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Tunneling study of superconducting *A*15 V-Ga alloy films

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We report tunneling studies on evaporated *A*15 V-Ga alloy films as a function of gallium composition. T_c data and anomalies in the tunneling *I-V* characteristics as one deviates from the stoichiometric composition are presented and discussed from the point of view of the superconductivity and materials science of these alloys. We also report observations of Pauli splitting of the superconducting energy gap in high-magnetic-field measurements on these V-Ga tunnel junctions.

I. INTRODUCTION

The *A*15 V-Ga alloy system differs from all the other high-T_c *A*15 compounds [e.g., Nb-Sn and V-Si (Ref. 1)] in two respects. Firstly its superconducting properties can be studied on both the V-rich and Ga-rich sides of stoichiometry as it is believed to have an equilibrium *A*15 phase field from 20—30 at. % Ga. This situation is only realized in one other high-T_c *A*15 alloy Nb-Pt. Secondly V-Ga is strongly Pauli limited in the presence of large magnetic fields which makes possible the observation of Pauli splitting of the superconducting energy gap in tunneling measurements and hence a direct observation of the Cooper pair spin state in this important high-field superconductor.

In addition the V-Ga system would seem to display an extreme form of a behavior seen in other *A*15 systems [e.g., Nb-Sn (Ref. 2)] in which off-stoichiometric alloys within the equilibrium phase field contain material with a range of T_c's. While an understanding of this phenomenon is still wanting, the tunneling data reported here provide new insights into its character and possible origins.

II. SAMPLE PREPARATION AND PROPERTIES

The V-Ga films studied here were produced using the same *e*-beam codeposition techniques developed at Stanford by Hammond[3] that have been applied previously to many other *A*15 superconductors.[4–6] The films were deposited primarily on sapphire substrates held at 600—800 °C in a phase-spread configuration which makes possible the study of almost the entire *A*15 alloy phase field in a single evaporation. Some evaporations on amorphous Si_3N_4 substrates were also made as described below. The deposition rate was typically 30 Å/sec to a total thickness of 2000—5000 Å. Tunnel junctions were then made on these films using a modified version (see Sec. III) of a standard oxidized amorphous silicon artificial tunnel barrier[7] and a Pb counter electrode.

All the films[8] showed a single superconducting T_c when measured inductively (Fig. 1). This peaked at about 14.3 K for the stoichiometric composition compared with 15.9 K for the best reported bulk annealed V_3Ga.[9] The width of the inductive transition was typically about 1 K and reflected the spread in composition across each sample. Other measures of the transition temperature are discussed below.

The residual resistance ratio for the films was a strongly peaked function of composition rising to about 4 at stoichiometry, again very comparable with results for bulk V_3Ga.[10] Figure 2 shows a plot of T_c against the film resistivity ρ as measured by the van der Pauw technique. Note the strong symmetry with respect to the Ga-rich and Ga-poor sides of stoichiometry. A quantitative analysis of this data shows that the decrease in T_c is proportional to ρ^2. The possible significance of these results will be discussed in Sec. IV.

III. TUNNELING RESULTS

A. Zero-field data

Figure 3 shows a typical series of tunnel junction characteristics at 1.5 K for films deposited on sapphire substrates, as a function of nominal composition. For reasons that are not really understood, the resistances of

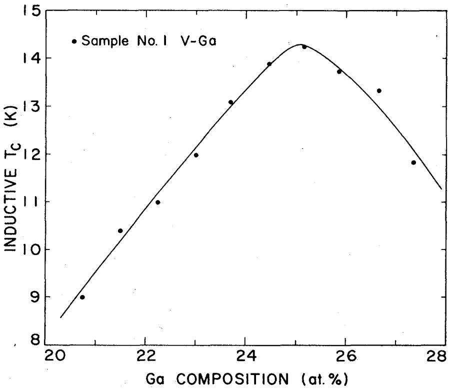

FIG. 1. Inductively measured critical temperature for a series of films deposited on sapphire substrates.

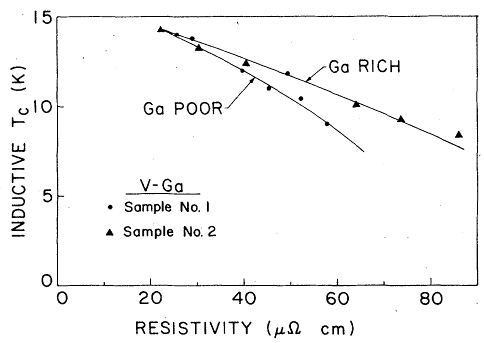

FIG. 2. Inductive critical temperature plotted against film resistivity for samples with various gallium compositions.

the junctions were reproducibly lower by about a factor of 10 than junctions made on other *A*15 systems studied at Stanford[4–6,11] 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 V-Ga films compared with the other *A*15 superconductors prepared with the same techniques. Even after small area junctions were defined by photolithography (250×175 μm^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 *A*15 film the standard 20-Å amorphous silicon 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.

Tunnel junctions made in this way had more convenient conductances (typically 50 mhos/cm^2) and were of comparable quality to our standard *a*-Si barrier. They also showed most of the nonidealities seen in the other *A*15 systems that have been studied (e.g., Ref. 11), for example, a small rise in the conductance at the lead gap (1.35 mV) of typically less than 5% of the total conductance. Another striking feature *not* seen in the other *A*15 systems is the structure 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 (see Fig. 4). Note that the dashed line on the 24.5 at. % Ga sample indicates that the tunneling *I*-*V* showed a low-voltage tail to the rise at the gap, but no resolvable second gap. On stoichiometry there is a single, albeit broadened rise at the gap voltage. The breadth of this rise at the sum of the gaps for stoichiometric V_3Ga 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. The relative weighting of the structures seen in the *I*-*V* curves was a strong function of the tunnel barrier processing. In all cases the lower gap structure was weaker when the thicker doubly oxidized barrier was used as opposed to the thinner singly oxidized one.

To try to establish the origins of this structure in the tunneling data the growth morphology of the films was studied. Figure 5(a) shows x-ray diffractometer data for a typical sample. For all Ga concentrations within the equilibrium phase field two distinct *A*15 lines, (200) and (210), were observed plus their next higher-order lines indicating a double-textured film growth. Pole plots generated with the same films in which the sample is rotated in the ϕ and χ directions while the diffractometer is held at a fixed 2θ angle indicate that the two texture directions are tilted with respect to one another by a few degrees. Preferred growth orientations are seen in other *A*15 films[11,12] but there is usually only one of them, e.g., (200) for Nb-Sn and (210) for V-Si. Suspecting that the sap-

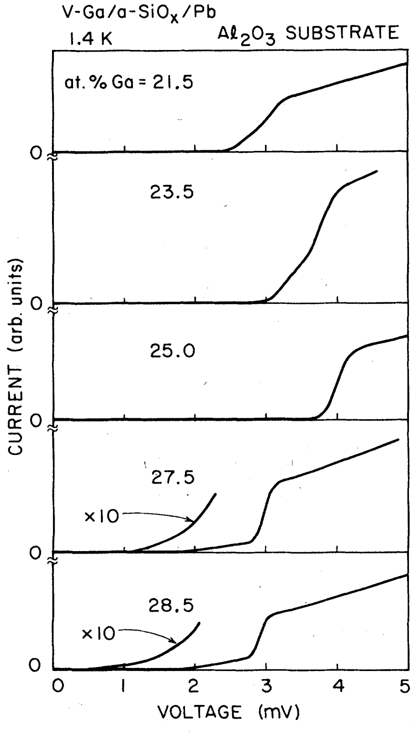

FIG. 3. Tunneling *I*-*V* characteristics as a function of gallium composition for films deposited on sapphire substrates.

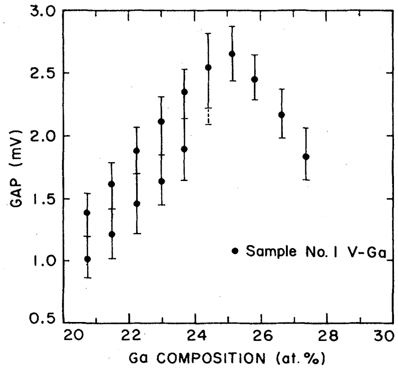

FIG. 4. Superconducting gap or gaps inferred from the tunneling characteristics as a function of gallium composition for films deposited on sapphire substrates.

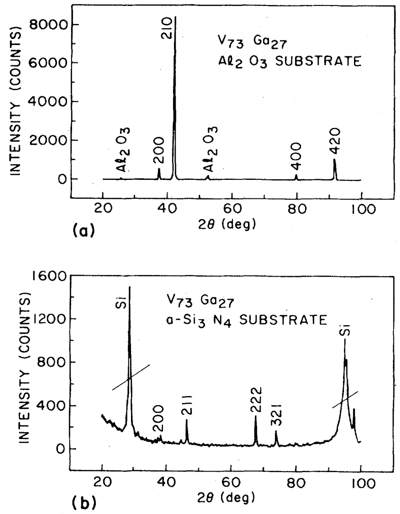

FIG. 5. X-ray diffractometer traces for films deposited (a) on single-crystal sapphire substrates, (b) on a-Si_3N_4 on Si substrates. The indicated lines are for the $A15$ structure.

phire substrate was having an influence on the growth morphology, films were made under identical conditions on α-Si_3N_4 substrates. The resulting films had lower residual resistance ratios (only rising to about 3 at stoichiometry) but almost the full value for the superconducting gap. More importantly the rise at the sum of the gaps was very sharp (0.4 mV) for all Ga concentrations. Ga-poor films no longer showed the second gap, and Ga-rich samples showed a much reduced normal component until the phase boundary was approached at 30 at. % Ga (see Fig. 6). Figure 5(b) is an x-ray diffractometer scan of one of these films. It shows no dominant texturing but weak lines corresponding to (200), (211), (222), and (321) crystal planes. The intensities of these lines were not consistent with having a random distribution of grain orientations, in fact certain normally strong lines, e.g., (210), were absent altogether. In the light of these data the existence of two gaps and two texture directions in films on the sapphire substrates suggests that they are correlated. However, it should be noted that such a correlation has not been proved directly.

Two possible explanations of these data, energy-gap anisotropy and the existence of two types of material with different T_c's, have been considered and evaluated. On the basis of the temperature dependence of the gap we believe we have distinguished between the two.

At first glance the facts would appear to point towards the existence of energy-gap anisotropy[13] in the well-ordered V-Ga films. That is, different crystal directions have different values for the superconducting energy gap which all fall to zero at the same critical temperature. This anisotropy is washed out by disorder, which might explain the behavior of the films made on amorphous substrates where only one gap was observed. These data were originally interpreted in terms of energy-gap anisotropy (see Ref. 14).

Alternatively the material may be composed of two distinct components with different T_c's. This could arise in various ways. $A15$ V-Ga films deposited on single-crystal sapphires may have a natural tendency to grow with two different texture directions simultaneously. Grains growing with different orientations may have different degrees of ordering, hence different T_c's. On the other hand, the V-Ga films may be separating into two distinct species with different Ga compositions as a consequence of modifications of the free energy at the surface or as a result of the nonequilibrium nature of vapor deposition film growth. The bulk diffusion rate in V-Ga alloys at typical substrate temperatures is extremely low, hence normally metastable material which may form at the growth face would tend to get frozen in as additional material is deposited. The existence of two T_c types need not show up in an inductive T_c measurement as the low-T_c material could be shielded by the high-T_c material.

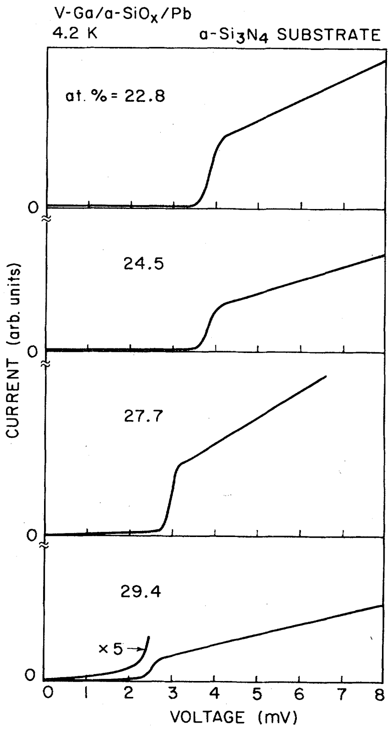

FIG. 6. Tunneling I-V characteristics as a function of gallium composition for films deposited on a-Si_3N_4 substrates.

If one could measure the energy gap of the films as a function of temperature it would be trivial to distinguish between these two possibilities. If the alloys were showing anisotropy the gaps would both vanish smoothly at one T_c, while if there were two T_c types the gaps would vanish at two visibly different temperatures. An easier experiment to do is a so-called "gap-opening" measurement, i.e., a measurement of the zero-bias conductance as one sweeps temperature through the superconducting transition.[11] This indirectly yields information about the energy-gap temperature dependence. Figure 7 shows gap-opening data for a range of V-Ga films all the way across the phase field. As was observed in the Nb-Sn system[11] the gap opening for stoichiometric V_3Ga is rather closely fit by the BCS theory indicative of homogeneous material with a single T_c. Away from stoichiometry the

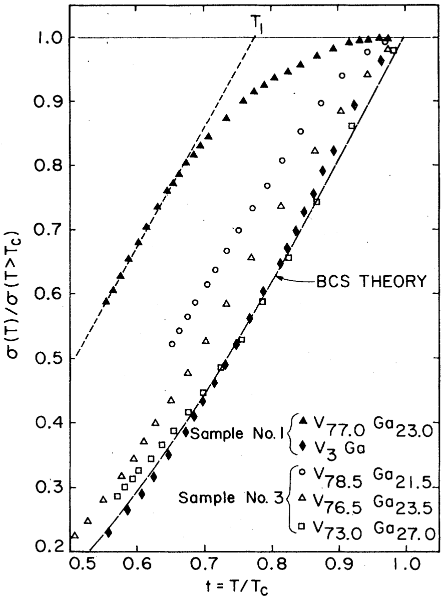

FIG. 7. Temperature dependence of the zero-bias conductance (gap opening) for tunnel junctions fabricated on films of differing gallium concentrations. Solid symbols have the standard tunnel barrier, open symbols have the double one.

behavior is nonideal showing pronounced rounding for temperatures close to T_c, a region where theory predicts a linear T dependence for the zero-bias conductance.[15] Like Nb-Sn this was interpreted as evidence for the existence of *A*15 material with a spread in T_c's, making gap anisotropy appear to be a rather unlikely candidate. Note that the deviation from theory is much greater for the sample with the thinner tunnel barrier (solid triangles) in which the second gap feature is much stronger. (Open symbols are films with the thicker doubly oxidized barrier.) As we shall show presently this does not necessarily imply a wider distribution of T_c's.

We performed a more sophisticated analysis of the data by adopting a model which assumes this rounding is dominated by just two T_c types. The contributions of the two species to the gap-opening data are weighted by their relative contributions to the measured tunneling current (i.e., according to the relative heights of their current rises at the gap in the I-V characteristics). Note that this is not necessarily their relative fraction of the total area of the film. Armed with this information and a linear extrapolation of the gap-opening data at temperatures below where the rounding is seen one can estimate the T_c of the low-gap material (see Appendix). Figure 8 is a plot of the transition temperature of both the high-gap material ($T_c^{(h)}$) and the low-gap material ($T_c^{(l)}$) evaluated in this way versus composition. This plot is satisfying in as much as data from films with both the thinner and thicker tunnel barriers which showed such markedly different gap-opening behavior come closer to falling on the same curves. Also the separation between these two T_c's is consistent with what one would expect from the total breadth of the rise at the gap voltage in the I-V characteristics (insert Fig. 8). The line drawn in the inset has the slope predicted by the BCS weak-coupling relationship.

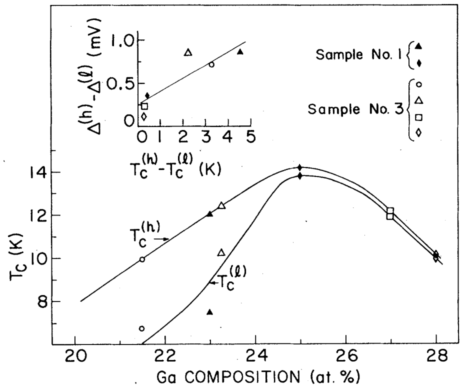

FIG. 8. Critical temperature of high-gap ($T_c^{(h)}$) and low-gap ($T_c^{(l)}$) material as inferred from gap-opening data as a function of composition. Inset: Breadth of rise at the gap voltage observed in the tunneling characteristics plotted against separation of T_c's as inferred from gap-opening data.

The possible origins of two types of material with different T_c's will be discussed in Sec. IV.

B. High-field data

As was mentioned previously V-Ga is a Pauli-limited system. This means that at high fields the effect of a magnetic field on the electron spins becomes an important pair breaker. As a consequence Pauli splitting[16] of the superconducting gap at 1.5 K was observed in a 100-kOe field parallel to the films (Fig. 9). Unfortunately, due to the relatively broad rise at the gap observed in our tunnel junctions even in zero field and the additional broadening due to orbital pair breaking as the applied field is increased, the splitting of the gap was substantially washed out. This makes simple estimates of the splitting ambiguous. However, using more sophisticated data-analysis procedures based on Fourier transform techniques[17] it is

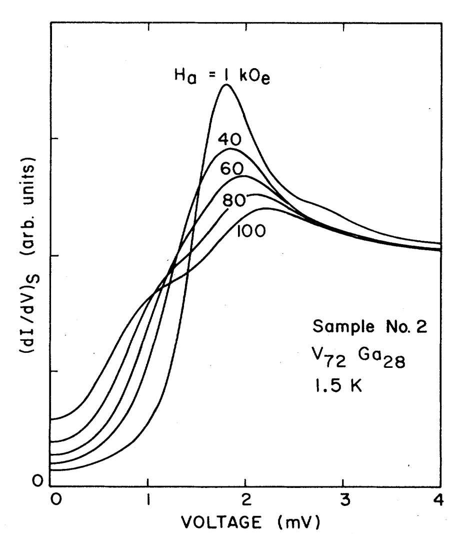

FIG. 9. Tunneling conductance for one V-Ga junction as the magnetic field is increased to 100 kOe.

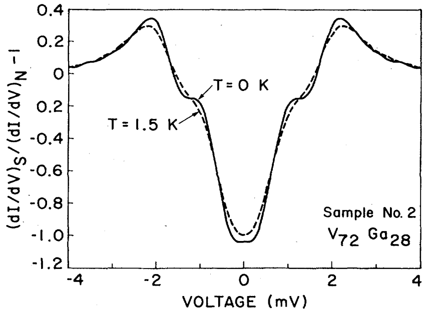

FIG. 10. Dashed line is original tunneling data in 100-kOe magnetic field. Solid line is same data with the temperature broadening removed by the Fourier-transform technique.

possible to extract both the gap splitting, the unsplit conductance curve (in any field), and a deconvolution of the thermal-broadening effects. An example of the results obtained with this technique for one of our junctions in a 100-kOe field is shown in Fig. 10. The dashed line is the original data, and the solid line is the same data with the thermal broadening deconvolved.

The split conductance curve for the V_3Ga tunnel junction in a 100-kOe field was compared with theoretically generated curves with a range of solid-state parameters. From this comparison it was estimated that $\lambda_{so} < 0.3$. Also $dH_{c2}/dT(T_c)$ was found to be about 40 kOe/K in agreement with that observed directly.

For the sample shown in Fig. 10 the gap splitting is found to be 1.08 mV at 100 kOe consistent with the result that the gap Δ splits to $\Delta \pm \mu_B H$ with no many-body corrections. These results agree with recent theoretical calculations based on weak-coupling theory which predicts that the gap splits by $2\mu_B H/(1+G^0)$ (where G^0 is a Fermi-liquid correction) only in the gapless region near the second-order phase boundary H_{c2}.[18] At the temperatures used here H_{c2} is about 220 kOe, so we are less than half the way towards it. None the less, these experiments show for the first time that quantitative tunneling studies of the spin splitting in V-Ga are possible.

IV. DISCUSSION

A. Film growth

We saw in Sec. III A that the growth of *A*15 V-Ga alloy films is rather sensitive to the substrate upon which they are deposited. Films on single-crystal sapphires are double textured and the data are suggestive that in off-stoichiometric material each texture direction is associated with material of a different T_c. One might argue, however, that since we inferred these two T_c's from tunneling measurements, which only probe material at the top of the film, that this could simply be a surface effect and not representative of the bulk of the material. It has recently been demonstrated,[19] for example, that when *A*15 superconductors are oxidized the composition just below the oxide surface can differ greatly from the bulk. The two texture directions may differ in their surface compositions due to different rates of oxidation at different crystal faces. Preliminary x-ray photoelectron spectroscopy (XPS) measurements carried out on some of our films by Talvacchio[20] suggest that this is not the case for our films. The data available indicate that there is no oxidation of the *A*15 V-Ga surface when covered with our standard 25-Å *a*-Si barrier; in fact there is even a thin layer (10–15 Å) of unoxidized silicon present. Moreover the measured average Ga composition at the surface agreed well with the bulk determination (i.e., microprobe.)

It would seem, then, that we are dealing with an effect that permeates the entire film, and not just the surface. As was mentioned previously, if the two texture directions on sapphire substrates have different T_c's it must either be because they have different degrees of disorder or because they have differing Ga compositions. If there are two different compositions present even though still within the bulk equilibrium phase field, this is probably an effect arising at the growth surface which becomes frozen in when more material is added on top on account of the low bulk diffusion rate in the *A*15 materials.

The origins of the inhomogeneities observed in V-Ga and other *A*15 superconductors remains a subject of considerable interest.[2] Clearly, however, V-Ga provides an example of distinctive behavior that must be accounted for in any comprehensive theory of the film growth of these materials. Of particular interest is the question: What is so special about the stoichiometric composition that it shows material with a single T_c when off-stoichiometric alloys do not, even though it too shows two texture directions?

B. Dependence of T_c on resistivity

As shown in Fig. 2, the inductive T_c is nearly a symmetric function of the resistivity above and below stoichiometry. This is a striking result, but in light of the inhomogeneities found in these films we must ask if it is meaningful. There is no clear-cut answer to this question. However, despite the inhomogeneities, one might expect the inductive T_c to be a unique function of resistivity since high-T_c material will have a lower resistivity and hence will dominate the van der Pauw measurement. Note that, in general, T_c (inductive)$=T_c^{(h)}$. Universal behavior of T_c as a function of resistivity regardless of how the latter was introduced, has been observed in other *A*15 compounds,[21] and the interpretation of this effect is controversial, breaking down into three main schools of thought. It may be a chemical effect in which the Fermi level is shifted through a sharply peaked density of states by changes in the mean-electron–per–atom ratio. This point of view has been argued recently for V-Ga ternary alloys.[22] Alternatively the density of states at the Fermi level may be reduced as a consequence of disorder smearing of a sharp peak in the band density of states (see Ref. 23). Finally, localization-induced reductions in the screening of the Coulomb repulsion leading to an increased μ^* and a reduction in T_c have been proposed recently by Anderson, Muttalib, and Ramakrishnan.[24]

Although band-structure calculations for V_3Ga show a sharp peak located near the Fermi level, the behavior of these films with their nearly symmetric dependence of T_c on resistivity above and below stoichiometry, is unlikely to be solely a chemical effect. In order that this be true the density of states would have be fortuitously symmetric about the stoichiometric Fermi energy. This explanation also ignores the effect of resistive disorder smearing on peaks in the density of states.

However, if a peak does exist near the Fermi level, the effect of smearing by elastic scattering could be causing the observed symmetric T_c reduction. Moreover, in determining T_c, the electron-phonon coupling parameter λ tends to average the density of states over the Debye energy (Θ_D) about the Fermi energy. For all V-Ga films studied here resistive broadening is estimated to be on the order of or greater than Θ_D, thus presenting a plausible mechanism for degradation of T_c.

The fact that for resistivities less than 70 $\mu\Omega$ cm the decrease in T_c is proportional to ρ^2 is consistent with the functional form of the T_c reduction predicted from localization theory. However, this seems a rather unlikely mechanism given how small the resistivities are. Moreover, at least in one other A15 alloy Nb-Sn it has been shown that μ^* is essentially constant as T_c falls in Sn-poor samples.[25]

V. CONCLUSION

The structure of V-Ga alloy films is found to be very sensitive to the substrate on which they are grown. Films deposited on single-crystal sapphires are found to be double textured, and the data are suggestive that in off-stoichiometric alloys each texture direction is associated with material of a different T_c. The observed T_c reduction, as deviations are made from the stoichiometric composition, is found to be almost a universal function of resistivity on both sides of stoichiometry. Moreover, this reduction appears most consistent with the lowering of a sharp peak in the electronic density of states by resistive disorder smearing. Pauli splitting of the superconducting gap has been observed in parallel magnetic fields up to 100 kOe for the first time, with the amount of splitting consistent with recent theory.

Measurement of the electron-phonon spectrum $\alpha^2F(\omega)$ as a function of Ga concentration across the entire A15 phase field is in progress and will be published at a later date. It will be interesting to see if the mode-softening mechanism for T_c enhancement, which was observed for Nb-Sn (Ref. 26) as the stoichiometric composition was approached, is operating in this system. In addition, if softening is seen it will be interesting to see whether the phonon modes harden again on the Ga-rich side of stoichiometry.

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APPENDIX

Close to the transition temperatures the gap-opening data is modeled as two parallel conductance paths which individually vary linearly with temperature, i.e., $T < T_c^{(l)}$:

$$\bar{\sigma} = \frac{\sigma(T)}{\sigma(T > T_c^{(h)})} = \alpha\left[\frac{2T}{T_c^{(l)}} - 1\right] + (1-\alpha)\left[\frac{2T}{T_c^{(h)}} - 1\right] .$$

Here α is the fraction of conductance through the lower T_c channel and can be determined from the tunneling I-V at low temperatures. If we make a linear extrapolation to $\bar{\sigma} = 1$, we obtain a characteristic temperature $T(\bar{\sigma}=1) = T_1$. Simple algebra yields

$$T_c^{(l)} = \frac{\alpha T_1}{1-(1-\alpha)(T_1/T_c^{(h)})} .$$

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