Tunneling $\alpha^2F(\omega)$ as a function of composition in $A15$ V-Si

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High-quality $A15$ V-Si/SiO_x/Pb tunnel junctions on electron-beam codeposited V_3Si have been fabricated. $2\Delta/k_BT_c$ remains near the weak-coupled Bardeen-Cooper-Schrieffer limit as stoichiometry is approached. These junctions have satisfactory characteristics for taking derivative measurements. The data were reduced with use of the modified McMillan-Rowell proximity-gap inversion analysis developed by Arnold and Wolf to generate $\alpha^2F(\omega)$ and related microscopic parameters. As T_c and the gap increase, there is no evidence of any qualitative change in the phonon spectra (such as phonon mode softening seen in other $A15$ compounds). Thus while in other $A15$ compounds such as Nb_3Ge, Nb_3Al, and Nb_3Sn there is evidence that mode softening is a major factor in the high transition temperatures, in V_3Si the high density of states at the Fermi surface (and not mode softening) is probably primarily responsible for the high T_c.

INTRODUCTION

Since the discovery of high-T_c superconductivity in V_3Si (17 K) by Hardy and Hulm[1] in 1953, the record T_c has remained in the $A15$ family (now with Nb_3Ge, $T_c=23$ K). What leads to the high T_c in the $A15$ compounds is an interesting question. As a result of early heat-capacity measurements on V_3Si (by Kunzler *et al.*[2]) and Nb_3Sn (by Vieland and Wicklund[3]), which showed high values for γ, the coefficient for electronic specific heat (62.8 and 52.4 mJ/mole K, respectively) and thus a high $N(0)$, the density of states at the Fermi surface, it was believed that a peak in the density of states at the Fermi surface was responsible for the high T_c's in the $A15$ compounds. Subsequent heat-capacity data began to confuse the picture. Nb_3Al (by Cort *et al.*[4]) and Nb_3Ge (by Stewart *et al.*[5] and Kihlstrom *et al.*[6]) showed only moderate values for γ (36 mJ/mole K for Nb_3Al, 30.3—34.5 mJ/mole K for Nb_3Ge). Thus these higher-T_c materials showed lower values for $N(0)$. Furthermore, more recent heat-capacity data taken by Stewart *et al.*[7] on Nb_3Sn in an applied magnetic field (used to partially suppress the transition to better determine γ) gave a significantly lower value for $\gamma=35$ mJ/mole K, although this number also is controversial. Recent heat-capacity measurements on V_3Si by Junod and Muller[8] somewhat lowered the value of γ to 52.8 mJ/mole K but it still remains high. The same group revised upward the γ value for Nb_3Al (Ref. 9) to 44 mJ/mole K. The net result is that while V_3Si remains a high density-of-states material, many of the other high-T_c $A15$ compounds show significantly lower values for $N(0)$, thus calling into question the idea that $N(0)$ is the universal cause for high T_c in the $A15$ compounds.

Tunneling is the most direct probe of superconductivity. Because of advances in the formation of insulating silicon barriers (by Rudman and Beasley[10]) progress has been made in making tunnel junctions of sufficient quality to produce $\alpha^2F(\omega)$, the electron-phonon spectral function, in several of the $A15$ compounds. The results from Nb_3Al (by Kwo and Geballe[11]), Nb_3Sn (by Rudman and Beasley[12]), and Nb_3Ge (by Kihlstrom *et al.*[6,13]) show the presence of phonon mode softening (a movement of the lowest-energy phonon peak to lower energies as the B element concentration increases toward stoichiometry (A_3B). This results in increases in both λ, the electron-phonon coupling constant, and T_c. Thus a second explanation was proposed, that rather than a peak in the density of states at the Fermi surface, it is mode softening that causes the high T_c for the $A15$ compounds. But this then raises the question of V_3Si. While the other $A15$ compounds mentioned arguably have only moderate values for the density of states, V_3Si certainly does have a high value for $N(0)$ (as does V_3Ga). Thus one would not think it would need mode softening to produce its high T_c. Whether there is mode softening in V_3Si was the prime question of this work.

A second issue is addressed. Conflicting results were obtained for the shape of $\alpha^2F(\omega)$ for V_3Si by McKnight

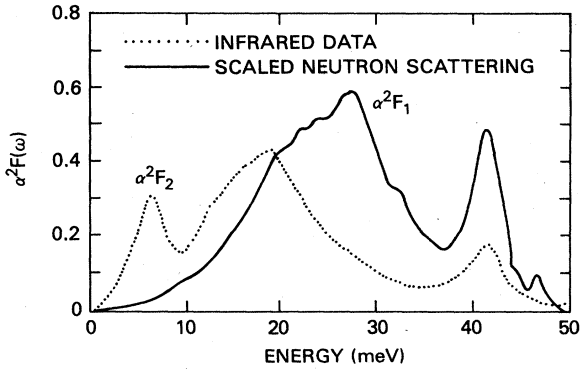

FIG. 1. Model $\alpha^2F(\omega)$ spectra for V_3Si. The solid curve (α^2F_1) has λ equal to 1 and is proportional (by a constant factor) to the phonon density of states $G(\Omega)$ in V_3Si measured by Schweiss *et al.* (Ref. 16). Dotted curve (α^2F_2) has $\lambda=1.29$ and is equal to α^2Ftr given in Ref. 14. This figure is from Ref. 15 by Mitrovic and Carbotte.

et al.[14] (using far-infrared absorption) and Mitrović and Carbotte[15] (who scaled the phonon density of states obtained by Schweiss *et al.*[16] from neutron scattering). The discrepancy is shown in Fig. 1. Mitrović and Carbotte found, when they calculated thermodynamic properties using the scaled phonon spectra versus the $\alpha^2F(\omega)$ from far-infrared absorption measurements, better agreement was obtained with the scaled phonon spectra. With tunneling we can measure $\alpha^2F(\omega)$ more directly, thus we can hopefully resolve this question as well.

EXPERIMENTAL DETAILS

These samples were prepared at Stanford University by electron beam coevaporation (see Hammond[17]). Substrate temperature was 850 °C, deposition rate 16.7 Å/s, and background pressure was 2×10^{-7} Torr. Sample thicknesses of both 700 and 2500 Å were prepared (both thicknesses gave excellent tunneling characteristics). The samples while still under vacuum were cooled to 100 °C and the barrier of 25—30 Å silicon (as per Ref. 10) was deposited. The samples were then removed from vacuum, and the silicon barrier was allowed to oxidize in air for 29 h. Then the junction area was defined by a dielectric (photoresist) and a Pb counterelectrode was deposited.

The current-voltage (I-V) curves for the three junctions studied are shown in Fig. 2. Leakage current at zero bias was negligible (of order 0.2%). Excess conductance below the sum gap was typically ~5%. The dV/dI data from the lowest-gap sample showed evidence of a slight proximity knee (which is difficult to see in the I-V). Later in the Arnold-Wolf proximity analysis, this resulted in larger values for the proximity parameters than in the other junctions. The differential conductance for these samples was measured in the superconducting state with the Pb electrode driven normal by an applied magnetic field (0.1 T), and then with the temperature elevated above T_c so that both electrodes were normal. The reduced tunneling density of states was then input into the modified McMillan-Rowell gap inversion analysis program (originally developed by McMillan and Rowell[18] and modified by Arnold and Wolf[19–21]).

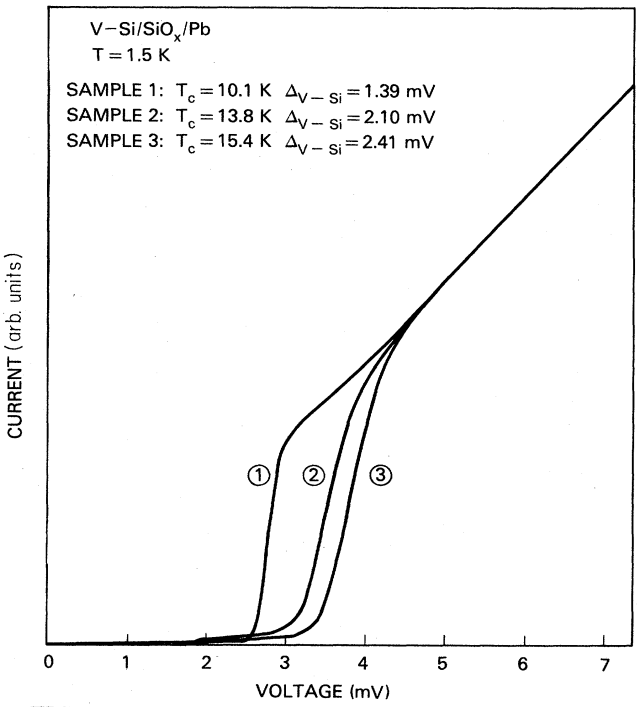

FIG. 2. Current-voltage characteristics for the three V-Si samples measured in this study.

EXPERIMENTAL RESULTS

The ratio $2\Delta/k_BT_c$, a measure of the coupling strength, for these samples is shown in Table I. Unlike Nb-Ge, Nb-Al, or Nb-Sn (which become strong coupled),

TABLE I. Physical parameters for various samples.

Parameter	Sample 1	Sample 2	Sample 3
at. % Si	18.2	22.0	21.7
Thickness (Å)	2500	700	2500
$\Delta_{V\text{-}Si}$	1.39	2.10	2.41
T_c (gap open)	10.1	13.8	15.4
$2\Delta/k_BT_c$	3.2	3.5	3.6
L (excess conductance below sum gap in % of the above-gap conductance)	6.0%	6.0%	4.5%
Proximity parameter			
R	0.013	0.0135	0.015
d/L	0.220	0.125	0.150
λ	0.76±0.15	0.91±.07	0.89±.06
μ^*	0.14±0.07	0.14±.06	0.11±.04
$\langle\omega\rangle$	21.1±1.7	20.9±1.7	21.5±0.6
ω_{log}	19.2±1.6	19.0±1.5	19.9±0.6
$\langle\omega^2\rangle$	512 ±30	507 ±40	520 ±15
T_c (McMillan)	7.6	11.3	13.6
T_c (Allen and Dynes)	7.1	10.7	13.2

$2\Delta/k_BT_c$ remains relatively constant at about the weak-coupled BCS limit of 3.5 as stoichiometry is approached. The gap is determined by the minimum of the derivative (dV/dI) through the gap region (after subtracting off the Pb gap). The T_c's quoted are determined by measuring dV/dI at zero bias as a function of temperature to see where the gap opens up. Thus the T_c is measured on the same material that is being tunneled into. This constant value for coupling strength is in contrast to the results for Nb_3Al,[11] Nb_3Sn,[12] and Nb_3Ge,[6,13] all of which showed a distinct change from weak coupling to strong coupling as stoichiometry was approached.

Figure 3 shows the $\alpha^2F(\omega)$ traces for the three samples. The first thing to note is there is no evidence of mode softening in these samples. While there is some overall enhancement, there is no movement of the lowest-energy phonon peak as T_c and Si concentration increase. Correspondingly there is only a small change in the value for λ, the electron-phonon coupling constant from 0.76 to 0.91. This is in contrast to the results of Nb_3Al,[11] Nb_3Sn,[12] and Nb_3Ge,[13] where mode softening was clearly present and the λ values increased from around 1.0 to ~ 1.7. The parameters from the $\alpha^2F(\omega)$ measurements are given in Table I.

Comparing these results with those of McKnight *et al.*[14] and Mitrović[15] (see Fig. 1), there was no sign of the low-energy phonon peak at 7 meV as seen by McKnight *et al.* Some caution is necessary, however, because this is close enough to the gap that the data is difficult to obtain accurately (since dV/dI is changing rapidly). In fact, in the $\alpha^2F(\omega)$ analysis we used a parabolic fit through this region. Nonetheless, the second derivative d^2V/dI^2, which is used to determine peak positions and the cutoff value, showed no evidence of a peak in that region (although this also is changing rapidly and a small peak could be washed out, we would expect to see that one is the size shown in McKnight *et al.*). On the other hand, the main peak is at about 21 meV, more in agreement with McKnight *et al.* (although a shoulder at about 27 meV may correspond to the main peak in Schweiss *et al.*[16]).

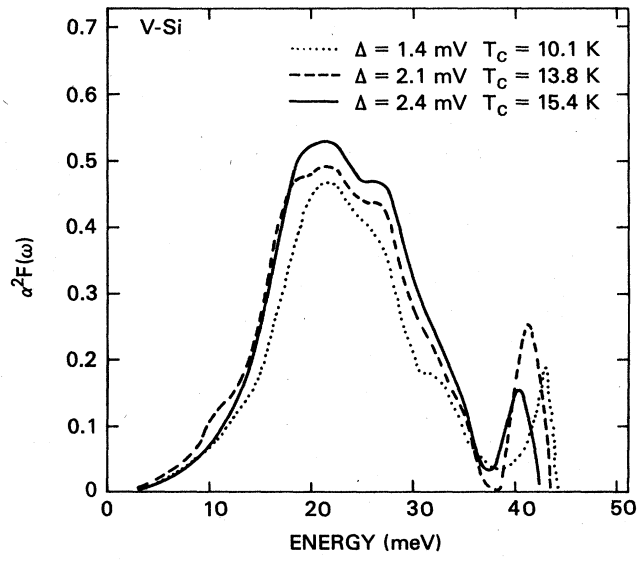

FIG. 3. Electron-phonon spectral function $\alpha^2F(\omega)$ for three V-Si samples.

Recently Mitrović *et al.*[22–24] have discussed the possible effects of a varying density of states near the Fermi level on tunneling results. The conventional analysis (which is used in this paper) assumes a constant $N(E)$. This has seemed reasonable since inhomogeneity (which is always present to some extent) will smear out the density of states and wipe out structure that would be in a pure material. On the other hand, it is difficult to know quantitatively whether this is entirely true. In particular, a test proposed by Mitrović and Perkowitz[24] to look at $\alpha^2F(\omega)$ at energies above the cutoff was not possible because of the difficulty in having the program converge when the extra energies were included. Thus the question raised by Mitrović *et al.* will have to be answered separately from this work.

CONCLUSIONS

The main result seen from this work is the absence of mode softening in V_3Si. In one sense this is not unexpected in that since V_3Si is a high density-of-states material, its high T_c can be explained by that alone, rather than needing mode softening as an explanation. This is in contrast to Nb_3Ge which has a significantly lower $N(0)$ yet a higher T_c. Presumably if V_3Si showed mode softening as well, it would have a significantly higher T_c than Nb_3Ge. In another sense this is surprising in that it leads to the conclusion that there are two different mechanisms at work in the $A15$ compounds. It may be that vanadium-based $A15$ compounds rely on a high density of states to produce their high T_c's while niobium-based compounds, with only a moderate density of states, depend on mode softening to produce their high T_c's. Otherwise the crucial element may be that the onset of a phase boundary in the metastable $A15$ compounds (i.e., Nb_3Al and Nb_3Ge) results in mode softening, thus the equilibrium $A15$ compounds would not show mode softening but the metastable $A15$'s would. Nb_3Sn which does show mode softening yet is believed to be an equilibrium compound would seem to eliminate this, but results from Hellman *et al.*,[25] Maher *et al.*,[26] and Schiffman *et al.*[27] suggest Nb_3Sn is much more complicated than previously thought and probably is not an equilibrium compound in much of the range where tunneling was done.

The second main result is V-Si is a weak-coupled superconductor throughout its $A15$ range as seen both in the BCS limit values for $2\Delta/k_BT_c$ as well as the low values of λ of about 1. This is consistent with the lack of mode softening (which in Nb_3Ge, Nb_3Sn, and Nb_3Al produced a change from weak coupling to strong coupling as stoichiometry was approached). Finally, we were not able to support the finding of McKnight *et al* of a low-energy peak in V_3Si although we are in reasonable agreement with the rest of their spectrum.

Finally, it should be noted that Klein *et al.*,[28] in 1978, found from band-structure calculations the remarkable result that Nb_3Ge ($T_c = 23$ K) had a low density of states, while V_3Si ($T_c = 17$ K) had a high density of states. They thus suggested that another mechanism, such as phonon softening, must be at work in Nb_3Ge. They appear to have been correct.

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[1]G. F. Hardy and J. K. Hulm, Phys. Rev. **87**, 884 (1953); **93**, 1004 (1954).

[2]J. E. Kunzler, J. P. Maita, H. J. Levinstein, and E. J. Ryder, Phys. Rev. **143**, 390 (1966).

[3]L. J. Vieland and A. W. Wicklund, Phys. Rev. **166**, 424 (1968).

[4]B. Cort, G. R. Stewart, C. L. Snead, Jr., A. R. Sweedler, and S. Moehlecke, Phys. Rev. B **24**, 3794 (1981).

[5]G. R. Stewart, L. R. Newkirk, and F. A. Valencia, Solid State Commun. **26**, 417 (1978).

[6]K. E. Kihlstrom, D. Mael, and T. H. Geballe, Phys. Rev. B **29**, 150 (1984).

[7]G. R. Stewart, B. Cort, and G. W. Webb, Phys. Rev. B **24**, 3841 (1981).

[8]A. Junod and J. Muller, Solid State Commun. **36**, 721 (1980).

[9]A. Junod, J. L. Jorda, M. Pelizzone, and J. Muller, Phys. Rev. B **29**, 1189 (1984).

[10]D. A. Rudman and M. R. Beasley, Appl. Phys. Lett. **36**, 1010 (1980).

[11]J. Kwo and T. H. Geballe, Phys. Rev. B **23**, 3230 (1981).

[12]D. A. Rudman and M. R. Beasley, Bull. Am. Phys. Soc. **26**, 211 (1981); Phys. Rev. B **30**, 2590 (1984).

[13]K. E. Kihlstrom and T. H. Geballe, Phys. Rev. B **24**, 4101 (1981).

[14]S. W. McKnight, S. Perkowitz, D. B. Tanner, and L. R. Testardi, Phys. Rev. B **19**, 5689 (1979).

[15]B. Mitrović and J. P. Carbotte, Phys. Rev. B **26**, 1244 (1982).

[16]B. P. Schweiss, B. Renker, E. Schneider, and W. Reichardt, in *Superconductivity in d- and f-Band Metals*, edited by D. H. Douglass (Plenum, New York, 1976).

[17]For details on the *e*-beam evaporator, see R. H. Hammond, IEEE Trans. Magn. **MAG-11**, 201 (1975); J. Vac. Sci. Technol. **15**, 382 (1978).

[18]W. L. McMillan and J. M. Rowell, in *Superconductivity*, edited by R. D. Parks (Dekker, New York, 1969), Vol. 1, p. 561.

[19]G. B. Arnold, Phys. Rev. B **18**, 1076 (1978).

[20]E. L. Wolf, J. Zasadzinski, J. W. Osmun, and G. B. Arnold, Solid State Commun. **31**, 321 (1979).

[21]E. L. Wolf, J. Zasadzinski, G. B. Arnold, D. F. Moore, J. M. Rowell, and M. R. Beasley, Phys. Rev. B **22**, 1214 (1980).

[22]B. Mitrović and J. P. Carbotte, Solid State Commun. **40**, 249 (1981).

[23]B. Mitrović and J. P. Carbotte, Can. J. Phys. **61**, 784 (1983).

[24]B. Mitrović and S. Perkowitz, Phys. Rev. B **30**, 6749 (1984).

[25]F. Hellman, D. A. Rudman, R. H. Hammond, and T. H. Geballe, Bull. Am. Phys. Soc. **28**, 261 (1983); F. Hellman and T. H. Geballe, *ibid.* **29**, 385 (1984).

[26]D. M. Maher, M. Hong, M. B. Ellington, D. L. Stubbs, T. H. Geballe, and G. W. Hull, Jr., Bull. Am. Phys. Soc. **28**, 261 (1983).

[27]R. A. Schiffman and D. M. Bailey, High Temp. Sci. **15**, 165 (1982).

[28]B. M. Klein, L. L. Boyer, D. A. Papaconstantopoulos, and L. F. Mattheiss, Phys. Rev. B **18**, 6411 (1978).