

Direct Observation of Enhanced Lattice Stability in V_3Si under Hydrostatic Pressure

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The lattice transformation temperature T_L of single-crystal V_3Si was directly observed to decrease linearly with hydrostatic pressure at a rate of $-(1.5 \pm 0.1) \times 10^{-4} \text{ }^\circ\text{K bar}^{-1}$. To explain the pressure dependence of T_L and the elastic behavior, the Labbé-Friedel model must be extended to include interband charge-transfer effects as a new variable, in agreement with a recent calculation of Ting and Ganguly. We give a discussion of these results related to structural instability and superconductivity.

Soft phonon modes have been observed upon cooling in almost all A15 compounds with high superconducting transition temperature T_c .¹ For some extreme cases, the phonon mode becomes so soft that a lattice distortion corresponding to a cubic-to-tetragonal lattice transformation results. V_3Si is one such example. Its lattice distorts when the shear mode $C_s = \frac{1}{2}(C_{11} - C_{12})$ decreases to a very small value at a temperature T_L slightly above T_c . T_L is defined as the lattice transformation temperature. By analyzing the elastic properties and the specific heat, Testardi *et al.*² predicted a strong, quadratically strain-dependent T_c in cubic V_3Si in agreement with the later thermal-expansion study by Fawcett.³ It was further suggested that T_c of V_3Si was promoted by the soft phonon mode.⁴ However, T_c was found to be enhanced by the application of hydrostatic pressure⁵ in contradiction with the above prediction of a quadratically strain-dependent T_c . It was later proposed^{1,6} that the effect of hydrostatic pressure on T_c could be related to the hydrostatic effect on T_L . The purpose of this experiment is to examine directly the hydrostatic-pressure effect on lattice instability in transforming V_3Si and the role of soft phonon modes in its high T_c .

Our study of the hydrostatic-pressure effect on T_L of V_3Si was carried out using the newly developed temperature-modulation technique.⁷ It is a combination of the high-pressure clamp technique and an ac calorimetric method. This makes possible the determination of the relative specific heat C_p and the temperature slope of resistance $R' = dR/dT$ of a metallic sample under hydrostatic compression. A sample of size 1.2

mm \times 0.8 mm \times 5 mm was spark cut from a V_3Si single crystal. The resistance ratio between room temperature and 18 K of the sample investigated was 26. At zero pressure, $T_c = 16.7^\circ\text{K}$ and $T_L = 21.6^\circ\text{K}$, typical for a transforming V_3Si crystal. Four electrical leads and a Chromel-(Au + 0.07% Fe) thermocouple were soldered onto the sample. The temperature of the sample was modulated by an ac voltage fed through a wire heater closely coupled to the sample. By properly adjusting the thermal links between the sample and the heat reservoir (the high-pressure cell for our experiment) and the frequency of the ac heat source, the amplitude of the ac temperature modulation of the sample, ΔT_{ac} , was approximately inversely proportional to the specific heat C_p . ΔT_{ac} was measured by a thermocouple attached to the sample. The ac component of the voltage across the potential leads gave $IR' \Delta T_{ac}$, where I represents the dc current passing through the sample. The self-clamp technique provided the hydrostatic environment in a 1:1 mixture of *n*-pentane and isoamyl alcohol. The pressure was generated by a press and locked by the clamp at room temperature. The high-pressure clamp was then removed from the press and cooled slowly inside a cryostat. A superconducting-Pb manometer situated next to the sample was used to determine the pressure at low temperature. All electrical leads were brought out from the high-pressure cell with Stycast 2850 FT epoxy seals. The ambient temperature of the sample was measured by a Ge thermometer and/or a Chromel-(Au + 0.07% Fe) thermocouple, depending on the temperature range.

In Fig. 1, we show the temperature dependence

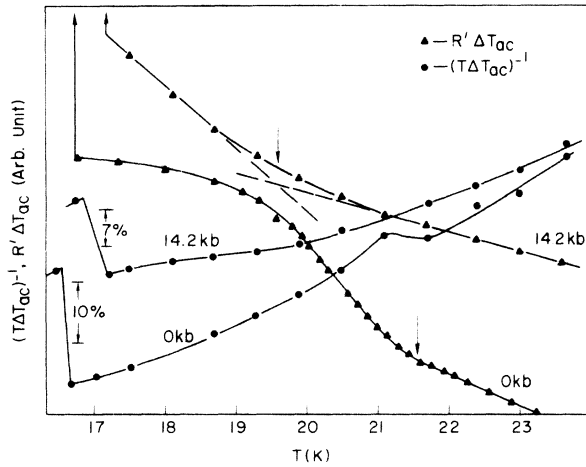


FIG. 1. Temperature dependence of the relative specific heat and the temperature slope of resistance of a V_3Si single crystal at different hydrostatic pressure.

of $(T\Delta T_{ac})^{-1} \propto C_p/T$ and $R'\Delta T_{ac}$ of V_3Si at different pressures. The lattice transformation is evidenced by large changes in the slopes of the C_p and R' curves.⁸ Under pressure, the lattice transition width increases and the anomaly weakens. We define T_L as the temperature at which the slopes increase drastically, as shown by the arrows in Fig. 1.

The results are summarized in Fig. 2. The number represents the sequential order of the experimental run and the bar denotes the experimental error. T_L decreases linearly with hydrostatic pressure with $dT_L/dP = -(1.5 \pm 0.1) \times 10^{-4} \text{ } ^\circ\text{K bar}^{-1}$ up to 18 kbar. We have also determined T_c inductively under hydrostatic compression and found $dT_c/dP = +(3.65 \pm 0.05) \times 10^{-5} \text{ } ^\circ\text{K bar}^{-1}$ in excellent agreement with previous studies.⁵ By extrapolation as shown in Fig. 2, a critical pressure of 24 kbar was obtained for a complete suppression of lattice transformation in V_3Si down to the superconducting state.

In view of the highly anisotropic nature of V_3Si ,¹ it is not surprising at all to find that the hydrostatic-pressure effect on the lattice transformation differs greatly from the uniaxial-pressure effect. It was observed^{2,9} that low uniaxial stress suppresses the lattice transformation but leaves T_L unchanged. Assuming an Ehrenfest second-order transition at T_L , Ehrenfest's equation gives

$$dT_L/dP = vT_L \Delta\alpha / \Delta C_p = \Delta\kappa / \Delta\alpha,$$

where α is the thermal volume-expansion coeffi-

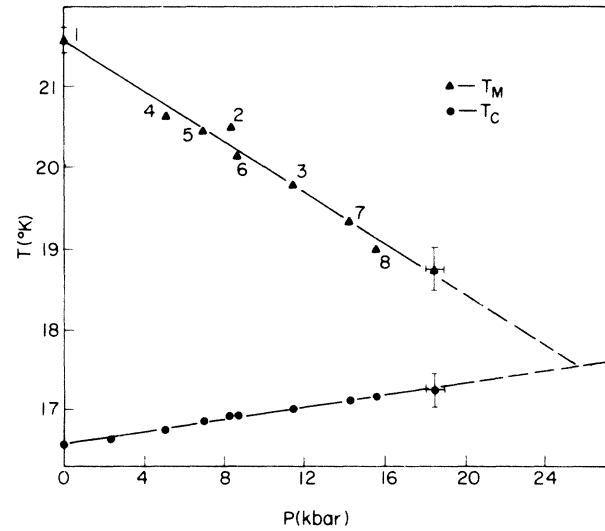


FIG. 2. Pressure dependence of the lattice-transformation temperature T_L and the superconducting transition temperature T_c of a V_3Si single crystal.

cient, κ the compressibility, and v the molar volume of V_3Si . Since $\Delta C_p = 0.054 \text{ cal mole}^{-1} \text{ } ^\circ\text{K}^{-1}$, $\Delta\alpha$ is thus expected to be -5×10^{-7} and $\Delta\kappa/\kappa = +1.33 \times 10^{-4}$ as the lattice transforms from cubic to tetragonal symmetry. These values of $\Delta\alpha$ and $\Delta\kappa$ are too small to have been observed in the previous studies of thermal expansion³ and elastic moduli.¹

The lattice transformation occurs when $C_s(P, T)$ reduces to some small critical value in the cubic state. Assuming this critical value is pressure independent, and expanding $C_s(P, T_L)$ to its first-order terms, one has

$$\partial T_L / \partial P = -(\partial C_s / \partial P)_T (\partial C_s / \partial T)_P^{-1}.$$

With $\partial T_L / \partial P = -1.5 \times 10^{-4} \text{ } ^\circ\text{K bar}^{-1}$ and $(\partial C_s / \partial T)_T = 20 \text{ kbar } ^\circ\text{K}^{-1}$, we obtain

$$(\partial C_s / \partial P)_T = +3.$$

This shows that the application of hydrostatic pressure will stiffen the shear mode at low temperature, in agreement with the recent observation by Carcia and Barsch¹⁰ for the transforming sample, but in disagreement with that by Larsen and Ruoff¹¹ for the nontransforming one. Carcia and Barsch¹⁰ examined the temperature variation of $(\partial C_s / \partial P)_T$ between 37 and 298°K and found that $(\partial C_s / \partial P)_T$ becomes negative below $\sim 100^\circ\text{K}$, exhibits a minimum at $\sim 80^\circ\text{K}$, and finally changes sign back to positive below $\sim 50^\circ\text{K}$.

The unusual behavior of $C_s(T)$ at atmospheric

pressure has been explained¹² in terms of the fine structure of the d band in the Labbé-Friedel linear-chain model.¹³ On the basis of this model, Schuster¹⁴ calculated the pressure effect on C_s by taking into account the intrachain charge transfer through the overlap integral and the change of density of states $N(0)$ through the shift in Fermi energy under pressure. By choosing an unrealistically large q_0a (Slater coefficient times the interatomic distance) of 4.2, $\partial C_s/\partial P$ was made negative below $\sim 100^\circ\text{K}$. Lattice stiffening under pressure at low temperature can be achieved from the above formulism with $q_0a < 2.4$ which is a reasonable choice. However, the pressure-promoted lattice softening between 100 and 50°K ¹⁰ can still not be accounted for.

The simplicity of the Labbé-Friedel model in describing the anomalous properties of A15 lies partially in neglecting the interchain coupling and the interband charge transfer. The close distance between the Fermi level and the density-of-states peak makes the interchain coupling and interband charge transfer important under pressure because of the broadening of the narrow d band. Recently, using the Labbé-Friedel model, Ting and Ganguly¹⁵ have calculated $\partial C_s/\partial P$ as a function of T by taking into consideration the charge transfer between the s and the d bands and obtained excellent agreement with our results on $\partial T_L/\partial P$ and those of Carcia and Barsch¹⁰ on $(\partial C_s/\partial P)_T$.

Making use of the strong-coupling theory for superconductivity, where the electron spectrum plays only a minor role, Testardi^{1,4,6} has tried to explain the pressure-enhanced T_c of cubic V_3Si in terms of a pressure-promoted soft phonon mode. The recent results of Larsen and Ruoff¹¹ showed a large negative value for $\partial C_s/\partial P$ of cubic V_3Si at low temperatures, demonstrating an increased mode softening under pressure. For a transforming V_3Si , however, no predictions on the pressure dependence of T_c or T_L based on sound-velocity measurements could be made because of complications arising from the domain structure in the transformed state. The conjecture has been made,⁶ however, that a maximum in T_c would occur with the state of maximum lattice softness, i.e., when $T_L \rightarrow T_c$. This leads to the suggestion of opposite pressure effects on T_c and T_L for $T_L > T_c$. Figure 2 provides some support for it.

A more complete test would require measurements at higher pressure to see if T_c reaches a maximum when $T_L = T_c$ and then falls for a further

reduction in T_L . Close examination of Smith's $T_c(P)$ results,⁵ which were extended to 24 kbar, reveals a tendency of T_c to saturate above 22 kbar. However, further experiments are required to determine if this is indeed the suggested behavior or just the reflection of the difference in the pressure behavior between the cubic and the tetragonal phases.

It should also be noted that for cubic V_3Si , Larsen and Ruoff¹¹ have concluded from measurements of $\partial C_s/\partial P$ (< 0) that hydrostatic pressure would induce the structural transformation (i.e., $dT_L/dP > 0$ for the nontransforming V_3Si). Measurements at sufficiently high pressure (~ 25 kbar) to test this prediction have yet to be made.¹⁶ Similar relations among T_c , T_L , and P were also observed in V-Ru B2 compounds¹⁷ and $(\text{Zr}_x\text{-Ta}_{1-x})\text{V}_2$ Laves phase,¹⁸ in spite of the fact that T_L is much higher than T_c and the strain saturates long before the temperature reaches T_c from above.¹⁹

In conclusion, we have for the first time directly determined the pressure effect on T_L of V_3Si . T_L was found to be suppressed by the application of hydrostatic pressure. An extrapolated critical pressure of 24 kbar was obtained for complete suppression of the lattice instability down to the superconducting state. The results can be explained in terms of the Labbé-Friedel model by taking into account the interband charge transfer under pressure, in agreement with the calculation of Ting and Ganguly. On the other hand, the pressure effects on T_L and T_c up to 22 kbar are consistent with the conjecture that T_c is enhanced by the pressure-induced lattice softness. However, crucial tests on this latter suggestion lie in further experiments extending to higher pressure.

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Specific Heat of Tetrathiofulvalinium-Tetracyanoquinodimethane (TTF-TCNQ) in the Vicinity of the Metal-Insulator Transition*

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Measurements of the specific heat of tetrathiofulvalinium-tetracyanoquinodimethane have been made from 45 to 70 K using ac calorimetric methods. A steplike anomaly in the specific heat is observed with transition temperature 54.8 K. The results compare favorably with predictions from a mean-field model when the crystal undergoes a Peierls distortion.

Since the report of unusual conductivity phenomena by Coleman *et al.*¹ in the organic charge-transfer salt tetrathiofulvalinium-tetracyanoquinodimethane (TTF-TCNQ), considerable attention has been focused on the possibility of a Peierls transition²⁻⁵ in this material. To date, no direct evidence of such a transition has been found. In this Letter, we report evidence for a phase transition at ~ 55 K in single crystals of TTF-TCNQ, manifested by a step change in the specific heat. We compare this result with the theoretical predictions based on a mean-field, one-dimensional, tight-binding model, agreement with which

gives evidence that a Peierls transition does indeed occur.

The temperature-dependent specific heat of TTF-TCNQ was determined using the ac calorimetric method⁶ on single crystals and pressed-powder samples. The data we present in this Letter were taken using a 47- μ g single crystal grown from solution which was provided by the University of Pennsylvania group,⁷ and a 12- μ g single crystal which was prepared by the authors using vapor-phase reaction techniques. In Fig. 1 we show the specific heat of the Penn sample in the vicinity of the phase transition. Repeated