# Superconductive tunneling in vanadium with gaseous impurities*

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Electron-tunneling measurements have been made in vanadium films containing varying amounts of gaseous impurities. Transition temperatures $T_c$ vary from near the bulk value to more than 2 K below it. After corrections are made for spurious leakage conductivity, tunneling characteristics are in all cases consistent with a simple BCS superconducting density of states. $T_c$ and the zero-temperature energy gap $\epsilon$ (0) vary in accordance with $2\epsilon(0)/kT_c = 3.5 \pm 0.1$. In consequence, it does not appear that gaseous impurities enter the vanadium lattice in a paramagnetic configuration.

## I. INTRODUCTION

The effect of dissolved gases on the superconducting properties of the group-V transition metals V, Nb, and Ta is well known. As little as 1-at.% oxygen dissolved in Nb lowers the transition temperature $T_c$ by nearly 1 K.[1,2] Similar effects occur in[3] V and Ta,[4,5] though they have not been as carefully studied. By contrast, nontransition metals are little affected by such impurities.

The mechanism by which interstitial impurities effect reductions of $T_c$ in the group-V metals is not well understood. Proposed explanations have generally invoked lattice disorder and consequent electron scattering[6] or phonon spectrum changes.[7] An alternative mechanism is suggested by the known magnetic properties of the oxides of these elements.[8] Magnetic impurities have drastic effects on the properties of superconducting metals, bringing about strong reductions in $T_c$ and even gaplessness.[9] If gaseous impurities were to dissolve in V, Nb, and Ta in a paramagnetic configuration, this would provide a ready explanation for their strong effects on $T_c$.

In addition, several previous experiments have exposed anomalies in the superconducting behavior of vanadium which might be attributable to a magnetic character of dissolved gaseous impurities. Giaever[10] found a smearing of the energy gap in V tunneling experiments using films which were condensed in the presence of a nonnegligible residual gas pressure. Noer and Knight[11] interpreted their failure to observe any change below $T_c$ in the nuclear spin-lattice relaxation time of their impure V films as possible evidence for gapless behavior. Meyers and Little[12] failed to observe long-range order in flux quantization experiments with V and Nb; though their films were evaporated in a high vacuum, the reduced $T_c$'s observed suggest the possibility of gaseous impurities.

Motivated by the possibilities suggested above that gaseous impurities might interact magnetically with the transition metals V, Nb, and Ta, we have investigated the effects of such impurities on the electron tunneling characteristics of vanadium. Electron tunneling is particularly sensitive to paramagnetic impurities[9]; vanadium was chosen because it can be evaporated and condensed into films of reasonable purity in a conventional high-vacuum system, because its critical temperature is conveniently near the liquid-helium temperature range, and because of the particular anomalies mentioned in the preceding paragraph.

The work discussed in this paper constitutes the first detailed examination of the superconducting density of states in vanadium films. Previous attempts to observe and analyze electron tunneling in this metal have been only partly successful. Giaever,[10] using V films in a V-$VO_x$-Pb configuration, "did not obtain any negative resistances at all, and the gap could only be roughly determined." Thompson and von Molnar[13] observed tunneling into bulk vanadium using a Schottky barrier on GaAs; their work was complicated by excess currents and they attempted no detailed analysis. Hansma and Rochlin[14] used bulk V to observe phonon structure in the tunneling density of states; they report difficulties due to the low barrier height of vanadium oxide and the difficulty in maintaining a sharp metal-oxide interface. Seifarth and Rentsch[15] studied Josephson tunneling from V films; their junctions showed leakage currents, and they report no attempt at examining the non-Josephson part of the tunneling.

## II. EXPERIMENTAL

### A. Vanadium evaporation

Vanadium films were formed on glass substrates by evaporation from resistance-heated tungsten boats in a conventional diffusion pumped vacuum system. The starting material was 99.98% vanad-

ium wire obtained from Materials Research Corp. By varying the conditions of evaporation, we could obtain films whose $T_c$'s could be fairly well controlled. With a combination of the best vacuum attainable (about $5\times10^{-7}$ Torr during evaporation, achieved by preevaporating a quantity of vanadium to act as a getter while the substrate was covered with a shutter), rapid evaporation (about 250 Å/sec), and a heated substrate (estimated at about 300 °C), we were able to achieve a maximum $T_c$ of about 4.8 K. Relaxing these conditions resulted in lower $T_c$'s; in fact, it was only too easy to evaporate films which showed no superconductivity at all down to 1.2 K. Generally speaking, to produce $T_c$'s in the range between about 4.0 and 4.8 K, the evaporation rate was reduced slightly; to make $T_c$'s between 3 and 4 K, the substrates were left at ambient temperature, the pressure during evaporation was allowed to remain as high as the low $10^{-6}$ Torr range, and the evaporation rate was cut by as much as a factor of two.

Film thicknesses were measured with an interferometrically calibrated quartz crystal monitor. Since $T_c$ of even very-pure V films deposited on glass decreases markedly for thicknesses less than about 1000 Å,[15] we concentrated primarily on films with thickness greater than 2000 Å so as to ensure that the observed $T_c$ reductions resulted predominantly from impurities.

### B. Tunnel junction fabrication

Our first junctions were made in the configuration V-$VO_x$-$M$ (where $M$ is another metal, usually Sn); the vanadium was oxidized by heating in an oxygen atmosphere or, less successfully, by glow discharge. None of these junctions was satisfactory; the resistance of the vanadium films showed a good superconductive transition, but there was never any evidence of a vanadium energy gap in the tunneling characteristics. (The more successful of the thermally oxidized V-$VO_x$-Sn junctions exhibited clear structure due to the Sn gap, indicating that these were not short circuited or otherwise improperly made.) In addition, all such junctions showed large zero-bias anomalies in both normal and superconducting states,[16] with high-bias voltage shifts.[17] Presumably this has to do with the antiferromagnetic and semiconducting properties of vanadium oxides[8]; the apparent lack of an energy gap in the vanadium metal is probably due to diffusion of oxygen into the metal immediately adjacent to the oxide tunneling barrier, suppressing its superconductivity.

To avoid these difficulties arising from the use of vanadium oxide as a tunneling barrier, we turned to Al-$AlO_x$-V junctions. The high melting temperature of vanadium and its consequent high condensation energy makes its use as the top layer of a junction rather difficult; the vanadium tends to "eat through" the oxide layer onto which it condenses. It appears that aluminum is the only metal with an oxide tough enough to withstand this sort of treatment. Even then, we found it necessary to oxidize our aluminum films at 100 °C in pure oxygen for 2–12 h to produce junctions with no obvious short circuits and a reasonable resistance. Successful junctions had a normal-state resistance of typically 5–50 Ω, showed little or no zero-bias anomaly or voltage shift, and exhibited clear structure due to a vanadium energy gap. (A few percent Mn was added to the Al to suppress its superconductivity at the lowest temperatures.)

### C. Measurements

Samples were immersed directly in liquid helium, and could thus be examined at temperatures between 4.2 K and about 1.2 K. A conventional four-terminal circuit[18] was used to measure resistance $dV/dI$ vs voltage $V$ characteristics for the tunnel junctions as well as to monitor the resistances of the strips comprising the junctions as the temperature was changed. A bridge circuit[19] was also used for more precise $dV/dI$-vs-$V$ tunneling characteristics, particularly near $T_c$ where the superconducting structure in $dV/dI$ was small.

## III. ANALYSIS

From our measurements of $dV/dI$ vs $V$ in both normal ($N$) and superconducting ($S$) states, we calculated the normalized conductivity

$$\sigma_{\exp} = \left(\frac{dV}{dI}\right)_S \Big/ \left(\frac{dV}{dI}\right)_N .$$

Although these curves appear to agree qualitatively with the expected BCS form,[20] a more careful quantitative examination shows serious discrepancies. That these discrepancies can be attributed to ohmic "leakage currents" was established for each curve by the following procedure: (i) *Assuming* that the tunneling contribution to the measured normalized conductivity $\sigma_{\exp}$ follows the ideal BCS behavior, a value of the energy gap $\epsilon$ was derived from the voltage at which this conductivity is maximum. This voltage is not affected by any voltage-independent parallel conductance. (ii) From this $\epsilon$, the predicted normalized BCS conductivity $\sigma_{\mathrm{BCS}}(V)$ was calculated. In particular, its value at zero bias $\sigma_{\mathrm{BCS}}(0)$ was noted. (iii) The leakage conductivity $\sigma_l$ was then taken to be $\sigma_l = \sigma_{\exp}(0) - \sigma_{\mathrm{BCS}}(0)$. Values thus obtained ranged in an apparently random fashion from 0.3 to 0.9. (That is, the leakage conductivity varied between 30 and 90% of the total measured normal-state conduc-

tivity.) These values were unrelated to $T_c$.
(iv) Assuming $\sigma_t$ to be independent of $V$, we then calculated a corrected conductivity $\sigma_{corr}(V) = \sigma_{exp}(V) - \sigma_t$.

The validity of the above calculations can be argued from the following results obtained: (a) $\sigma_{corr}(V)$ agrees well with $\sigma_{BCS}(V)$ in nearly every case. (Figure 1 shows a representative example.) They have, of course, been forced to have their maxima at the same voltage and to have the same value at $V=0$. However, the good agreement in the heights of the maxima and the closeness of the fit elsewhere is reassuring. (b) Using the values of $\epsilon$ derived for a given junction at a number of different temperatures, a plot of $\epsilon(T)$ can be made. In each case, the agreement with BCS[21] was acceptable. Figure 2 shows a typical fit. (c) For a given junction, $\sigma_t$ is only weakly temperature dependent, decreasing typically by about 10% as the temperature is lowered from $T_c$ to 1.2 K.

Results a and b appear to validate our assumption

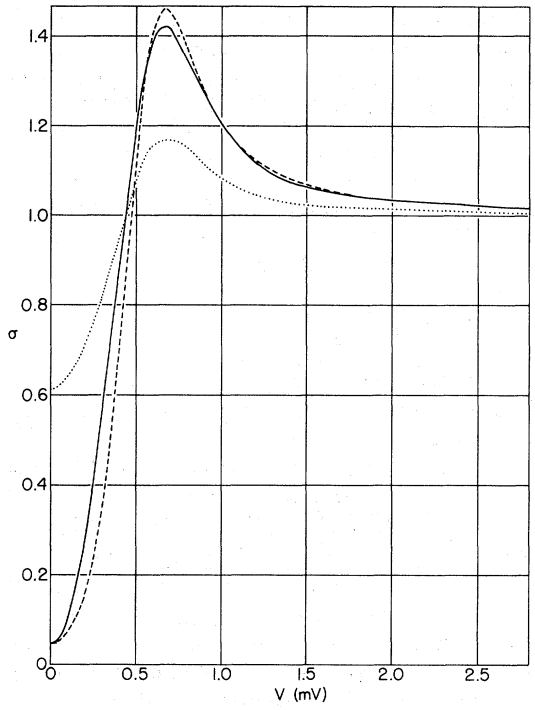


FIG. 1. Normalized conductivity vs bias voltage for representative Al-$AlO_x$-V junction; $T = 1.23$ K. Dotted curve: $\sigma_{exp}$, calculated from uncorrected data. Dashed curve: $\sigma_{BCS}$, calculated for ideal BCS superconductor with energy gap chosen (0.52 mV) to give maximum at same voltage as maximum of $\sigma_{exp}$. Solid curve: corrected $\sigma_{corr} = \sigma_{exp} - \sigma_t$, where $\sigma_t$ is a voltage-independent leakage conductivity, chosen to give agreement of $\sigma_{corr}$ and $\sigma_{BCS}$ at $V=0$. (Here $\sigma_t = 0.60$.)

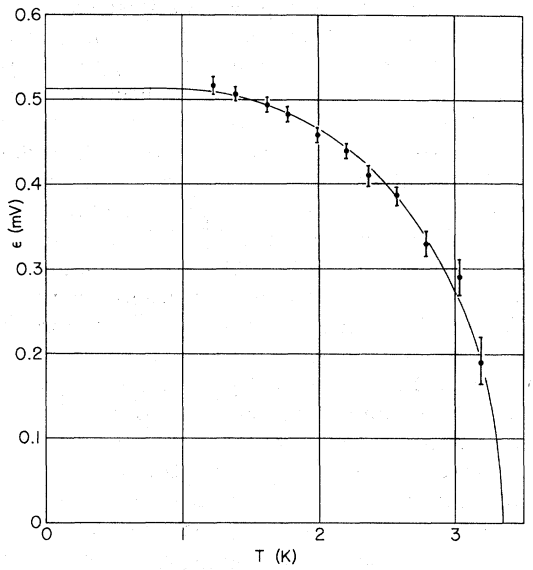


FIG. 2. Energy gap vs temperature. Data points are for same junction as in Fig. 1. Solid curve is fit of BCS $\epsilon(T)$ to data points.

that the superconductive tunneling part of the measured conductivity does in fact correspond to a classic BCS density of states. They also support our assumption that the excess current is at least approximately independent of bias voltage. This would be the case if this current came either from some sort of normal-state "short circuit" through the oxide layer or from a portion of the vanadium film adjacent to the oxide layer which was in the normal state. Result (c) above would tend to support the latter hypothesis; if the vanadium tunneling electrode contains significant areas which do not superconduct, it would not be surprising to find other small areas with transition temperatures lower than that of the main superconducting part of the electrode. As the temperature is lowered, one would then expect a slightly smaller surface area to remain in the normal state, and hence a slightly smaller leakage conductivity.

## IV. RESULTS

As can be seen from Fig. 2, $T_c$ for a given junction can, in most cases, be determined rather less precisely than $\epsilon(0)$. There are two reasons for this. First, for temperatures near $T_c$, the maximum in the measured conductivity is broad and $\epsilon$ is correspondingly more difficult to determine. This allows some latitude in the best $\epsilon(T)$ fit and hence in $T_c$. Second, the vanadium films were not ideally homogeneous. For a given junction, a transition temperature can be determined

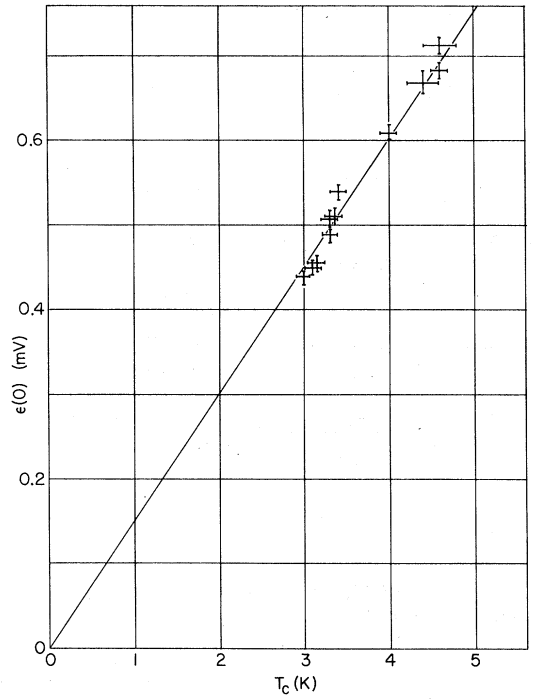


FIG. 3. Zero-temperature energy gap vs critical temperature for vanadium films of varying purity. Solid curve is straight-line fit with $2\epsilon(0)/kT_c = 3.50$.

by extrapolating to its normal-state value the zero-bias tunneling resistance determined at temperatures near the superconducting transition[22]; this $T_c$ tends to be slightly above the $T_c$ determined from the $\epsilon(T)$ curve. The latter method for obtaining $T_c$ represents a weighted average over the various regions of the sample, and appears to be a better (though probably not ideal) one to use.

Figure 3 shows $\epsilon(0)$ vs $T_c$ for a number of films covering the full range of $T_c$'s analyzed. The points shown are in reasonable agreement with the relation $2\epsilon(0)/kT_c = 3.5 \pm 0.1$. Other films gave comparable results.[23] This relation is consistent with the BCS prediction $2\epsilon(0)/kT_c = 3.53$, and also with previous measurements for relatively pure vanadium.[10,24]

Thus $\epsilon(0)$ is seen to remain proportional to $T_c$ even in films whose $T_c$ is reduced by more than 2 K from the bulk value [5.4 K (Ref. 24)]. This result, together with our ability to fit the tunneling characteristics with a BCS superconducting density of states, shows that vanadium containing gaseous impurities remains a classic BCS superconductor. Whatever the mechanism responsible for the sensitivity of $T_c$ in vanadium (and, one assumes, Nb and Ta) to gaseous impurities, it appears not to be magnetic.

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