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# Unusual Strain Dependence of $T_c$ and Related Effects for High-Temperature ($A$-15-Structure) Superconductors: Sound Velocity at the Superconducting Phase Transition

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The sound velocities (elastic moduli) of $V_3Ge$ and $V_3Si$ are found to have very large discontinuities in their temperature derivatives at the superconducting transition. A thermodynamic treatment of these data (with the specific-heat behavior) for a second-order phase transition is shown to yield a general dependence of $T_c$ on strain. It is found that all strains greater than roughly $10^{-3}$ will lower $T_c$ for cubic $V_3Si$ and raise $T_c$ for $V_3Ge$. The results show that these strain dependences are very large, mainly quadratic, and directly responsible for some of the anomalous behavior of the superconductors. They predict, quantitatively for $V_3Si$: (a) the reduction in $T_c$ which results from the structural transformation, (b) the arrest of the structural phase transformation at $T_c$, (c) the strain dependence of the specific-heat discontinuity at $T_c$, (d) the strain dependence of the structural-transformation temperature, and (e) the anisotropic stress dependence of $T_c$. The predicted dependence of $T_c$ upon the lattice parameter is a major factor in accounting for the different $T_c$'s among the $A$-15-structure compounds. The microscopic source of this large strain dependence is discussed in terms of the Labbe-Friedel (density-of-states peak) model. It is a surprising result that this model does *not* predict the large strain dependence of $T_c$ for $V_3Si$.. Finally, the "approximate" nature of the sound velocity data at a phase transition is discussed and the general thermodynamic form for the corrections to the nonideal case is given.

## I. INTRODUCTION

The $A$-15- ($\beta$-tungsten)-structure superconductors have yielded a plethora of "anomalies", [1-12] singularly outstanding in magnitudes and perplexing in their physical origins because they occur in those materials which, today, have the highest known temperatures for superconductivity. It is known, for example, that the high-$T_c$ superconductors exhibit elastic softening, while those with low $T_c$ do not. [13] Some samples of $V_3Si$ and $Nb_3Sn$ undergo a cubic-to-tetragonal transformation at temperatures $T_m$ somewhat above (but never below) $T_c$. For $V_3Si$, where extensive studies have been made, it was found that for nontransforming crystals, the very large elastic softening on cooling is arrested with the onset of supercondivity. [14] In transforming crystals, which exhibit of continuous increase in the degree of tetragonality when cooled below $T_m$, the transformation itself is arrested at $T_c$. [9,14]

In this paper we attempt to reduce the number of seemingly independent anomalies. This we do by analyzing the behavior of the sound velocity near the superconducting transition, and, by thermodynamic arguments, extending these results to "predictions" of some "anomalies" outstanding. Some new and unexpected correlations also occur, and these are presented here and in the following paper (which also lists much of the data relevant to our findings).

It is known that for a second-order phase transition (superconductivity) one may expect some discontinuities in the behavior of the sound velocities (elastic moduli). These discontinuities are analytically related to the strain dependence of the thermodynamic critical field. [15] In Sec. II we show a simple extension of this usual result to yield the general strain dependence of the transition temperature if the specific heat is known. For longitudinal strains the linear and quadratic strain dependences of $T_c$ are related to the discontinuities in magnitudes and temperature derivatives, respectively, of the elastic moduli. For shear strains, only the quadratic dependence of $T_c$ is allowed and only the "slope" discontinuities may occur.

Sound velocity measurements of phase transitions are increasingly popular although the precision of measurement may sometimes outdistance the reliability of interpretation. In the latter part of Sec. II we discuss the "approximate" nature of the sound velocity results in describing the phase transition. We state the form of the corrections to the idealized case from general thermodynamic arguments and briefly extend these results to cases beyond those of interest in this paper.

Experimental description and results for $V_3Si$ and $V_3Ge$ are given in Secs. II and III. Fortunately, the behavior is "anomalously" large in magnitude and the analysis of Sec. II may proceed unencumbered by the corrections earlier discussed.

The strain dependence of $T_c$ is found to be very large, mainly quadratic, and directly responsible for several distinctive behaviors of these superconductors. These include the arrest of the structural transformation at $T_c$, the strain dependence of the specific-heat discontinuity, and the anisotropic stress dependence of $T_c$. The remarkable dependence of $T_c$ upon interatomic spacing (for hydrostatic strain) is shown to be a major factor in accounting for the different $T_c$'s among the $A$-15-structure compounds. Further applications of the results of this paper, particularly to alloying of these materials, are given in the following paper.

The experiment and interpretation developed thus far are not necessarily restricted to superconductivity, and the process is repeated for the structural transformation to yield its strain dependence. The results so obtained are not inconsistent with experimental findings but the argument is tinged with an assumption not wholly at ease with the experimental data.

Finally, the microscopic source of these large strain dependences of $T_c$ is sought. The Labbé-Friedel model,[16] successful in yielding many of the observed anomalies, is a narrow ($\sim 20\,^{\circ}$K) peak in the density of states wherein the Fermi level lies. Such fine structure might easily appear to be the source of a large strain dependence. It is a surprising result of Sec. IV that this is not so.

## II. THEORY

The isothermal[17] elastic moduli are obtained from the Helmholtz free energy $F(T, V_0\epsilon, X_i)$ by

$$c_{ij} = \left(\frac{1}{V_0}\,\frac{d^2F}{d\epsilon_i d\epsilon_j}\right)_{T,Xi}\,, \tag{1}$$

where $\epsilon$ is the strain, $V_0$ is the unstrained volume, and $X_i$ are the remaining extensive variables of the system. The difference in free energy between the normal and superconducting states near but below $T_c$ can be written[18,19]

$$F^N - F^S = V_0\,\frac{H_c^2(T,\underline{\epsilon})}{8\pi} = \frac{\alpha^2(\underline{\epsilon})}{8\pi}\,[T_c(\underline{\epsilon}) - T]^2\,. \tag{2}$$

We expand $T_c$ in linear and quadratic functions of strain:

$$\begin{aligned} T_c(\underline{\epsilon}) &= T_c(0) + \underline{\Gamma}\,\underline{\epsilon} + \tfrac{1}{2}\underline{\epsilon}\,\underline{\underline{\Delta}}\,\underline{\epsilon} = \underline{\Gamma}\,\underline{\underline{S}}\,\underline{\sigma} + \tfrac{1}{2}\underline{\underline{S}}\,\underline{\sigma}\,\underline{\underline{\Delta}}\,\underline{\underline{S}}\,\underline{\sigma} \\ &= T_c(0) + \Gamma_1(V-V_0) + \tfrac{1}{2}\Delta_{11}(\epsilon_1^2+\epsilon_2^2+\epsilon_3^2) \\ &\quad + \Delta_{12}(\epsilon_1\epsilon_2+\epsilon_2\epsilon_3+\epsilon_1\epsilon_3) + \tfrac{1}{2}\Delta_{44}(\epsilon_4^2+\epsilon_5^2+\epsilon_6^2) \\ &\quad \text{(for cubic symmetry).} \end{aligned} \tag{3}$$

We define $\underline{\Gamma}$ as a $1\times 6$ matrix whose components are

$$\Gamma_i = \frac{\partial T_c}{\partial \epsilon_i} \tag{4}$$

and $\underline{\underline{\Delta}}$ as a $6\times 6$ symmetric matrix whose form is similar to the $\underline{\underline{c}}$ matrix but with components

$$\Delta_{ij} = \frac{\partial^2 T_c}{\partial\epsilon_i\,\partial\epsilon_j}\,, \tag{5}$$

where $\underline{\epsilon}$ is the usual $6\times 1$ strain matrix. For cubic symmetry

$$\begin{aligned} &\Gamma_1 = \Gamma_2 = \Gamma_3, \quad \Gamma_4 = \Gamma_5 = \Gamma_6 = 0, \\ &\Delta_{11} = \Delta_{22} = \Delta_{33}, \quad \Delta_{44} = \Delta_{55} = \Delta_{66}\,, \\ &\Delta_{12} = \Delta_{13} = \Delta_{23} \qquad (\Delta_{ij} = \Delta_{ji}) \end{aligned}$$

and all other $\Delta_{ij} = 0$. In Eq. (3) $\underline{\underline{s}}$ is the $6\times 6$ compliance matrix and $\underline{\sigma}$ is the $6\times 1$ stress matrix.[20] We consider two special cases. For volume strains

$$\begin{aligned} &(V-V_0)/V_0 = 3\epsilon_h\,, \\ &T_c(V-V_0) - T_c(0) = 3\Gamma_1\epsilon_h + \tfrac{3}{2}(\Delta_{11}+2\Delta_{12})\epsilon_h^2\,. \end{aligned} \tag{6}$$

For a tetragonal strain where $(c/a-1) = \delta$ and $\epsilon_1 = \frac{2}{3}\delta$,

$$\begin{aligned} &\epsilon_2 = \epsilon_3 = \tfrac{1}{3}\delta, \quad \epsilon_4 = \epsilon_5 = \epsilon_6\,, \\ &T_c(\delta) - T_c(0) = \tfrac{1}{3}(\Delta_{11} - \Delta_{12})\delta^2\,. \end{aligned} \tag{7}$$

From Eqs. (1)–(3) one finds that the components of the isothermal elastic modulus tensor undergo a discontinuity in magnitude:

$$c_{ij}^S - c_{ij}^N = (-\alpha^2/4\pi)\Gamma_i\Gamma_j \tag{8}$$

and a discontinuity in temperature derivative:

$$\frac{dc_{ij}^S}{dT} - \frac{dc_{ij}^N}{dT} = -\frac{\alpha^2}{4\pi}\,\Delta_{ij} - \frac{\alpha}{2\pi}\left(\frac{d\alpha}{d\epsilon_i}\,\Gamma_j + \frac{d\alpha}{d\epsilon_j}\,\Gamma_i\right). \tag{9}$$

For high-symmetry shear waves (deformations) the discontinuity in $c$ and the last term in Eq. (9) are zero since all first-order strain derivatives vanish. We show in the Appendix that in our studies the last term in Eq. (9) may also be neglected for longitudinal waves.

The coefficient $\alpha$ is given by the specific-heat (at constant volume) discontinuity at $T_c$,

$$C_V^N - C_V^S = -T\frac{d^2}{dT^2}(F^N - F^S)\Big|_{T_c} = \frac{-\alpha^2 T_c}{4\pi}. \quad (10)$$

Finally, for strain $\underline{\epsilon}$ the elastic modulus is related to velocity of sound $V_s$ by

$$\underline{\underline{c}} = \rho V_S^2(\underline{\epsilon}) \ , \quad (11)$$

where $\rho$ is the mass density. In Table I we give the strains and associated elastic moduli for high-symmetry directions in a cubic crystal.

### "Approximate" Nature of Sound Velocity Data at a Phase Transformation

The elastic moduli obtained in a sound velocity experiment are given in general by

$$\underline{\underline{c}} = \left[\frac{1}{V_0}\frac{d^2\Phi}{d\underline{\epsilon}^2}(X_i, I_j)\right]_{X_i, I_j} , \quad (12)$$

where $X_i$ and $I_j$ represent all the thermodynamic extrinsic and intrinsic variables, respectively, which are held constant during the experiment and

$$\Phi(X_i, I_j) = U(X_i, X_j) - \sum X_j I_j \quad (13)$$

is the thermodynamic potential minimized under the experimental conditions ($U$ is the internal energy). The "approximate" nature of sound velocity data arises because a change in experimental conditions may (inadvertently) lead to a change in the variables $X_i, I_j$ held constant and, thereby, the function $\Phi$ which determines the measured moduli. This change of experimental condition is quite likely to happen at (or near) a phase transition, and leads to variations of the moduli which are not intrinsically due to the unique properties of the transformed state. Thus, for example, before obtaining the strain dependence of $F^N - F^S$ one must correct the data because the elastic contribution from $F^N$ at $T < T_c$ is not measured under the same conditions as for $T > T_c$. This is now formalized.

In general, if the proper thermodynamic potential for the experiment changes from one of $X_i$ (entropy, volume, mole number,...) to one of constant $I_i$ (temperature, stress, chemical potential,...), the change in the measured modulus is [21]

TABLE I. Strains and associated elastic moduli for high-symmetry sound waves.

| Propagation directions | Particle motion | Strain type | Elastic moduli |
|---|---|---|---|
| [001] | [001] | Longitudinal | $c_{11}$ |
| [001] | ⊥ [001] | Shear | $c_{44}$ |
| [110] | [110] | Longitudinal | $\frac{1}{2}(c_{11}+c_{12}+2c_{44})$ |
| [110] | [001] | Shear | $c_{44}$ |
| [110] | [1$\bar{1}$0] | Shear | $\frac{1}{2}(c_{11}-c_{12})$ |
| [111] | [111] | Longitudinal | $\frac{1}{3}(c_{11}+2c_{12}+4c_{44})$ |
| [111] | ⊥ [111] | Shear | $\frac{1}{3}(c_{11}+c_{44}-c_{12})$ |

$$c_X - c_I = \left(\frac{d\sigma}{dX}\right)_\epsilon \left(\frac{dX}{d\epsilon}\right)_I \quad (14)$$

Normally, plane-wave propagation occurs at constant $X$ at low frequencies and "relaxes" to constant $I$ at high frequencies. At intermediate frequencies $\omega$, we can write for the modulus

$$c(\omega) = c_X - (c_X - c_I) f(\omega/\omega_r) \ , \quad (15)$$

where $f(0) = 0$ and $f(\infty) = 1$. The dispersion function $f$ and the "crossover" frequency $\omega_r$ must come from a physical model. In many cases

$$f = (1 + \omega_r^2/\omega^2)^{-1} \ . \quad (16)$$

When $\omega_r$ is caused to change by the experimental conditions (i.e., by a change of the $I_i$) one obtains the change in modulus[22]:

$$dc(\omega) = \sum_i \frac{\partial c_X}{\partial I_i} dI_i - \sum_i \left( f \frac{\partial (c_X - c_I)}{\partial I_i} dI_i + (c_X - c_I)\frac{\partial f}{\partial \omega_r}\frac{\partial \omega_r}{\partial I_i} dI_i \right) \quad (17)$$

[$\partial f/\partial\omega_r = -2f^2\omega_r/\omega^2$ for the $f$ of Eq. (16)]. The low-frequency behavior, generally treated theoretically,[23] is given by the first term on the right-hand side of Eq. (17). The remaining term describes the modifications which arise because of the finite frequency of the measurements. This term depends upon properties other than the elastic behavior (see below), properties which also vary at a phase transition. To obtain the elastic behavior alone the data must be corrected to remove these effects. Although $\omega_r$ (a function of $X$ or $I$) may never shift through $\omega$, the "corrections" given by Eq. (21) may be relatively large. Two remarks are pertinent. The "corrections" given by Eq. (17) always appear in the form of dispersion ($V_s$ a function of $\omega$). No "corrections" occur for high-symmetry shear waves when $X$ is a scalar since $dX/d\epsilon = 0$ in Eq. (14).

Several particular cases are now considered. For $X = S$ (entropy), $I = T$ and the "adiabatic-isothermal" difference, from Eq. (14), is easily obtained:

$$c_S - c_T = \frac{T}{C_v}\left(\frac{\partial \epsilon}{\partial T}\right)_\sigma^2 c_T^2 \ . \quad (18)$$

The adiabatic-to-isothermal relaxation occurs when the thermal diffusion time over a sound wavelength is less than the sound period. Thus, $\omega_r = C_v V_s^2/K$, where $K$ is the thermal conductivity. For our samples we estimate $(c_S - c_T)/c_T \sim 10^{-4}$, but $\omega/\omega_r \sim 10^{-3}$ in both the normal and superconducting states. Thus, the adiabatic moduli are measured in both the normal and superconducting states for $T \sim T_c$ and these are slightly ($\sim 10^{-4}$) larger than the isothermal moduli derived in Sec. II. However, the very small change in adiabatic-

isothermal relaxation on passing through $T_c$ contributes velocity changes which are negligible compared to the observed behavior.

For $X$ = mole number $N$, and $I$ = electrochemical potential $\mu$, one obtains with the aid of some Maxwell relations

$$c_N - c_\mu = \left(\frac{\partial \mu}{\partial \epsilon}\right)_N^2 \left(\frac{\partial N}{\partial \mu}\right)_\epsilon \quad . \tag{19}$$

This change can be very large. For a free-electron gas where $\mu$ is the Fermi level, one obtains for the bulk moduli

$$B_N - B_\mu = \tfrac{2}{3}\mu N = \tfrac{10}{9} U = B_N \quad .$$

$U$ is the internal energy. (In a typical metal the electronic part of the total elastic modulus is ~ 10%.) A fuller discussion of this case (including charge transfer effects) will be given elsewhere[24]; its contribution to our experimental results, however, is found to be negligible.

Although unrelated to the present work, the case of $X = M$ (magnetization component parallel to $H$) and $I = H$ (applied field) is interesting since it yields

$$c_M - c_H = - c_M^2 \left(\frac{\partial \epsilon}{\partial M}\right)_\sigma^2 \left(\frac{\partial M}{\partial H}\right)_\epsilon \quad , \tag{20}$$

which is a general relation between the magnetic, magnetostrictive, and magnetoelastic behaviors of a substance. This relation can give, for example, the change in sound velocity for a metal in a magnetic field.[25] For $X = P$ (electric moment) and $I = E$ (external electric field) analogous equations and effects occur.

Finally, one may treat the case $X = V_0\epsilon$ and $I = \sigma$. Although no physical relaxation is associated with these parameters, the quantity $C_{V_0\epsilon} - C_\sigma$ does give the change in modulus which arises because experimentally it is $\sigma$ rather than $V_0$ which is usually held constant. In general, if $\epsilon$ is the strain which accompanies an experimental change in one of the intensive parameters, then

$$dc = \sum_{ij} \frac{\partial c}{\partial \epsilon_i} \frac{\partial \epsilon_i}{\partial I_j} dI_j \tag{21}$$

gives the "strictive" contribution to $c$ due to the fact that measurements are not made at constant strain. For example, in measurements made as a function of temperature on a cubic crystal, $dc/dT = (dc/dV)(dV/dT)$ is that part of the temperature dependence which arises from thermal expansion via the crystal anharmonicity. This contribution is part of the normal "background" temperature dependence. At a phase transition, however, $\partial c/\partial \epsilon$ and $\partial \epsilon/\partial I_j$ may change and one would obtain the "strictive" corrections

$$\frac{d(c^N - c^S)}{dT} = \frac{dc^N}{dV^N}\left(\frac{dV^N}{dT} - \frac{dV^S}{dT}\right) \quad , \tag{22}$$

where $N$ and $S$ refer to the two phases. Like those corrections described above, the quantity given by Eq. (22) [26] arises from the $N$-state behavior because the measurement conditions differ in the $S$ state. In this sense it is not directly related to the thermodynamics of the phase transformation and should be removed from the data before analysis for this purpose. Since the third-order elastic moduli ($d\ln c/d\epsilon$) are normally ~ 1 to 10, these corrections may be considerably larger than those normally taken to be due to thermal expansion. For $V_3Si$ some of the third-order elastic moduli may be large. However, the experimental results are anomalously large and it is estimated that the strictive "corrections" amount to less than 10% of the observed magnitudes.

In conclusion, corrections to sound velocity data generally must be applied before analysis because the experimental conditions are normally not those specified by the theory. These corrections are of two types, "dispersive" and "strictive" and are given by Eqs. (17) [with Eq. (14)] and (21). For the materials in our studies the corrections are found to be relatively unimportant.

## III. EXPERIMENTAL

Crystals of $V_3Si$ and $V_3Ge$ were grown by reacting the elemental constituents in water-cooled silver boats followed by a "floating zone" pass to induce the single-crystal growth. Two pairs of plane-parallel faces, {001} and {110}, were prepared on each specimen.

For some samples of $V_3Si$ a cubic-to-tetragonal transformation occurs for $25\ ^\circ\mathrm{K} \gtrsim T > 17\ ^\circ\mathrm{K}$. To avoid this complicating effect when studying the elastic behavior[27] near $T_c (= 17\ ^\circ\mathrm{K})$ we have chosen samples which do not exhibit the structural transformation (as determined by x-ray and acoustic measurements). Some of the properties of the transforming crystals will be deduced from these data.

Pulse-echo measurements of 20-MHz sound velocities were made using the McSkimin pulse-superposition method. For $V_3Si$ the measurements are described in Ref. 14. For $V_3Ge$ the measurement technique was modified for FM and automatic frequency control (AFC) operation. Velocity measurements were made for longitudinal waves along [001] and [110] and for shear waves along [110] with particle motion along [$1\bar{1}0$]. These modes, strains, and elastic moduli are given in Table I. The precision was generally $10^{-5}$. No correction for length changes was made. Errors arising from this are insignificant.

## IV. RESULTS

In Fig. 1 we show the behavior near $T_c$ of the longitudinal wave sound velocity in $V_3Ge$ for $\vec{q}_L$ ∥

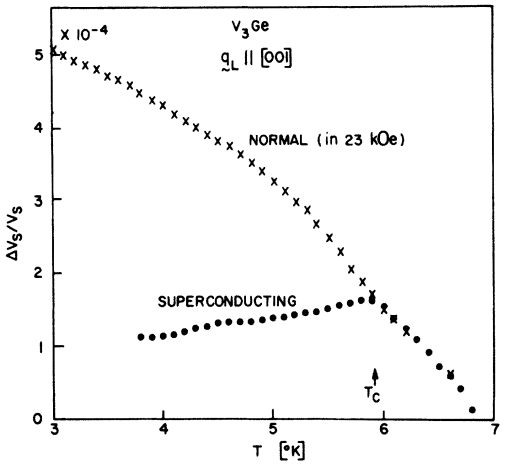


FIG. 1. Sound velocity of [001] longitudinal waves in $V_3Ge$ vs temperature. The discontinuity of the slope at $T_c$ arises from the quadratic strain dependence of $T_c$. The zero position of $\Delta V/V$ is chosen arbitrarily.

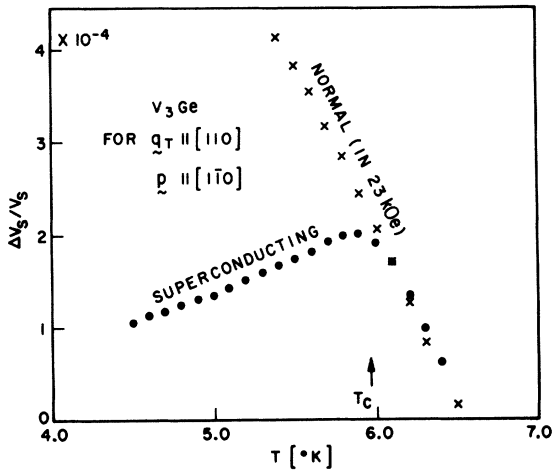


FIG. 2. Sound velocity of [110] shear waves with $[1\bar{1}0]$ particle motion in $V_3Ge$ temperature. The discontinuity of slope at $T_c$ arises from the quadratic strain dependence of $T_c$. The zero position of $\Delta V/V$ is chosen arbitrarily.

[001]. The normal-state results below $T_c = 5.9\,^{\circ}K$ were obtained for all modes by applying a magnetic field of 23 kOe transverse to $\vec{q}$. This may result in a slight stiffening ($\Delta c/c \sim 10^{-5}$) over the zero-field result when longitudinal modes are used.[25] The data have been corrected to remove this slight (temperature-independent) shift when present.

According to Eqs. (8) and (9), a discontinuity in both magnitude and slope may occur at $T_c$. The data of Fig. 1 show a transition "width" of $\sim 0.1\,^{\circ}K$ but no discontinuity in magnitude. In view of the width (a comparable width has been observed in magnetic measurements) the discontinuity in modulus $c^N - c^S \lesssim 10^{-5}\, c^N$. The prominent feature in this (and all other elastic) behavior is the large change in $dc/dT$ at $T_c$. The data show

$$\frac{d(c^N - c^S)}{dT} = (-4.8\times 10^{-4})c^N$$

for $c_{11}$ at $T = T_c$. This is two orders of magnitude larger than that found for typical superconductors.

Figure 2 shows the allowed [Eq. (9)] discontinuity in slope arising from the quadratic shear strain dependence of $T_c$. The wave in this case is $\vec{q}_T \parallel [110]$ and particle motion $\vec{p} \parallel [1\bar{1}0]$. From the data we obtain

$$\frac{d(c^N - c^S)}{dT} = -(8.9\times 10^{-4})c^N$$

for $\frac{1}{2}(c_{11} - c_{12})$ at $T = T_c$.

The behavior for this shear wave in $V_3Si$ (nontransforming) is extraordinary. In Fig. 3 we give the elastic modulus for this wave from 4.2 to 100 °K. The results for $T > T_c$ have been discussed previously.[9,14] At $T = T_c$ (17 to 17.2 °K for nontransforming $V_3Si$ – see following paper) the discontinuity in $(1/c)(dc/dT)$ is $+450\times 10^{-4}$, about four orders of magnitude larger than typical values.

The complete data for $(1/c)(dc/dT)$ at $T_c$ for the three elastic moduli of $V_3Ge$ and $V_3Si$ are listed in Table II. No discontinuities in the magnitude of $c$ (permitted for longitudinal waves only) were observed. The minimum discontinuity which would be detected was severely limited by the large slope $dc/dT$ at $T_c$ and the temperature "width" of the transition ($\sim 0.1 - 0.2\,^{\circ}K$). On this basis we estimate the fractional discontinuity in $c_{11}$ to be $\lesssim 10^{-5}$ and $5\times 10^{-5}$ for $V_3Ge$ and $V_3Si$, respectively.

We have chosen in Table II $\frac{1}{2}(c_{11} - c_{12})$ as one of

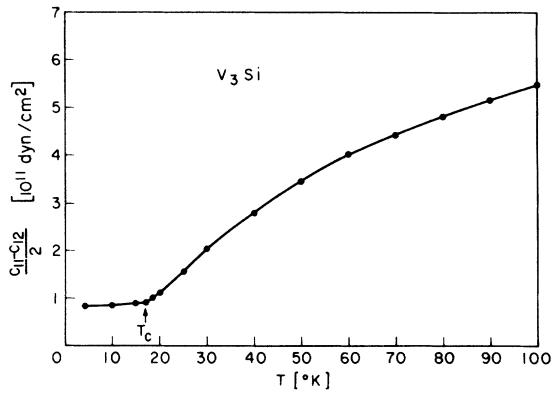


FIG. 3. Sound velocity of [110] shear waves with $[1\bar{1}0]$ particle motion in $V_3Si$ vs temperature. The large softening above $T_c$ has been discussed in Refs. 9 and 14.

TABLE II. Elastic moduli at the superconducting phase transition.

| | | $V_3Ge$ | | |
|---|---|---|---|---|
| $c$ | $c(T_c)$ | $\frac{1}{c}\frac{dc^N}{dT}\Big\vert_{T_c}$ | $\frac{1}{c}\frac{dc^S}{dT}\Big\vert_{T_c}$ | $\frac{d(c^N-c^S)}{dT}\Big\vert_{T_c}$ |
| | ($10^{12}$erg/cm$^3$) | ($10^{-4}$/°K) | | ($10^8$erg/cm$^3$ °K) |
| $c_{11}$ | 3.04 | −4.1 | +0.7 | −14.6 |
| $\frac{1}{2}(c_{11}-c_{12})$ | 0.983 | −7.5 | +1.4 | − 8.7 |
| $c_{44}$ | 0.723 | −0.76 | +0.11 | − 0.63 |
| Specific-heat discontinuity[a] at $T_c$ ($C_p^S - C_p^N$) = $9.25\times10^4$erg/cm$^3$°K ($7.25\times10^{-2}$cal/mole °K) | | | | |
| Lattice parameter 4.78 Å | | | | |
| Density 6.88 g/cm$^3$ | | | | |
| | | $V_3Si$ (nontransforming) | | |
| $c_{11}$ | 1.82 | +58 | +8 | 91 |
| $\frac{1}{2}(c_{11}-c_{12})$ | 0.08 | +600 | +150 | 36 |
| $c_{44}$ | 0.766 | +2 | −3 | 3.8 |
| Specific-heat discontinuity[a] at $T_c$ ($C_p^S - C_p^N$) = $6.5\times10^5$erg/cm$^3$ (0.49 cal/mole °K) (nontransforming) | | | | |
| $6.1\times10^5$erg/cm$^3$ (0.46 cal/mole °K) (transforming) | | | | |
| Lattice parameter 4.72 Å | | | | |
| Density 5.72 g/cm$^3$ | | | | |

[a]See following paper for specific-heat data.

the three independent components necessary to describe the elastic behavior of a cubic crystal. This particular modulus describes the very anomalous shear behavior of these crystals.[7,14,28] Many of the interesting physical results come from the behavior of this modulus and it is a satisfying aspect of the data that neither the corrections of Sec. II nor the discontinuity uncertainties just discussed apply to this shear modulus. But it can be further remarked from the data in Table II, that although this modulus was the most important in describing the elastic instability at $T > T_c$, the slope discontinuities at $T_c$ (and therefore, the strain dependence of $T_c$) are, in fact, larger for $c_{11}$.

The specific-heat data for $V_3Si$ and $V_3Ge$ are given in the following paper.

## V. DISCUSSION

The values of $\alpha^2/4\pi$ for $V_3Ge$ and $V_3Si$ obtained from the discontinuities in the specific heats are given in Table III.

For longitudinal strains, the failure to see a discontinuity in the related moduli allows an upper limit only on the magnitude of $\Gamma = dT_c/d\epsilon$. (The algebraic sign of the first-order strain dependence cannot be obtained from sound velocity measurements.) The limits for the magnitude of $\Gamma$ are given in Table III.

The major feature of the elastic behavior, which is the very large discontinuity in $dc/dT$, implies [from Eq. (9)] either a large quadratic strain dependence of $T_c$ or else [using Eq. (8)] that

$$\frac{d\ln\alpha}{d\epsilon} \gg \frac{d\ln T_c}{d\epsilon} .$$

We shall assume in what follows that the former is true and give in the Appendix the evidence which makes this choice reasonable.

The complete first- and second-order strain dependence of $T_c$ for $V_3Ge$ and $V_3Si$ is given in Table III. Several observations can be made before specific applications of these results:

(i) For both compounds, the quadratic strain dependence is very large and dominates the linear term at $\epsilon_1$ uniaxial strains of $10^{-3}$ and $4\times10^{-4}$ for $V_3Ge$ and cubic $V_3Si$, respectively.[29] The general strain dependence of $T_c$ upon tetragonality and lattice parameter $a$ for $V_3Si$ can be described in both cases by parabolas. The maximum $T_c$ is at $\delta = 0$ for the former and at $a$ approximately equal to, or slightly less than (inferred from alloy behavior – see following paper) the lattice parameter of $V_3Si$.

(ii) For the cubic $V_3Si$ sample all shear strains, and all longitudinal strains greater than $\sim 4\times10^{-4}$,[29] will lower the superconducting transition temperature. For $V_3Ge$, all shear strains, and all longitudinal strains (of the high-symmetry types) greater than $10^{-3}$,[29] raise the transition temperature.

(ii) For $V_3Si$, all shear strains, and all longitudinal strains greater than $\sim 4\times10^{-4}$,[29] lower the superconducting transition temperature. For $V_3Ge$, all shear strains, and all longitudinal strains (of the high-symmetry types) greater than $10^{-3}$,[29] raise the transition temperature.

(iii) The largest longitudinal strain dependence occurs for $\epsilon$ along $\langle 001\rangle$ for $V_3Si$ and $V_3Ge$. The largest shear strain dependence occurs for (110) planes sheared in $[1\bar{1}0]$ directions in both cases. The largest shear and the largest longitudinal strain dependences are comparable.

(iv) The $V_3Si$ data presented above are for nontransforming crystals. From these results the be-

TABLE III. Quantity $\alpha^2/4\pi$ and the components of the tensor describing the strain dependence of $T_c$.

| | $V_3Ge$ | $V_3Si$ |
|---|---|---|
| $\alpha^2/4\pi$(erg/cm$^3$ °K$^2$) | $1.56\times10^4$ | $3.82\times10^4$ |
| $\Delta_{11}$(°K) | $+9.4\times10^4$ | $-24\times10^4$ |
| $\Delta_{12}$(°K) | $-1.8\times10^4$ | $-5\times10^4$ |
| $\Delta_{44}$(°K) | $+0.4\times10^4$ | $-1\times10^4$ |
| $\vert\Gamma_1\vert$ (°K) | < 45 | < 50 |
| $T_c(\epsilon) - T_c(0) = \Gamma\epsilon + \frac{1}{2}\epsilon\Delta\epsilon$ | | |

havior of transforming crystals is easily obtained (see below). There is, in fact, little distinction to be made between transforming and nontransforming crystals for the effects described here. For high tetragonal stress levels ($\sigma > 5\times 10^8$ dyn/cm$^2$) there is little difference in the elastic behavior of transforming and nontransforming crystals at $T_c$. Indeed, at these stress levels there is little difference structurally between transformed and nontransformed crystals since both have single-crystal tetragonal structures with comparable distortions. Therefore, one does not expect the results of Table III to be grossly in error when applied to a transforming crystal. At lower stress levels, however, the behavior in a transforming crystal is complicated by the stress-strain relation. An applied stress may first cause (in part) domain rotation which can lead to "macroscopic" sample strains but little or no microscopic strains. (Such effects would not generally exhibit cubic or tetragonal symmetry.) With further stress the domain size may change. In either case the microscopic strains (which cause the change in $T_c$) would be difficult to calculate. Further uncertainties at small strains are introduced by the (unknown) $\Gamma$ terms. Thus, for transforming $V_3Si$ the important results will find verification at strains $>10^{-3}$ and, in that case, will not be essentially different from that given by the results for the nontransforming crystal (Table III).

The quantities given in Table III essentially exhaust the numerical data directly obtained by this experiment. Their relevance to the superconducting behavior, however, is broad. We cite some examples.

### Change in $T_c$ Due to Structural Transformation in $V_3Si$

For the structural transformation of $V_3Si$ the tetragonal deformation is[7]

$$(c/a) - 1 \approx 2.5\times 10^{-3} \equiv \delta.$$

Since no volume change occurs,

$$(c - a_0)/a_0 = \epsilon_1 = \tfrac{2}{3}\delta$$

and

$$(a - a_0)/a_0 = \epsilon_3 = \tfrac{1}{3}\delta$$

(with $\epsilon_4 = \epsilon_5 = \epsilon_6 = 0$), where $a_0$ is the cubic unit cell size. The change in $T_c$ due to the structural transformation, then, from Eq. (7), is

$$T_c(\text{tetr}) - T_c(\text{cub}) = \tfrac{1}{3}(\Delta_{11} - \Delta_{12})\delta^2 = -0.38\ ^\circ\text{K}. \quad (23)$$

We have ignored the linear term $\Gamma\epsilon$ since no volume change occurs with the structural transformation.

Since not all samples of $V_3Si$ transform, one can attempt to check this result by comparing $T_c$'s of transforming and nontransforming samples. It has been shown[30] that transforming samples (a) have a small amount of second phase, (b) have a higher resistance ratio $R(300^\circ\text{K})/R(4.2^\circ\text{K})$, and (c) are elastically softer. In checking the result of Eq. (27) as described above, one assumes that these differences do not alter $T_c$ by a comparable amount. For (a) and (b) this seems reasonable. Furthermore, the value of $\delta$ given above is a representative one. Observed values vary among samples; presumably $\delta$ may vary from zero to values somewhat greater than $2.5\times 10^{-3}$. One then expects, from Eq. (23), that the reduction in $T_c$ for tetragonal $V_3Si$ will vary from zero to $\sim 0.4\ ^\circ$K. In the following paper we present evidence in support of this result.

The reduction in $T_c$ expressed by Eq. (23) is based only on the tetragonal strain. It does not consider the possible effect on $T_c$ of atomic displacements within the unit cell, if such should occur. A search for some of the displacements which are possible in the transformation has yielded essentially negative results.[31]

### Stress Dependence of $T_c$

Since the quadratic strain effects exceed the linear effects at small strain levels, one expected result is that the shift in $T_c$ with stress will no longer exhibit the isotropy (i.e., proportional to volume change only) expected for a cubic crystal. This has been observed by Weger, Silbernagel, and Greiner.[6] The direct test of this result, by the measurement of $dT_c/d\sigma$, is partly encumbered by the nonlinear stress-strain relation at large strains, particularly for $V_3Si$. Fortunately, sufficient data for $V_3Si$ exist for a quantitative test of Eq. (3). Patel and Batterman[7] have shown that for $V_3Si$ at low temperatures, nonlinear elastic behavior occurs for strains greater than $10^{-4}$. Their data show that for stress $\sigma_1$ (along [001]) the strain $\epsilon_2$ (along [010]) at $T \sim 25\ ^\circ$K is given approximately by

$$\sigma_1(\text{dyn}) \approx (5\times 10^{11})\epsilon_2 + (10^{15})\epsilon_2^{\,2}.$$

Thus, for $\sigma_1 > 5\times 10^8$ dyn/cm$^2$ (500 atm) the elastic behavior is roughly quadratic. At low stress levels,

$$\epsilon_1/\epsilon_3 = \epsilon_1/\epsilon_2 = r \approx -2.$$

From Eq. (3) we calculate uniaxial stress dependence of $T_c$ for the [001] at stress levels $\sim 5 - 10\times 10^8$ dyn/cm$^2$:

$$T_c(\sigma) - T_c(0) = (\Delta_{11}/2)\epsilon_2^{\,2}(r^2+1) + \Delta_{12}\epsilon_2^{\,2}(1-2r)$$

$$\approx -5.5\times 10^{-10}\sigma_1\ \text{deg cm}^2/\text{dyn}. \quad (24)$$

This compares reasonably well with the experi-

mental result $(-5\times10^{-10})\sigma_1$ deg cm$^2$/dyn obtained by Weger, Silbernagel, and Greiner.[6] These workers also found that comparable levels of [111] uniaxial and hydrostatic stress produced no detectable change (to within ± 0.5 °K) in $T_c$. This is in agreement with the calculated behavior using the $\Delta$ in Table III and the elastic moduli. Physically, the effect is small for these types of stresses because the crystal is much stiffer and the resulting strains are smaller.

For $V_3Ge$ the interesting result is that all high symmetry strains $>10^{-3}$ increase $T_c$ and at a relatively rapid rate. Uniform strains ($\epsilon_1$ type)~ 1 % would raise $T_c$ by about 9 °K. Such strains are difficult to produce uniformly by mechanical means. In the following paper we show the behavior of $T_c$ when such strains are achieved by alloying. These surprising results show that for superconductivity the major effect of alloying (to replace the Ge atoms) comes from changes in lattice parameter rather than the change in chemical composition. Unfortunately, no direct test (e.g., $dT_c/d\sigma$) is known to the author which would allow a check of the quadratic strain dependence of $T_c$. (Nor is any information available on the elastic behavior of $V_3Ge$ at high stress levels.)

### Other Strain Effects on $T_c$ and Width of Transition

The degradation of $T_c$ due to accidental strain will be serious, particularly for $V_3Si$. Strains $\gtrsim 5\times10^{-3}$ will greatly depress the superconducting transition in $V_3Si$. Such strains may occur in very thin films and these effects will be at least partly responsible for the low $T_c$'s of $V_3Si$ films thinner than 1000 Å.[32] With comparable values of strain one would expect the $T_c$ of $V_3Ge$ to be raised about 2 °K. $V_3Ge$ thin films are superconducting down to at least 200 Å with $T_c$'s comparable to or greater than bulk sample values.[32]

Inhomogeneous strain will appreciably "broaden" the superconducting transition. This is expected and observed, again, for thin films. Other occurrences in "stress effect" measurements are discussed in the following paper.

### Order of Superconducting Transition, Thermal Expansion Effects, and Arrest of Structural Transformation at $T_c$

Consider the free energy of the system written to show the strain-dependent part near $T_c$:

$$F(\underline{\epsilon}) = F^N(0) + \tfrac{1}{2}\underline{\epsilon}\,\underline{\underline{c}}^N\underline{\epsilon} - (\alpha^2/8\pi)[T_c(\underline{\epsilon}) - T]^2, \qquad (25)$$

where $\underline{\epsilon}$ the strain relative to the "normal" cubic state and the last term is set equal to zero for $T > T_c(\underline{\epsilon})$. For $T > T_c(\underline{\epsilon})$, $F$ initially increases with strain. If $dT_c/d\underline{\epsilon} > 0$, however, the crystal will become superconducting at some finite strain and further strain may, depending upon the magnitude of the last term in Eq. (29), eventually lead to the condition $dF/d\underline{\epsilon} < 0$. If $T_c$ exhibits a positive quadratic strain dependence then, at sufficiently large strain, the free energy given by Eq. (29) will always be less than that at zero strain. Thus, for a sufficiently large positive strain dependence of $T_c$, superconductivity will occur as a first-order transformation. (In this case, of course, it is necessary to reexamine the thermodynamics of the elastic behavior.) To calculate the strain which minimizes the free energy one must include higher-order strain terms (anharmonic effects) in Eq. (25). This equation, applied to the data for $V_3Ge$, shows that at $T > T_c(0)$ the free energy under strain will be less than that at zero strain for strains of the order of unity. This is far too large a strain to ignore the (unknown) anharmonic terms and it is these terms, no doubt, which prevent the first-order transition. For $V_3Si$, the magnitudes of the relevant terms in Eq. (25) are far more favorable for a first-order transition. This is particularly applicable to the term $\frac{1}{2}\underline{\epsilon}\,\underline{\underline{c}}\,\underline{\epsilon}$ since for certain strains the modulus and the corresponding elastic energy are very small. However, $dT_c/d\underline{\epsilon} < 0$. Had $dT_c/d\underline{\epsilon}$ been positive one could expect a first-order transition at $T_c$ with a spontaneous cubic to tetragonal deformation[33] of considerably smaller (and more reasonable) magnitude than that calculated for $V_3Ge$.

An interesting consequence of the large quadratic strain dependence of $T_c$ occurs in the thermal expansion behavior. From Eq. (25) at equilibrium, one obtains when $T$ is near but below $T_c$

$$\frac{dF}{d\underline{\epsilon}} \equiv \underline{\sigma} = \underline{\underline{c}}^N\underline{\epsilon} - \frac{\alpha^2}{4\pi}[T_c(\underline{\epsilon}) - T] \times \frac{dT_c}{d\underline{\epsilon}} - \frac{\alpha}{4\pi}[T_c(\underline{\epsilon}) - T]^2\frac{d\alpha}{d\underline{\epsilon}} = 0. \qquad (26)$$

At $T = T_c$ the change in thermal expansion is then given by

$$\underline{\underline{c}}^N\frac{d\underline{\epsilon}}{dT} = -\frac{\alpha^2}{4\pi}\frac{dT_c}{d\underline{\epsilon}} - \left(\frac{d\underline{\underline{c}}^N}{dT}\right)\underline{\epsilon}\ . \qquad (27)$$

For the cubic state $\underline{\epsilon} = 0$ the discontinuity in $d\underline{\epsilon}/dT$ at $T = T_c$ arises only from the linear strain dependence of $T_c$ (i.e., the coefficient $\Gamma$) and is $\lesssim 10^{-6}$ °K$^{-1}$. The large quadratic strain dependence of $T_c$ will affect $d\underline{\epsilon}/dT$ at lower temperatures only.

For a crystal which has undergone a cubic to tetragonal transformation at $T > T_c$, the strain at $T_c$ (relative to the cubic state) is

$$\epsilon = (\tfrac{2}{3}\delta,\ -\tfrac{1}{3}\delta,\ -\tfrac{1}{3}\delta, 0, 0, 0),$$

where $\delta \equiv (c/a - 1)$. In this case, by Eqs. (27) and (7), the temperature dependence of this deforma-

tion will undergo a discontinuity

$$\frac{d\delta}{dT} = -\frac{\alpha^2}{4\pi}\left(\frac{2}{c_{11}-c_{12}}\right)\frac{2}{3}(\Delta_{11}-\Delta_{12})\delta - \left[\frac{d\ln}{dT}(c_{11}^N - c_{12}^N)\right]\delta \ . \quad (28)$$

For a transforming crystal of $V_3Si$ some typical values are $\delta \approx 2.5\times10^{-3}$ and

$$\tfrac{1}{2}(c_{11}-c_{12}) \approx 5\times10^{10}\ \text{dyn/cm}^2$$

(which is smaller than for nontransforming crystal). The last term in Eq. (28) is negligible for a transforming crystal. One obtains for the discontinuity,

$$\frac{d\delta}{dT} \sim +2.6\times10^{-4}\,^\circ\text{K}^{-1}.$$

Experimentally, one finds that the tetragonal distortion at $T>T_c$ resulting from the phase transformation is increasing quite rapidly with decreasing temperature and has an approximate value[7]

$$\frac{d\delta}{dT} \sim -3\times10^{-4}\,^\circ\text{K}^{-1}$$

just above $T_c$.[34] Thus, the large quadratic strain dependence of $T_c$ causes a discontinuity in $d\delta/dT$ which largely cancels that due to the transformation. This curious result, due to the large quadratic strain dependence of $T_c$, explains why the onset of superconductivity "arrests" the progress of the structural transformation at $T_c$. For nontransforming crystals which exhibit a large elastic softening above $T_c$, the large quadratic strain dependence of $T_c$, of course, "leads" to an arrest of the lattice instability at $T_c$.

### Strain Dependence of Specific-Heat Discontinuity at $T_c$

The strain dependence of the specific-heat discontinuity $\Delta C_v = C_v^S - C_v^N$ at $T_c$ is readily obtained from Eq. (10):

$$\frac{\Delta C_v(\epsilon) - \Delta C_v(0)}{\Delta C_v(0)} = \frac{T_c(\epsilon) - T_c(0)}{T_c(0)}\ , \quad (29)$$

where, for reasons given in the Appendix, we have ignored the strain dependence of $\alpha$. This simple result is compared to published data in the following paper. Fair agreement with experimental results is obtained.

### Strain Dependence of Structural-Transformation Temperatures

The analysis given in Sec. II is not restricted to the superconducting transition but may apply to any second-order phase transition accompanied by a discontinuity in the specific heat. In this section we shall assume that the structural transformation observed in some crystals of $V_3Si$ is of this type. The assumption may be questionable because the observed specific-heat increase occurs over about 2 deg around the temperature $T_m$ of the structural transformation. However, it is quite reasonable to believe that this is "spreading" due to sample inhomogeneity since $T_m$ is known to vary appreciably with small changes in sample preparation. The specific-heat samples are sufficiently large to incorporate inhomogeneities known to be related to the structural transformation. Furthermore, except for this transition region the specific-heat behavior does not differ greatly from that in the cubic state. We assume, therefore, that the structural transformation is of the type discussed in Sec. II.

The calculation of the shear strain dependence of $T_m$ is now identical to that for $T_c$. One obtains for the structural transformation the results given in Table IV. The shear strain dependence of the structural-transformation temperature is roughly at least a factor of 5 smaller than that for the superconducting transition temperature. For the longitudinal strain of $c_{11}$, however, one can no longer ignore the strain dependence of $\alpha$ and only an upper limit on $\Delta_{11}$ can be estimated.

It is easy to show that the calculated strain dependence of $T_m$ is too small to have been seen in previous experiments. If the applied stress in such an experiment leads to strains at $T \gtrsim T_m$ comparable to those which result from the transformation, then the crystal will be "in" the transformed state at $T \gtrsim T_m$ and no transformation anomalies will occur. To observe the strain dependence of $T_m$ in $V_3Si$, then, the "applied" strain ([001] type, for example) must be less than $(c/a)-1 \approx 2.5\times10^{-3}$. From Table IV and Eq. (7) the resulting shift in

TABLE IV. Quantity $\alpha^2/4\pi$, the elastic behavior, and the components of the tensor describing the strain dependence of $T_m$ for $V_3Si$.

| |
|---|
| $\alpha^2/4\pi \sim 8\times10^3\ \text{erg/cm}^3\,^\circ\text{K}^2$ |
| $\frac{1}{c}\frac{d(c^c-c^t)}{dT}\Big\vert_{T_M}$ ($^\circ\text{K}^{-1}$) |
| $\frac{1}{2}(c_{11}-c_{12}) \sim 0.25\,^\circ\text{K}^{-1}$ |
| $c_{44} \sim 0\,^\circ\text{K}^{-1}$ |
| $\frac{1}{2}(\Delta_{11}-\Delta_{12}) \approx -2\times10^4\,^\circ\text{K}$ |
| $\Delta_{44} \approx 0\,^\circ\text{K}$ |
| $\lvert\Delta_{11}\rvert$ (estimated) $\lesssim 10^4\,^\circ\text{K}$ |
| $\lvert\Gamma\rvert < 10^2\,^\circ\text{K}$ |

$T_m$ will be less than ~0.08 °K which is too small to have been observed in previous experiments.

One defect of this treatment for the strain dependence of the structural transformation is that Eq. (27) does not lead to a breakdown of symmetry at $T_m$ unless the shear modulus $c_{11} - c_{12} \to 0$ at $T_m$. Although this modulus becomes unusually small on cooling to this temperature range, its value at $T_m$ is finite. This inconsistency would be removed if a small "spontaneous" tetragonal distortion[16] occurred at $T_m$.[35] In view of past measurements,[7] this distortion must be $\lesssim 5\times10^{-4}$.

### Dependence of $T_c$ upon Lattice Parameter

The elastic behavior near $T_c$ of all of the high-temperature (A-15) superconductors is quantitatively similar to that found for $V_3Si$.[13] It is, therefore, a general feature of these compounds that (i) they possess a very large negative quadratic strain dependence of $T_c$; and (ii) as grown, the lattice parameter is that which nearly maximizes $T_c$[36] (i.e., they have a small $\Gamma\epsilon$ term). The magnitude of the strain dependence of $T_c$ accounts for much of the differences in $T_c$ among some of the compounds. Figure 4 shows the dependence of $T_c$ upon lattice parameter (hydrostatic strain) for $V_3Si$ and $V_3Ge$ calculated from the results of Table III. The large shifts in $T_c$ for strains which do not break the symmetry is unexpected from current models proposed to explain other anomalies. For example, although the elastic instability previously reported is largest for symmetry breaking strains, the effect predicted here is related to small changes in magnitude of the bulk modulus. On a fractional basis these changes were insignificant compared to those for the soft shear modulus.

The magnitude of the strain dependence can be judged by comparing the effects of a typical change in lattice parameter for a metal between 300 and 4 °K (see Fig. 4). Although the low-temperature lattice parameters are called for, only the values for room temperature are available for both compounds. Some relative displacement of the curves will occur because of possible slightly different thermal contractions. For $V_3Ge$ the lattice parameter is reported as both 4.77 and 4.78 Å. The latter value has also been obtained recently by Levinstein of our laboratory and has been used in the figure.

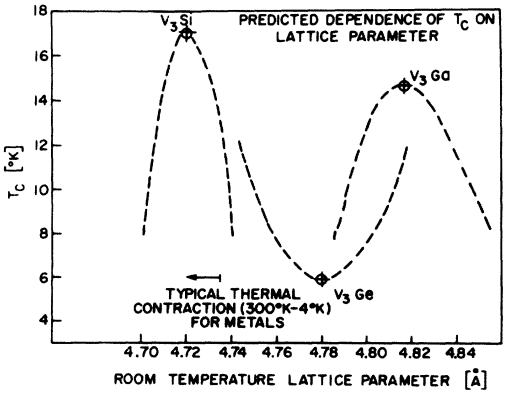


FIG. 4. Predicted dependence of $T_c$ on lattice parameters are called for, only the values for room temperature are available for both compounds. Some relative displacement of the curves will occur because of possible slightly different thermal contractions. For $V_3Ge$ the lattice parameter is reported as both 4.77 and 4.78 Å. The latter value has also been obtained recently by Levinstein of our laboratory and has been used in the figure.

Also given in Fig. 4 are results for $V_3Ga$. For this compound no single-crystal elastic moduli data are available. The curve in Fig. 4 has been obtained by scaling the longitudinal wave polycrystalline data relative to that for polycrystalline $V_3Si$.[13] This could lead to errors of a factor of 2 or so but this does not alter the major features of the figure. For comparison, the strain dependence for $V_3Ga$ is about four times smaller than that for $V_3Si$.

### Microscopic Source of Strain Dependence of $T_c$

Many of the anomalous properties of the A-15 structure high-temperature superconductors have been explained by assuming that the Fermi level lies near a large narrow peak in the density of states.[2,16] Labbé and Friedel[16] have applied the tight-binding approximation to the linear chains of $A$ atoms in the $A_3B$ compound for which there occurs the singular density of ($d$-band) states

$$n(E) = B(E - E_b)^{-1/2}\,, \tag{30}$$

where $B$ is a normalization constant and the $E$'s are measured from the Fermi level. It might be supposed that such a singularity could readily yield a large strain dependence. I now show this not to be the case for shear deformations.

Consider $T_c[Q(\epsilon), V(\epsilon)]$ to be a general function of $Q$, the number of electrons present in the band referred to in Eq. (30), and $V$, an electron-phonon coupling constant. (In what follows, the symbol $Q$ may equally well represent the density of states at the Fermi level.) The quadratic strain dependence of $T_c$ is then written

$$\frac{d^2T_c}{d\epsilon^2} = \frac{\partial^2T_c}{\partial Q^2}\left(\frac{dQ}{d\epsilon}\right)^2 + 2\,\frac{\partial^2T_c}{\partial Q\partial V}\,\frac{dQ}{d\epsilon}\,\frac{dV}{\partial\epsilon} + \frac{\partial^2T_c}{\partial V^2}\left(\frac{dV}{d\epsilon}\right)^2$$

$$+\frac{\partial T_c}{\partial Q}\,\frac{d^2Q}{d\epsilon^2} + \frac{\partial T_c}{\partial V}\,\frac{d^2V}{d\epsilon^2}\,. \tag{31}$$

For high-symmetry shear deformations, $\partial/\partial\epsilon \equiv 0$ and all terms on the right side of Eq. (31) vanish except the last two. Of the two remaining terms, that term proportional to $d^2Q/d\epsilon^2$ would be the source of the large quadratic strain dependence of $T_c$ arising from (bare) band-structure effects. However, in the Labbé-Friedel model the coefficient for this term $\partial T_c/\partial Q$ has been found to be nearly zero for $V_3Si$.[37] Thus, the large shear-

strain dependence of $T_c$ does not arise from the density of states in the Labbé-Friedel model or from any parameter $x$ in which $\partial T_c/\partial x = 0$.

The conclusion that the large quadratic strain dependence of $T_c$ does not arise from peaks in the density of states is not strongly tied to the details of the Labbé-Friedel model. The only result of this model which is used $\partial T_c/\partial Q \approx 0$ is a fair representation of the experimental fact that there is little one can do (either chemically or mechanically) to raise the $T_c$ of $V_3Si$. As such, it should be the result of any realistic theory for $V_3Si$.

These findings show that the unusually large strain dependence of $T_c$ does not arise because energy shifts of $(E - E_b)$ near the singularity in $n(E)$ due to strain cause large changes. Indeed, these shifts have little effect because, physically, the details of the fine structure are washed out by the thermal broadening ($kT_c \sim$ fine structure in the density of states). The large strain dependence of $T_c$ is, in this model, related to a very large (quadratic) strain dependence of BV, and, quite likely, V alone.

It will be shown in a future publication that these superconductors exhibit a remarkable degree of anharmonicity. This anharmonicity has had considerable (but unrecognized) influence in some, and perhaps many, of the properties of these superconductors. Its importance to superconductivity is not clearly understood, but it probably represents the macroscopic manifestation of the large strain dependence of V noted above.

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APPENDIX

The difference in elastic moduli between the normal and superconducting states is given quite generally by Eq. (2) for an unspecified function $H_c(T, \epsilon)$. We now assume that the temperature dependence of this function is given by the usual "critical field" behavior

$$H_c(\epsilon, T) = H_0(\epsilon)[1 - T^2/T_c^2(\epsilon)] \quad . \tag{A1}$$

This assumption can be checked using the specific-heat behavior, and the evidence showing that it is largely correct (to ~ 10%) can be found in the data in the following paper. From Eq. (2) we find $H_0 = -\frac{1}{2}\alpha T_c$ for $T \approx T_c$. At $T = 0$

$$c^N - c^S\big|_{T=0} = \frac{-1}{4\pi}\left[\left(\frac{\alpha}{2}\frac{dT_c}{d\epsilon}\right)^2 + \tfrac{3}{4}\alpha T_c \frac{d\alpha}{d\epsilon}\frac{dT_c}{d\epsilon} + \left(\tfrac{1}{2}T_c\frac{d\alpha}{d\epsilon}\right)^2 + \tfrac{1}{4}\alpha T_c^2\frac{d^2\alpha}{d\epsilon^2} + \tfrac{1}{2}\alpha^2 T_c\frac{d^2T_c}{d\epsilon^2}\right] \quad . \tag{A2}$$

For high-symmetry shear deformations the first three terms on the right-hand side vanish by symmetry. The fifth term is one-half the value $c^N - c^S$ obtained by extrapolating the behavior near $T_c$ [Eq. (9)] and represents (by extrapolation to within 10%) the observed value. Therefore,

$$\frac{d^2\alpha}{d\epsilon^2} < \frac{2\alpha}{T_c}\frac{d^2T_c}{d\epsilon^2}$$

(for the shear deformations in our study) and probably with a considerably large difference.

In the interpretation of the data for longitudinal waves described by Eq. (9) I assumed

$$\frac{d^2T_c}{d\epsilon^2} \gg \frac{4}{\alpha}\frac{d\alpha}{d\epsilon}\frac{dT_c}{d\epsilon} \quad . \tag{A3}$$

I now wish to justify this using Eq. (A2). For longitudinal waves, the first, second, and fifth terms on the right-hand side of Eq. (A2) represent (to within a factor of $\sim \frac{3}{2}$) one-half of what is obtained by extrapolating the behavior at $T_c$ [Eq. (9)] to $T = 0$. The latter result is, to within ~ 20%, just the observed behavior. If Eq. (A3) is not correct, however, it is then easily seen that the third term of Eq. (A2) exceeds the second term, as well as the (experimental) sum of all terms, by the factor

$$\frac{T_c}{(c^N - c^S)}\frac{d(c^N - c^S)}{dT}\bigg|_{T_c} \approx 100 \quad .$$

It does not seem likely that this is almost exactly canceled out (over a range in temperature) by the fourth term. Thus, the assumption given by Eq. (A3) is probably correct and only the fifth term in Eq. (A2) is important.

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[17]The adiabatic moduli are obtained in our experiments. The adiabatic-isothermal difference is discussed below.
[18]$H_c$ is the thermodynamic critical field. The proportionality of $F^N - F^S$ to $[T_c - T]^2$ just below $T_c$ is quite general for a second-order phase transition with a discontinuity in the specific heat.
[19]For the parabolic relation $H_c = H_0(1 - T^2/T_c^2)$, $\alpha = 2H_0/T_c$.
[20]Where the matrix products should yield a scalar, the transposed form is assumed when necessary (and not indicated).
[21]We omit tensor notation in what follows.
[22]This is accomplished by a loss $Q^{-1} = [(c_X - c_I)/c_X] \times (\omega_r/\omega)f$.
[23]What follows applies equally well, of course, if the high-frequency behavior is desired.
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[26]And similar quantities obtained from Eq. (21).
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[28]See the following paper for a discussion of the $V_3Ge$ elastic behavior.
[29]This value arises from the uncertainty of magnitude and sign of $\Gamma$. The value given is for ⟨001⟩ longitudinal strain. For tetragonal and for cubic $V_3Si$ with different $T_c$'s these strain values (as well as the $\Gamma$'s) will differ from the above values but can be calculated from Eq. (3).
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[34]This strain measurement must, of course, be a microscopic one (see Ref. 7). Macroscopic measurements (of a sample length) are complicated by domain structure and alignment.
[35]It would remain to be shown, however, that the treatment of Sec. II is still largely correct in the presence of small "first-order" transformation effects.
[36]For the Nb based compounds this statement must be qualified because of a larger experimental error. This will be discussed in a future paper on the anharmonic behavior of these superconductors.
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