Evidence for pressure-induced electronic changes in V_3Si

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We report for the first time direct evidence for pressure-induced electronic changes in transforming and nontransforming V_3Si. These observations may be understood qualitatively in terms of interband charge-transfer effects.

The origin of a high superconducting transition temperature T_c in $A15$ V_3Si has been attributed both to a high density of electronic states at the Fermi energy[1] E_F and to an anomalously large softening of the elastic shear modulus[2] that, in extreme cases, can lead to a cubic-to-tetragonal crystallographic transformation at temperatures just above T_c.[3] The relative importance of these two mechanisms in determining the transition temperature has been the subject of considerable debate.[4] A similar controversy[5] arises in attempting to explain the observed[6] pressure enhancement of T_c in V_3Si. Arguments given for pressure-enhanced superconductivity fall roughly into three categories: (1) pressure enhances phonon mode softening that, in turn, promotes stronger electron-phonon coupling[7]; (2) pressure removes lattice defects that are responsible for inhibiting soft phonon modes[8]; and (3) pressure induces a shift in the Fermi energy as a result of charge transfer between s and d subbands,[9] thereby altering the density of states at E_F. There is an increasing body of indirect evidence[5,10,11] favoring the role of interband charge transfer in determining the pressure dependence of T_c; however, experimental results are still inconclusive. If pressure does produce electronic changes in V_3Si, these may be manifest by a systematic variation in the electronic coefficient of the heat capacity γ as a function of pressure. Using appropriate Ginzburg-Landau relationships, we have obtained values of γ as a function of pressure through measurements of the slope of the upper critical field near $T_c(H'_{c2})$, T_c, and the residual resistivity ρ_0.

Samples of V_3Si were obtained from a single, large arc-melted button. Weight analysis of starting and final products indicated that the button was probably no more than 0.5-at.% Si deficient. High-angle x-ray diffraction on powdered pieces taken from the button gave a lattice parameter of 4.723 Å. Second-phase content was less than the detectable limit of ~5%. Samples were sliced from the button in the form of parallelopipeds having approximate dimensions of $1\times1\times4$ mm^3. One piece was sealed under vacuum and annealed for 300 h at 1000 °C. Compared to the unannealed, nontransforming sample (NT), annealing had the effect of raising T_c by about 0.15 K and increasing the residual resistance ratio (RRR) from 14.5 to 26. Annealing also induced a kinklike resistance anomaly[10] at ~21 K that we associate with the occurrence of a structural transformation. This anomaly was not detected in the NT sample, as expected,[2] because of its lower RRR.

The upper critical field near T_c and T_c were measured resistively as functions of pressure using a four-terminal ac technique. Hydrostatic pressure was generated in a self-clamping beryllium-copper cell.[12] The pressure at low temperatures was determined by a lead manometer located in close proximity to the sample. Before measuring the lead transition temperature, we carefully demagnetized the cell to ensure that any remanent field in tungsten-carbide components was removed. All measurements on V_3Si were performed with the pressure cell immersed in a pumped liquid-hydrogen bath to guarantee thermal equilibrium between the cell and sample. The residual resistivity was measured at 19.40 K before applying a magnetic field.

Results of our measurements on both transforming (T) and nontransforming (NT) samples of V_3Si are summarized in Fig. 1. Like previous investigators,[13,14] we find that T_c is enhanced linearly with pressures up to 16 kbar and that this effect is more pronounced in the T sample. ($\partial T_c/\partial P = 4.5\times10^{-5}$ K/bar compared to $\partial T_c/\partial P = 2.4\times10^{-5}$ K/bar in the NT sample). The upper critical-field slope also is enhanced by pressure for both samples.[15] We note that for $P > 10$ kbar, H'_{c2} begins to show a negative-pressure derivative in the NT sample. In contrast to the behavior of T_c and H'_{c2}, the residual resistivity *decreases* with increasing pressure.

From the data in Fig. 1, the electronic heat-capacity coefficient may be calculated using the Ginzburg-Landau relationship[16]

$$-H'_{c2} = [\eta_{H_{c2}}(T_c)/R(\lambda_{tr})][9.55\times10^{24}\gamma^2 T_c(n^{2/3}S/S_F)^{-2} + 5.26\times10^4\gamma\rho_0] \ , \quad (1)$$

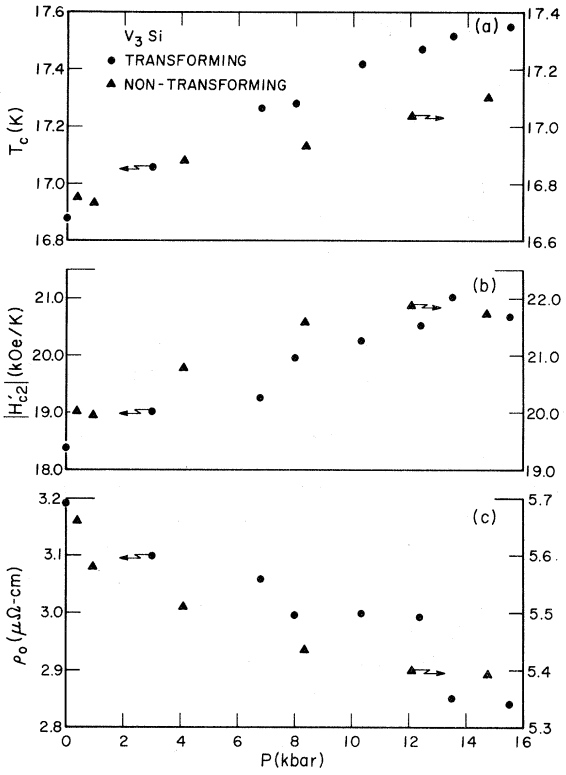

FIG. 1. (a) Midpoint transition temperature, (b) temperature derivative of the upper critical field near T_c, and (c) residual resistivity of transforming and nontransforming samples of V_3Si as functions of pressure.

where n is the conduction-electron density, S is the Fermi-surface area, S_F is the Fermi surface of an electron gas of density n, and $R(\lambda_{tr})$ is a correction factor of order unity [$R(\lambda_{tr}) \simeq 1.006$ and decreases slowly toward unity with increasing pressure]. $\eta_{H_{c2}}(T_c)$ is the strong-coupling factor to H_{c2} given by

$$\eta_{H_{c2}}(T_c) = 1 + (\pi T_c/\omega_0)^2(0.6 \ln \omega_0/T_c - 0.26) \quad , \qquad (2)$$

where ω_0 is a frequency characteristic of the phonon distribution. In the absence of available data for ω_0, we take as representative values ω_{log}, a logarithmic average phonon frequency, calculated from heat-capacity measurements[17] on T and NT V_3Si. Neglecting any moderate pressure dependence of ω_{log} does not affect our conclusions. Orlando *et al.*[16] have shown that a value of $S/S_F = 0.5$ is characteristic of NT V_3Si at ambient pressures. In our calculations we assume that $n^{2/3}S/S_F$ is pressure independent which is probably reasonable for NT V_3Si, but would tend to underestimate changes in γ for transforming samples if we believe that pressure suppresses a gap[17,18] induced on the Fermi surface by the structural transformation.

We show, in Fig. 2, γ as a function of pressure. Within our estimated uncertainty ($\pm 10\%$) in determining the absolute value of γ, the ambient pressure results agree well with the heat-capacity measurements.[17] The enhancement of γ is primarily a reflection of the pressure dependence of H_{c2}'. We reiterate that changes in γ for T V_3Si are probably underestimated by our assumption of the constancy of S/S_F.

What fraction of γ enhancement is due to changes in the bare density of states $N(0)$ may be calculated from the relationship $N(0) = \gamma/[\frac{2}{3}\pi^2 k_B^2(1+\lambda)]$, where λ is the usual electron-phonon mass-renormalization parameter. The pressure dependence of λ can be estimated by inverting the modified[19] McMillan equation

$$T_c = \left[\frac{\omega_{log}}{1.2}\right] \exp\left[-\frac{1.04(1+\lambda)}{\lambda - (1+0.62\lambda)\mu^*}\right] \quad , \qquad (3)$$

where μ^* is a measure of the Coulomb interaction that we take to be 0.1 and pressure independent. Because the pressure dependence of ω_{log} is unknown, we arbitrarily assume that it changes linearly with pressure by $\pm 4\%$ up to 16 kbar.[20] $N(0)$ calculated in this manner is shown in Fig. 3 as a function of pressure. It is apparent that pressure produces small, but measureable, electronic changes in V_3Si. We note that $N(0)$ appears to reach a maximum near 10 kbar in NT V_3Si.

Band-structure calculations[21] on cubic V_3Si reveal a sharp structure in the density of states near E_F. Detailed analysis[22] of the density-of-states behavior in

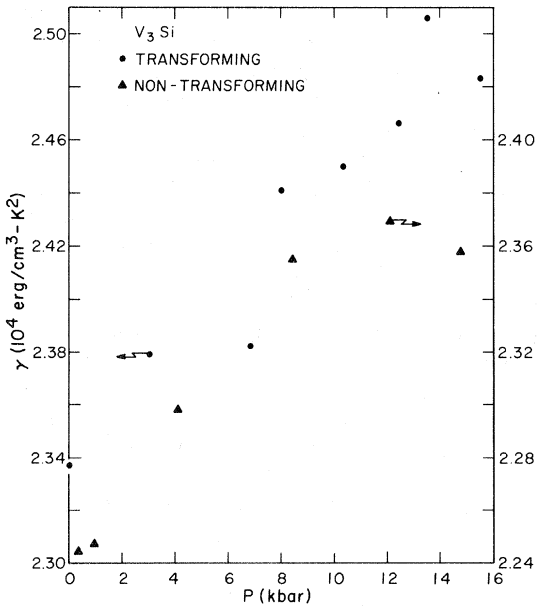

FIG. 2. Electronic coefficient of the heat capacity as a function of pressure.

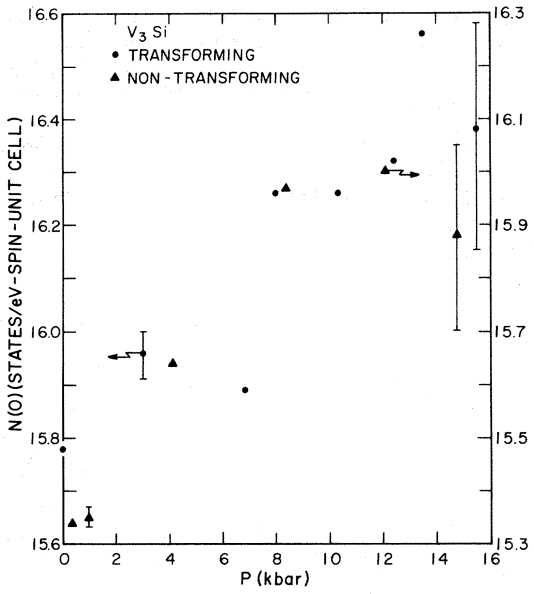

FIG. 3. Bare density of electronic states at the Fermi energy as a function of pressure. Error bars correspond to an assumed variational dependence of $\omega_{\log}$.

the immediate vicinity of E_F shows that E_F falls on a rapidly increasing portion of the density-of-states curve. Pressure-induced charge transfer, which successfully explains[9] the pressure and thermal dependence of the shear modulus, moves E_F to higher energies. Considering the band-structure results, this implies that $N(0)$ for cubic V_3Si should be enhanced by moderate hydrostatic pressures, in agreement with our observations. The maximum in $N(0)$ at ~ 10 kbar also may reflect fine structure in the density of states near E_F found in the calculated band structure.[22] This sharp structure will be smeared at very high pressures because of band broadening. New band-structure calculations for a 2% compression of cubic V_3Si show[23] that $N(0)$ is indeed reduced to $\sim 77.5\%$ of its ambient pressure value. We note that a linear extrapolation of our data on NT V_3Si, for pressures greater than 10 kbar, to a 2% lattice compression, also gives a reduction in $N(0)$ of $\sim 22\%$. We would expect a similar maximum in $N(0)$ to occur in T V_3Si at pressures larger than 16 kbar.

It is interesting to consider the role defects may play. We see from Figs. 1(a) and 1(c) that annealing reduced the ambient pressure resistivity by nearly 50% and produced about 0.15 K increase in T_c. If we assume that the structural transformation is responsible for a decrement in T_c of about 0.3 K,[2,18] then an approximately 50% decrease in the defect concentration results in an effective enhancement of $T_c \sim 0.45$ K. These same figures show that pressure reduces ρ_0 in NT V_3Si by about 5% and in T V_3Si by about 10%, yet T_c is enhanced by approximately 0.38 and 0.65 K, respectively. Therefore a correlation appears between the pressure effects on T_c and ρ_0, but not between ambient and high-pressure results. In all cases, the reduced resistivity is expected to enhance any sharp features in the density of states. It therefore appears that some mechanism, presumably interband charge transfer, in addition to defect concentration, is influencing the pressure enhancement of T_c in V_3Si.

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