junction resistance and quality were observed to change with time. The resistance decreased and the quality of the junction increased and then decreased. This suggested the following model for oxidation in Nb\(_3\)(Al\(_{75}\)Ge\(_{25}\)). The oxygen was adsorbed and dissolved by the ribbon and only a fraction of it formed a stable oxide. The depth of the oxygen penetration into the ribbon was initially determined by the temperature of the ribbon or the electric field imposed on it. As time progressed, the dissolved oxygen diffused into the bulk, leaving the stable oxide behind. This caused a decrease in resistance of the junction and also made the ribbon adjacent to the barrier more bulk-like since the oxygen concentration had decreased. The process probably proceeded faster than bulk diffusion; possibly porosity allowed surface diffusion to occur. Eventually enough oxygen had diffused away so that the resistance of the junction was too low for it to serve as an effective tunneling barrier.

We believe junction quality was also impaired by impurities in the ribbon. Ferromagnetic impurities are known to suppress superconductivity markedly and it was impossible to remove all the cupronickel tubing due to the "flashing" and subsequent folding under of the surface during swaging. Also, in sample AB, copper sputtered onto the sample from the cathode may have dissolved in the ribbon, degrading the surface layer of the ribbon. If this occurred and also decreased T\(_c\) to a few tenths of a degree above 4.2 K it could explain the small energy gap of the A15 material and the
strong dependence of the gap on temperature (Table II).

The small values obtained for the half-gap of lead-bismuth might be explained by depositing a counter-electrode that was not 70 at. % lead, that is, not in equilibrium with the melt. This phenomenon has been observed previously in the lead-bismuth system\(^{(27)}\). The energy gap obtained with junction DJ yielded \(2\Delta = 2.88\) mV which corresponds to a composition of over 80 at. % lead\(^{(32)}\).

The five junctions which showed sum and difference peaks had one aspect in common: they had all been cleaned by ion bombardment. We believe the glow discharge removed the oxidized and cold worked material, smoothed the surface locally, and allowed an oxide to be formed on a bulk-like surface. At present we cannot say there is any correlation between quality of the junction and its position on the ribbon relative to the aluminum clamp in the glow discharge system.

It also seems at this time that there is no correlation between method of oxidation and the gap values obtained for \(\text{Nb}_3(\text{Al}_{0.5}\text{Ge}_{2.5})\). Junctions with thermal oxide barriers (BF and AB) have given nearly the same gap values as those with anodic oxide barriers (CD and DJ).

The largest gap values obtained were those using annealed ribbons (BF and CD). While a model has been proposed which indicates how a surface may lower the magnitude of the energy gap\(^{(33)}\) we cannot see how the surface could increase it, and therefore feel this gap \(2\Delta = 8.8\) mV is indicative of the bulk \(\text{Nb}_3(\text{Al}_{0.5}\text{Ge}_{2.5})\) ribbon. The anneal lowered \(J_c\) versus \(H\) of the ribbons\(^{(11)}\) which indicated that pinning centers were removed from the ribbon. Also \(T_c\) was raised from 17.5 K to 19 K and both of these effects
make the ribbon, and presumably its surface, more characteristic of the bulk.

The gap value of our ribbon results in $2\Delta/kT_c = 5.4$ which, while high, is not without precedent. The parameter $2\Delta/kT_c$ is as high as 5.2 in the Pb-Bi system\(^{(32)}\) and neutron scattering experiments on single crystal Nb\(_3\)Sn yield $2\Delta/kT_c = 4.4 \pm 0.6\(^{(34)}\)$. The experimental error is rather large in this case but the correct value is most likely in the strong coupling range $2\Delta/kT_c > 4.0$.

On the other hand, Nb\(_3\)Sn junctions have yielded values of $2\Delta/kT_c$ between 1.3 and 3.77, but these values are believed to reflect the energy gap of the surface region\(^{(35)}\). Thermal conductivity studies, which should reflect the bulk state, resulted in $2\Delta/kT_c = 3.56\(^{(36)}\)$. Clearly this collection of experimental contradictions cannot be resolved without further work.
VII. RECOMMENDATIONS FOR FURTHER RESEARCH

The tunneling work on A15's has only begun and we can see the following work to be done:

Vanadium-Gold Samples

Produce single phase material and develop new technology to make smoother surfaces, either by tensile failure or chemical or mechanical polishing. If accomplished, this work will allow us to study the effect of thermal processing on $T_C$.

Niobium-Aluminum-Germanium Samples

Attempt to clean the surfaces of the ribbon further by electropolishing, in order to fabricate junctions that will allow us to determine the phonon spectrum and density of states in $\text{Nb}_3(\text{Al}_{7.5}\text{Ge}_{2.5})$. Measurement of the temperature dependence of the gap above 9 K can be attempted by making a point contact from two crossed $\text{Nb}_3(\text{Al}_{7.5}\text{Ge}_{2.5})$ wires.

A15 System

Once these two alloy systems have been studied, other A15 compounds may be investigated by tunneling and it may be possible to determine if another mechanism besides surface degradation of superconductivity is responsible for the discrepancies in $2\Delta/kT_C$ for $\text{Nb}_3\text{Sn}$. 
In Figure 11, the resistor $R_s$ serves as a voltage divider to bias the junction in the ±20 mV range, $R_I$ serves as a current divider between the leg containing the junction, $R_x$, and the resistor, $R_c$. The voltage across $R_c$ goes to the input of the X axis of the Hewlett-Packard recorder or to the input of the HR-8. In the first instance, this voltage is displayed as current, since it is the same as the current through the junction and is measured across a known precision resistor and in the second, the a.c. component of the voltage is processed by the HR-8 whose d.c. output is proportional to $dI/dV$ of the junction. Resistors $R_K$ and $R_F$ act as current and/or voltage dividers for the signal going through the junction, depending on their values relative to each other and $R_x$. As seen from the small signal model in Figure 20, $R_K$ and $R_F$ each constitute one leg of a parallel circuit and the network of $R_S$, $R_I$, $R_c$, $R_x$ and the capacitor forms the third leg parallel to the a.c. voltage source.

The capacitors in series with $R_S$ has an impedance of 1.5Ω at 5 KHz, $R_S$ in practice is 1 KΩ and $R_I$ and $R_c$ are 100Ω or less so we approximate the a.c. voltage drop across any leg in parallel to the a.c. source by

$$V_e = \frac{(R_S || R_K || R_F)V_{ac}}{R_S || R_K || R_F + 1000 - R_F}$$

where $V_{ac}$ is the voltage across the secondary of the UTC-33. We note that $V_e$ is independent of $R_x$ and
Figure 20: Small signal model for derivative measuring electronics.
5 K Hz
20 mV

1000 Ω - R_F

R_F

R_K

R_I

R_S

R_C

23 μfd

TO BIAS
INPUT OF
RECORDER

TO HR-8
INPUT
\[
V_{Rc} = \frac{V_e (R_c + R_x) I}{(R_c + R_x) I + R_S} \cdot \frac{R_c}{R_c + R_x} = \frac{V_e I R_c}{(R_c + R_x) [R_S + R_c] [I (R_c + R_x)]}
\]

using the same order of approximation as before

\[
V_{Rc} = \frac{V_c I R_c}{(R_c + R_x) R_S}
\]

and solving for the conductance of the junction we get

\[
\frac{1}{R_x} = \frac{R_S V_{Rc}}{V_e I R_c - V_{Rc} R_S (R_c + R_x)}
\]

For two limiting cases the results are much simpler for \( R_x >> R_I + R_c \)

\[
V_{Rc} \approx \frac{1}{R_x} \frac{V_c I R_c}{R_S} \left( 1 - \frac{R_i + R_c}{R_x} \right)
\]

and for \( R_x << R_I + R_c \)

\[
V_{Rc} \approx \left( 1 - \frac{R_c}{R_I + R_c} \right) \frac{V_e I l R_c}{R_S}
\]

Thus at junction resistances high compared to \( R_I + R_c \) the input to the HR-8, \( V_{Rc} \), is proportional to \( 1/R_x \) and therefore like \( dI/dV \). At low junction resistances \( V_{Rc} \) is nearly constant with a small variation that is proportional to \( R_x \) or \( dV/dI \). The reference signal to the HR-8 is proportional to \( V_{ac} \) and, in the same approximation as above, \( V_e \) serves as a voltage source in the first case and as a current source in the second. This situation arises because when \( R_x >> R_I \) most of the current goes through \( R_I \) and fluctuations in \( R_x \) do not affect the voltage drop across \( R_I \) (and thus
When \( R_x \ll R_I \), then the changes in current going through \( R_x \) are small because \( R_I/R_I+R_C+R_x \), which is proportional to the current going through the junction, is nearly constant.

In between these two cases the location of maxima and minima on the curve that is ostensibly \( dI/dV \) or \( dV/dI \) could be shifted significantly by different values of \( R_I \) and \( R_C \). This is especially true near the sum peak where the conductance rises to a maximum and then falls.

The problem arises from not having the voltage across the junction constant or, more correctly, proportional to the HR-8 reference. The reference signal is what the input amplitude is compared to during integration of the input and serves as \( \Delta V \) in \( \Delta I/\Delta V \). Therefore, if we could use a reference signal proportional to \( V_x \) then the voltage across \( R_c \) would give \( dI/dV \) since \( V_{R_c} = V_x R_I/R_x \). There are two ways this can be accomplished: the circuitry can be constructed to have a feedback system so that the voltage is constant across the junction (37) (and therefore proportional to \( V_{ac} \) ) or \( V_x \) itself can be used as a reference. Care must be exercised with both of these methods to be certain that a change of phase or non-linearity is not introduced during signal processing, since this would lead to attenuated and inaccurate signals in the output of the HR-8.

At present, we do not compensate for the voltage dependence of \( R_x \) and our results are consistent with the others in the field. We have assumed that \( R_x \) does not change significantly enough compared to \( R_I \) and \( R_C \) to make a difference in our conductance plots, but further tests will have to be done to ascertain if this is true.
BIBLIOGRAPHY

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