Electron tunneling spectroscopy of superconducting $A15$ V-Ga alloy films

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The results of a tunneling study of the high-T_c, $A15$ superconductor V_3Ga are presented. The superconducting electron-phonon interaction spectral function $\alpha^2F(\omega)$ is obtained for a set of samples with compositions spanning stoichiometry. These results are of particular interest since V_3Ga is unusual among the high-T_c, $A15$ superconductors in that single-phase material can be formed on either side of stoichiometry. The results demonstrate that increased weight of $\alpha^2F(\omega)$ (or so-called mode softening) occurs at low energies as stoichiometry is approached either from above or below. Concomitantly $\omega_{\log}$ is found to show a minimum at stoichiometry. Interestingly, although T_c is a symmetric function of composition around stoichiometry, $\omega_{\log}$ is asymmetric. Hence, some other factor beyond mode softening is playing a significant factor in the systematics of the high T_c's exhibited by this superconductor as a function of composition.

I. INTRODUCTION

The origins of the high superconducting critical temperatures (T_c) in transition-metal-based $A15$ compounds and alloys are still incompletely understood. One important feature of the transition temperatures of these materials is the universally observed reduction in T_c due to deviations from the ideal 3:1 stoichiometry. One widely held explanation of this phenomenon is that it is a chemical effect in which, for example, changes in alloy composition lead to changes in the mean electron-per-atom ratio which sweeps the Fermi level through the band structure leading to changes in the density of states at the Fermi level $N(O)$.[1] Another widely held explanation is that it is a physical effect in which deviations of alloy composition from stoichiometry lead to increased disorder (e.g., site/antisite disorder) and the possibility of resistive lifetime smearing of structure in the density of states $N(E)$ and/or other physical effects such as localization.[2,3] Some workers[2,4] have claimed an almost universal degradation of T_c with film resistivity regardless of how the resistivity was introduced (e.g., by structural or chemical disorder)—a result which would appear to favor a physically based interpretation. Particular exceptions have been noted, however.[5]

The V-Ga system is nearly unique in that one can study T_c as a function of compositional disorder on both sides of the stoichiometric composition, since its equilibrium $A15$ phase field is believed to run from 20—30 at. % gallium. This situation is only realized in one other high-T_c $A15$ alloy, Nb-Pt, and means that the effects of compositional disorder can be compared on either side of the stoichiometric composition. As a consequence of this one can begin to differentiate between the relative roles of chemical and physical effects influencing the superconductivity.

The results of a more complete study of many of the V-Ga superconducting parameters have been reported earlier, including a discussion of the dependence of T_c with resistivity on both sides of stoichiometry.[6] A nearly symmetric dependence was noted. Here we report the microscopic superconducting parameters [i.e., $\alpha^2F(\omega)$ and μ^*], which have been extracted as a function of alloy composition using electron tunneling spectroscopy. While the data and their analysis are not completely trouble free, they do provide insights into the systematics of the dependence of T_c on composition in the $A15$ class of high-T_c superconductors.

II. SAMPLE PREPARATION

The V-Ga films studied here were produced using the same *e*-beam co-deposition techniques developed at Stanford by Hammond[7] that have been applied previously to many other $A15$ superconductors.[8–11] The films were deposited on sapphire substrates held at 750°C in a phase-spread configuration which makes possible the study of almost the entire $A15$ alloy phase field in a single evaporation. The deposition rate was typically 30 Å/sec to a total thickness of 2000—5000 Å in a background pressure of 1×10^{-7} Torr.

Tunnel junctions were then made on these films using a modified version of a standard oxidized-amorphous-silicon artificial tunnel barrier.[12] The modification was necessary because, for reasons that are not understood, the junction resistances were lower by about a factor of 10 than junctions made on other $A15$ systems studied at Stanford[8–11] which use an otherwise identical artificial barrier. Apparently the properties of the amorphous silicon barrier are not completely independent of the base electrode. While the reason for this difference is not known, it may be related to the superior smoothness observed for these films compared with the other $A15$ superconductors prepared with the same techniques. Even

after small-area junctions were defined by photolithography ($250\times175\ \mu m^2$), the resistances were still too low to obtain the electron-phonon spectrum at high bias voltages with any precision. This problem was overcome by a two-step oxidation process to increase the total oxide thickness. After fabricating the $A15$ film the standard 20-Å amorphous silicon (a-Si) barrier was deposited and then oxidized overnight *in situ* in 2 Torr of pure oxygen. The next day a further thin layer (approximately one monolayer) of silicon was deposited and the junctions oxidized in room air for about another 20 h. Finally, small area junctions were defined by photolithography, and strips of lead (Pb) were thermally evaporated on top as a counter electrode to complete the device. Tunnel junctions made in this way had more convenient conductances (typically 50 ohms/cm^2) and were, in most cases, of comparable quality to our standard a-Si barrier.

III. TUNNELING RESULTS

Tunnel junctions made in this way do display some nonidealities in their current-voltage (I-V) characteristics which were reported elsewhere.[6] In brief, the I-V curve of an ideal superconductor/insulator/superconductor ($S/I/S$) tunnel junction at very low temperatures should show almost no conductance until the bias voltage exceeds the sum of the superconducting energy gaps of the electrodes. There is then an almost discontinuous rise to nearly the full normal-state conductance for higher energies. In reality our tunnel junctions show some (5—10%) excess conductance below the sum of the gaps with an $S/I/N$-like onset at the Pb counter-electrode gap. Such behavior is typical of the $A15$ superconductors. Another nonideality, which is peculiar to these V-Ga samples, is the structure observed at the sum of the superconducting gaps. Below stoichiometry the V-Ga films deposited on sapphire appear to show two distinct gaps merging to a single, quite sharp gap at exactly 25 at.% Ga. At this stoichiometric composition there is a single, albeit broadened, rise in the sum-gap voltage, the breadth of which is about 0.5 mV, somewhat sharper than Nb_3Sn for which it is about 1 mV.[11] Above stoichiometry there appears to be one superconducting gap plus conductance below the gap indicative of a sizable normal component in the film. The weighting of this secondary lower-gap structure at the sum of the superconducting energy gaps was a strong function of the tunnel barrier processing, and was relatively weak (10—20%) with the thicker doubly oxidized barriers studied here. These nonidealities necessitated some care in the analysis of tunneling spectroscopy data from these films. Recent work by Hellman on inhomogeneities in vapor-deposited $A15$ thin films may shed some light on the origin of this multiple gap structure.[13]

In order to extract the microscopic superconducting parameters from our tunneling data, the differential conductance dI/dV was measured for each junction using a standard harmonic detection method.[14] The measurement was made first with the base electrode superconducting and the Pb counter electrode driven normal by a 0.1 T magnetic field, and then with both electrodes normal after the temperature had been stabilized above the T_c of the V-Ga film. These two conductance measurements were then adjusted for the small excess conductance found below the gap in the $S/I/S$ characteristic, and the ratio used as the tunneling density of states in the usual tunneling data inversion program. Representative data for deviations from the BCS reduced density of states are shown in Fig. 1.

The data were analyzed at Iowa State University, utilizing the standard McMillan program, followed by a modified proximity-effect Stage III program. Evidence for a proximity layer at the surface of the V-Ga films includes the familiar small peak in the I-V curve occurring just above the strong rise in the current at the sum of the gap voltages, especially in samples 1, 3, and 5 (see Table I); and also a high-energy phonon feature seen most strongly in the reduced density of states at 57.4 meV of sample 10 (see bottom of Fig. 1). Notice that, while still present, the structure is very much weaker in the 24.9 at.% Ga sample at the top of the figure. The phonon giving rise to this anomalous high-energy structure is unusual and appears to correlate with the optical phonon seen predominantly in Raman spectra of amorphous silicon at 59.5 meV.[15] This feature is not prominent in other tunneling data on the $A15$ superconductors reported by the Stanford group.

The proximity analysis used to treat approximately the effect of a weak proximity layer is the same as used previously (e.g., Wolf[16]), and treats the effect of a weak proximity layer ($\Delta_n=0$) of width d_N, Fermi velocity V_{FN}^*, and quasiparticle scattering length l—the latter incorporated as a fitting parameter d_N/l. The effect of such scattering is primarily to reduce the strength of observed phonon features in the normalized tunneling density of states

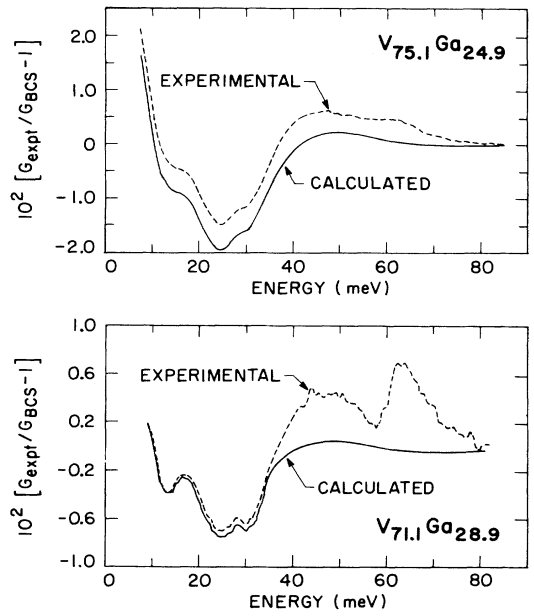

FIG. 1. Plots of experimentally measured (dashed line) and calculated (from output of the inversion program—solid line) deviations from the BCS density of states as a function of energy for two V-Ga films with different gallium compositions.

TABLE I. Sample characteristics.

Sample No.	Composition (at. % Ga)	T_c (K)	Δ_0 (meV)	R[a]	d_N^* (Å)	d/l	λ	μ^*	T_c^{calc} (K)	ω_{log}
1	21.3	9.94	1.49	0.0015	10	0.38	1.19	0.16	9.2	11.6
3	23.1	12.36	2.07	0.0015	10	0.35	1.17	0.089	11.2	10.6
5	24.9		2.55	0.00075	5	0.10	1.56	0.112	13.37	10.1
6	25.8	13.86	2.56	0.00075	50	0.15	1.44	0.072	15.8	11.4
8	27.3	12.09	2.15	0.00677	45	0.15	1.46	0.103	15.9	12.4
10	28.9	10.07	1.76	0.00677	45	0.15	0.81	0.014	13.3	14.8

[a]Obtained from $R = 2Z_N d_N / \hbar V_{FN}^*$, with choice $V_{FN}^* = 2 \times 10^8$, $Z_N = 1$.

$N_T(E)$. This model is incapable of treating an energy-dependent pair potential $\Delta_N(E)$ in the proximity layer, which would lead to structure in the observed $N_T(E)$ at phonon energies characteristic of the proximity layer. As mentioned above, it appears that such an N-layer phonon effect is observed near 57 meV in the 28.9 at. % Ga sample. This sample had the largest deposited thickness of Si due to the particular geometry of our evaporator. Since this phonon feature is very much weaker in the other samples, which received thinner deposits of Si, we believe that the $\Delta_N = 0$ approximation is justified in samples 1—8. Consequently, the region of unusually strong positive $N_T(E)$ ("overshoot") between 40—65 meV in these samples is presumed to arise from a separate mechanism. A similar enhanced $N_T(E)$ has been reported in tunneling studies of Nb-Sn junctions using an entirely different junction fabrication procedure.[17] These authors attribute the effect to the variation of the electronic band structure density of states on the scale of phonon energies. This "overshoot" effect has been discussed from a theoretical viewpoint by Kieselmann and Rietschel.[8] Their arguments are equally applicable to V_3Ga as to Nb_3Sn.

In fitting the $N_T(E)$ data, a uniform degree of agreement between measured and calculated values was sought over the entire experimental range of energies (8—60 meV), and inversions which might produce a closer fit between 8 and 40 meV, with a poorer fit between 40—60 meV (essentially no calculated overshoot), were rejected.

It was found, as in earlier work, that the use of proximity parameters was required to fit the data. The ranges of values for d_N between 5 and 45 Å (corresponding to somewhat arbitrary choices of 2×10^{-8} cm/sec for V_{FN}^* and $Z = 1.0$ for the N layer) tend to increase with Si coverage which increases across the sample set as mentioned above. These values are less than the value 65 Å adopted in earlier work on Nb_3Sn. The d/l values vary somewhat from sample to sample, as seen in Table I, but are generally similar to values used previously.

IV. RESULTS OF THE INVERSION PROGRAM

Figure 2 shows the "best fit" $\alpha^2F(\omega)$ spectra for the six Ga compositions studied. The data is presented in raw form and not "smoothed" as is common in this field. This was done so that problems with the data reduction would not be suppressed. One of these relates to the way the $\alpha^2F(\omega)$ spectrum is estimated at very low energies where the tunneling data is difficult to measure accurately. It is common to approximate the spectrum by ω^2 in this energy range, matching this form onto the measured data at some chosen energy (about 8 meV here). If this procedure is to be justifiable, the slopes should also be equal at the matching energy. This point shows up in the traces as a small "jog" in the curves at 8 meV. The slopes all appear to agree quite well at the matching point except in sample 10. However, the data for this sample is already seriously in doubt because of the strong phonon feature at 57.4 meV in the reduced density of states.

The position of the phonon peaks in the stoichiometric sample agree well with the previous results of Zasadinski *et al.*[19] Unfortunately, an examination of Fig. 2 does not reveal any obvious trends in the spectral peak heights. This may be a consequence of incorrect choices for the proximity layer fitting parameters. However, it is clear from this figure that, as the stoichiometric composition is approached from either side, the lowest phonon peak

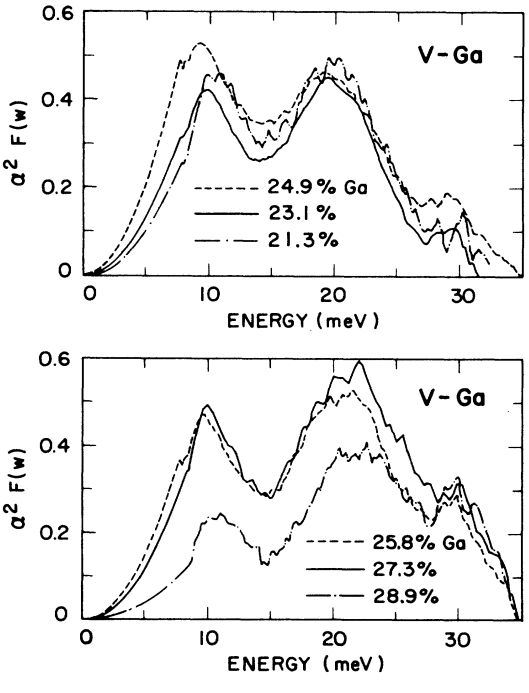

FIG. 2. "Best-fit" electron-phonon coupling spectra from the inversion program as a function of energy for six V-Ga films with different gallium compositions.

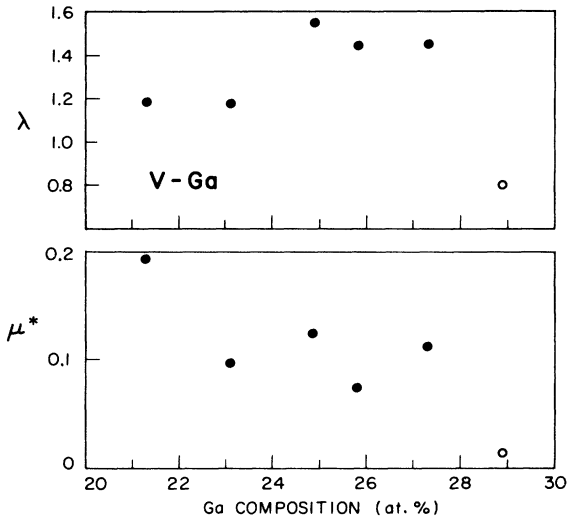

FIG. 3. Calculated values of electron-phonon coupling constant (λ) and Coulomb pseudopotential μ^* as a function of the gallium composition of the films. Note that, as described in the text, the last data point (open symbols) is on a much less firm footing than the others.

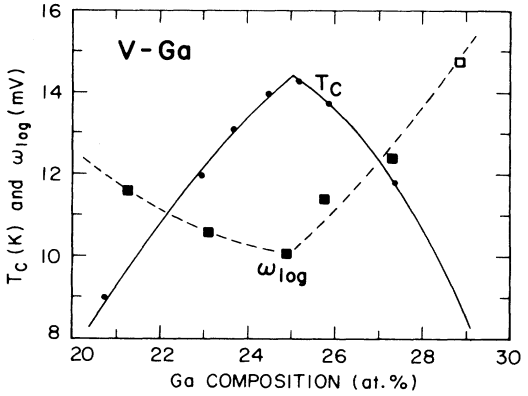

FIG. 4. Plot of experimentally measured T_c and calculated spectral moment of the electron-phonon coupling spectrum $\omega_{\log}$ as a function of the gallium composition of the films. Note that, as described in the text, the last data point (open symbols) is on a much less firm footing than the others.

shifts downward in energy. This phenomenon is known as "mode-softening" and has been seen in many Nb-based $A15$ alloys as stoichiometry is approached.[9–11]

The information contained in the calculated spectral functions can be efficiently parametrized by three quantities: the electron-phonon coupling constant,

$$\lambda=2\int[\alpha^2F(\omega)d\omega/\omega],$$

the renormalized Coulomb pseudopotential μ^*, and the spectral moment $\omega_{\log}$,

$$\omega_{\log}=(2/\lambda)\int\log(\omega)\alpha^2F(\omega)d\omega\ .$$

Calculated values for λ, μ^*, and $\omega_{\log}$ are shown for each sample in Table I, and plotted as a function of a composition in Figs. 3 and 4. Broadly speaking, λ follows the values of the energy gap Δ_0, but μ^* is considerably scattered between 0.013 and 0.194, possibly indicating problems with the data analysis. Because of these difficulties, values for these parameters should only be viewed as semiquantitative.

On the other hand, it has been shown[20] that $\omega_{\log}$ is relatively insensitive to the details of (or problems with) the inversion procedure, and hence should be viewed as a quantitative moment for all except sample 10. Note that in Fig. 4, $\omega_{\log}$ also reflects the mode softening seen in Fig. 2, this moment clearly falling to a minimum at the stoichiometric composition.

V. DISCUSSION

In the standard equations, the critical temperature of a superconductor T_c can be quite well-approximated by a two-parameter expression in terms of λ (the electron-phonon coupling constant), and μ^* (the normalized Coulomb pseudopotential). McMillan[21] has obtained the following expression for λ

$$\lambda=\frac{N_b(0)\langle I^2\rangle}{M\langle\omega^2\rangle}$$

where $N_b(0)$ is the band density of states at the Fermi level, $\langle I^2\rangle$ is the mean electron-phonon matrix element averaged over the Fermi surface, M is the ionic mass, and $\langle\omega^2\rangle$ is the second frequency moment of $\alpha^2F(\omega)$. From this we can see that changes in $\alpha^2F(\omega)$ can enhance T_c in one of two ways. There could either be an increase in $N_b(0)\langle I^2\rangle$ function, or a decrease in $\langle\omega^2\rangle$ (equivalent to a decrease in $\omega_{\log}$), i.e., "mode softening" of the spectrum. Problems with the data inversion prevent us from identifying any consistent trend in the behavior of $N_b(0)\langle I^2\rangle$ (or μ^*) as a function of Ga composition. However, we do see $\omega_{\log}$ falling to a minimum as the stoichiometric composition is approached from the Ga-poor or Ga-rich sides. Hence this must, as we observe, enhance the coupling constant and hence T_c, as one moves towards stoichiometry.

In addition to $\omega_{\log}$, Fig. 4 also shows a plot of T_c of our films as defined by the onset in a gap-opening measurement. Notice that T_c is almost a symmetric function of a composition about V_3Ga, while $\omega_{\log}$ certainly is not—increasing almost twice as fast on the Ga-rich side of stoichiometry. From this one infers that mode softening is not the only factor influencing T_c in the V-Ga system, and there must also be some "asymmetric" contribution either from $N_b(0)$, $\langle I^2\rangle$, or perhaps μ^*. Unfortunately, the problems with the data inversion encountered here prevent us from deciding which of these factors is most important.

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