

⁵³S. L. Norman and D. H. Douglass, Jr., Phys. Rev. Letters **18**, 339 (1966).

⁵⁴See, for example, Ref. 15 comments to this effect.

⁵⁵E. Abrahams and T. Tsuneto, Phys. Rev. **152**, 416 (1966).

⁵⁶P. C. Hohenberg, Phys. Rev. **158**, 383 (1967).

⁵⁷H. J. Mikeska and H. Schmidt (private communication).

tion).

⁵⁸W. E. Masker, S. Marčelja, and R. D. Parks, Phys. Rev. **188**, 745 (1969).

⁵⁹P. Fulde and K. Maki, Physik Kondensierten Materie **5**, 380 (1966).

⁶⁰P. G. de Gennes and S. Mauro, Solid State Commun. **3**, 381 (1965).

Thermodynamics of Pressure Effects in V₃Si and V₃Ge

L. J. Sham* and T. F. Smith†

*Department of Physics and Institute for Pure and Applied Physical Sciences,
University of California, San Diego, La Jolla, California 92037*

(Received 3 June 1971)

The thermodynamic relationships relating the pressure dependence of the superconducting transition temperature to the changes in the elastic constants at the transition are presented and their application to the compounds V₃Si and V₃Ge is discussed.

In a series of recent articles¹⁻³ Testardi and co-workers have made predictions of an unusually large quadratic strain dependence of the superconducting transition temperature for the A15 superconductors V₃Si and V₃Ge.⁴ Measurements^{5, 6} of T_c as a function of pressure for these compounds fail to reveal any evidence of the quadratic dependence, with T_c increasing linearly with pressure for both compounds. Since the predicted behavior follows directly from a purely thermodynamic treatment of the elastic properties, as determined from sound velocity measurements close to T_c , and is, therefore, completely model independent, the conflict is of the most fundamental nature. It is the purpose of this paper to make a critical evaluation of the circumstances surrounding the discrepancy in an attempt to isolate its origin.

We shall begin by considering the appropriate thermodynamic relationships linking the discontinuities in the compressibility and its temperature derivative at the superconducting transition with the pressure derivatives of T_c . Starting with the difference in the Gibb's energy between the normal (n) and superconducting states (s),⁷

$$G_n(T) - G_s(T) = \frac{V}{8\pi} H_c(T)^2,$$

and successively differentiating with respect to T and P we obtain expressions for the change in specific heat C , compressibility κ , thermal expansion α , and their various derivatives, in going from the superconducting to the normal state.

We have taken the temperature dependence of H_c to be of the general form

$$H_c(T) = B_1(T_c - T)/T_c + \frac{1}{2}B_2(T_c - T)^2/T_c^2 + \dots,$$

where the coefficients B_n are temperature independent. Although this expansion may be related to the more usual quadratic form

$$H_c(T) = H_0(1 - T^2/T_c^2)$$

by putting $B_1 = 2H_0$ and $B_2 = -2H_0$ we prefer to avoid this more restricted expression and obtain values for B_1 and B_2 from the heat-capacity data available using (1) and (2) given below. In actual practice we find that the values we obtain for B_1 and B_2 lead to a temperature dependence of H_c which is not very different from the quadratic form. It may be readily determined that at $T = T_c$

$$C_n - C_s = -\frac{V}{4\pi} \left(\frac{B_1}{T_c} \right)^2, \quad (1)$$

$$\frac{\partial}{\partial T} (C_n - C_s) = -\frac{V}{4\pi} (1 + 3\alpha T_c) \left(\frac{B_1}{T_c} \right)^2 + \frac{3}{4\pi} \frac{B_1 B_2}{T_c^2}, \quad (2)$$

$$\kappa_n - \kappa_s = -\frac{1}{4\pi} \left(\frac{B_1}{T_c} \right)^2 \left(\frac{\partial T_c}{\partial P} \right)^2, \quad (3)$$

$$\begin{aligned} \frac{\partial}{\partial T} (\kappa_n - \kappa_s) = & \frac{1}{4\pi} \left(\frac{B_1}{T_c} \right)^2 \frac{\partial^2 T_c}{\partial P^2} + \frac{3}{4\pi} \frac{B_1 B_2}{T_c^3} \left(\frac{\partial T_c}{\partial P} \right)^2 \\ & + \left[\frac{B_1}{\pi T_c} \frac{\partial}{\partial P} \left(\frac{B_1}{T_c} \right) - \frac{\kappa_s}{2\pi} \left(\frac{B_1}{T_c} \right)^2 \right] \left(\frac{\partial T_c}{\partial P} \right). \end{aligned} \quad (4)$$

On comparing (4) with the equivalent relationship derived by Testardi² we find only the first term on the right-hand side.⁷ The loss of the term in $(\partial T_c / \partial P)^2$ may be traced to his approximation that $H_c(T) = 2H_0(1 - T/T_c)$, which is equivalent to taking $B_2 = 0$. Since we find that $B_2 \approx -B_1$ for both com-

TABLE I. Quantities used in the relationships (3) and (4).

	V ₃ Ge	V ₃ Si
T_c (°K)	6.1	16.9
β (10^{12} dyn cm ⁻²)	1.73	1.71
$C_s - C_n$ (10^4 dyn cm ⁻² deg ⁻¹)	9.25	76.6
$\frac{\partial}{\partial T} (C_s - C_n)$ (10^4 dyn cm ⁻² deg ⁻²)	5.71	16.0
$\frac{1}{4\pi} \left(\frac{B_1}{T_c}\right)^2$ (10^4 dyn cm ⁻² deg ⁻²)	1.52	4.56
B_1/B_2	-0.92	-0.85

pounds under consideration, such an approximation is not valid. The third term does appear in his derivation, but it was argued that it was small enough to be neglected. Taking $B_1 \approx 2H_0$ and using the relationship $H_0/T_c \propto \gamma^{1/2}$ (where γ is the coefficient of the linear term in the low-temperature heat capacity) the coefficient of this term may be rewritten as

$$\frac{\kappa_s}{2\pi} \left(\frac{B_1}{T_c}\right)^2 (\gamma_e - 1),$$

where $\gamma_e = d \ln \gamma / d \ln V$ is the electronic Grüneisen parameter. For any normal value of γ_e (~1-2) the third term will only amount to a few percent of the second term and therefore may be safely neglected, as argued, though somewhat differently, by Testardi.² However, in the event that γ_e were anomalously large, say, ≥ 10 , then it would be necessary to take this term into consideration.

Using the heat-capacity data of Testardi *et al.*³ in (1) and (2) we obtain values for B_1 and the ratio B_2/B_1 . Relationships (3) and (4) then enable us to compare the pressure coefficients for T_c calculated from the elastic data and vice versa. All the relevant quantities used in the calculations are listed in Table I and the results are summarized in Table II. We can only quote upper limits on $|\partial T_c / \partial P|$ based upon the quoted fractional resolution $\Delta c/c$ of the elastic measurements, which were 10^{-5} and 5×10^{-5} for V₃Ge and V₃Si, respectively, since no discontinuity at T_c could be detected.² The limiting value in the case of V₃Si is in fairly reasonable agreement with the measured

value, but that for V₃Ge is a factor 3 smaller. In both cases the calculated pressure dependence of T_c is dominated by a large quadratic term which is positive for V₃Ge and negative for V₃Si. The considerable discrepancy between the calculated and observed variation of T_c with pressure is demonstrated in Fig. 1. The double lines for each calculated dependence reflect the inability to determine the sign of the linear term from (3).

We shall now consider to what extent the latitude in determining the quantities substituted into (3) and (4) can account for the failure to find consistency. Since the discrepancies involved amount to orders of magnitude and the uncertainties in B_1 and B_2 are no more than several percent we will confine our examination to the pressure and elastic data.

In Fig. 1 we show the linear dependences of T_c upon pressure which were originally reported by one of us.⁶ Certainly, in the case of V₃Ge, there is no evidence to suppose other than a linear variation. However, it must be admitted that for V₃Si there is a small deviation from the linear dependence at the highest pressure applied, but in view of the accompanying increase in transition width, its significance should be regarded as questionable. It may be noted that owing to the considerable anisotropy in the stress dependence⁸ of T_c for V₃Si it would only require a 1-2% deviation from a uniform stress distribution *within* the sample to account for the deviation. However, for the purpose of demonstration we have constructed extreme fits to the data in which we include a quadratic term. A significant deviation from the straight-line fit, in the pressure range of the measurements, only occurs for V₃Si above 20 kbar. This is indicated in Fig. 1 by the broken line. The pressure derivatives and the corresponding elastic quantities calculated from (3) and (4) are listed in parentheses in Table II. Clearly, this approach has done little to improve the situation. Indeed, the introduction of the quadratic term has led, in both cases, to an increase in the linear term, thus compounding the discrepancy with the bulk modulus. Furthermore, the sign of the quadratic term for V₃Ge is opposite to that required by the elastic data.

As there can be no doubt that there is a substantial linear term in the pressure dependence of T_c , a discontinuity in bulk modulus is expected at the

TABLE II. Comparison of calculated and observed quantities from relationships (3) and (4).

	$\partial T_c / \partial P$ (10^{-11} deg cm ² dyn ⁻¹)		$\partial^2 T_c / \partial P^2$ (10^{-20} deg cm ⁴ dyn ⁻²)		$\beta_n - \beta_s$ (10^8 dyn cm ⁻²)		$\partial(\beta_n - \beta_s) / \partial T$ (10^8 dyn cm ⁻² deg ⁻¹)	
	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed
V ₃ Ge	± 2.56	8.1 (8.5)	0.69	~ 0 (-0.045)	-3.0 (-3.3)	≤ 0.3	1.4 (1.7)	-3.0
V ₃ Si	± 2.61	3.7 (4.3)	-3.23	~ 0 (-0.064)	-1.8 (-2.4)	≤ 0.91	0.3 (1.3)	43

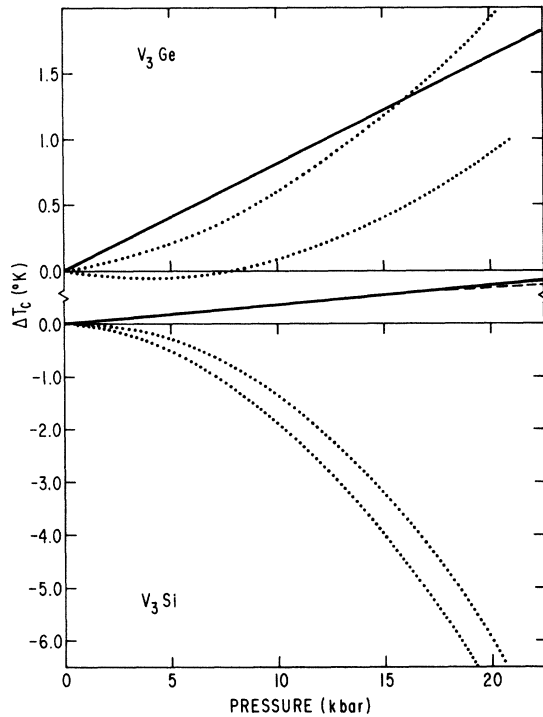


FIG. 1. Comparison of the directly measured variation of T_c with pressure (solid line) with that calculated from the elastic data (dotted line).

transition.⁹ In the case of V_3Si this would only amount to the order of twice the resolution available in the elastic measurements and it therefore seems reasonable to assume that the effect was too small to be resolved. However, it is disturbing that there is no apparent evidence of a discontinuity in the elastic data for V_3Ge , since here the expected effect should be an order of magnitude greater than the resolution in the measurements.

In considering the discontinuity in the tempera-

ture derivatives of the bulk modulus we note that

$$\frac{\partial}{\partial T} (\beta_n - \beta_s) = \frac{\partial}{\partial T} (c_{11}^n - c_{11}^s) - \frac{4}{3} \frac{\partial}{\partial T} \left[\left(\frac{c_{11} - c_{12}}{2} \right)^n - \left(\frac{c_{11} - c_{12}}{2} \right)^s \right],$$

where the two terms on the right-hand side are almost equal. Thus, even a modest error in the determination of either, or both, of these terms could lead to a large error in their difference. In the particular case of V_3Ge a reduction of the first term by 30% or an increase of the second by 37% (or the appropriate combination of a ~15% change in both) would reduce the predicted $\partial^2 T_c / \partial P^2$ to zero. The corresponding changes for V_3Si would be somewhat greater, amounting to a 50% decrease of the first term or a 90% increase of the second. We may note that an analysis of thermal expansion measurements¹⁰ on single-crystal V_3Si provides support for the value of the latter (shear) term, as determined from the elastic measurements, which would suggest that the problem may lie almost entirely with the first term (c_{11}). Since the expansion measurements clearly show that even for a nominally nontransforming single crystal a small proportion of the crystal still undergoes the cubic-to-tetragonal transition, the influence of the transformed material on the variation of c_{11} with temperature may well be quite significant.

In summary, it appears that a certain degree of reconciliation between the measured pressure dependence of T_c and that expected from a thermodynamic treatment of the elastic properties is possible, though unresolved discrepancies still exist for both compounds. A redetermination of the elastic behavior close to T_c is desirable, particularly for V_3Ge .

We wish to thank L. R. Testardi for stimulating correspondence and discussions.

*Supported in part by the National Science Foundation Grant No. GP-14912.

†Sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, U.S. Air Force, under Grant No. AF-AFOSR-631-67-A.

¹L. R. Testardi, J. E. Kunzler, H. J. Levinstein, and J. H. Wernick, *Solid State Commun.* **8**, 907 (1970).

²L. R. Testardi, *Phys. Rev. B* **3**, 95 (1971).

³L. R. Testardi, J. E. Kunzler, H. J. Levinstein, J. P. Maita, and J. H. Wernick, *Phys. Rev. B* **3**, 107 (1971).

⁴Throughout we shall consider nontransforming V_3Si , i.e., material which does not undergo the cubic-to-tetragonal transformation just above T_c .

⁵H. Neubauer, *Z. Physik* **226**, 211 (1969).

⁶T. F. Smith, *Phys. Rev. Letters* **25**, 1483 (1970).

⁷See, for example, D. Shoenberg, *Superconductivity* (Cambridge U. P., Cambridge, England, 1962), pp. 73-75. It may be noted that in Testardi's treatment (Ref. 2) he considers this relationship to be the difference in Helmholtz free energy, thus effectively neglecting a term $P(V_n - V_s)$. This term is not important unless the P -vs- V relationship is very nonlinear.

⁸M. Weger, B. G. Silbernagle, and E. S. Greiner, *Phys. Rev. Letters* **13**, 521 (1964).

⁹The discontinuity in the thermal expansion of V_3Si at T_c yields a value for $\partial T_c / \partial P$ which is in reasonable agreement with that determined from the pressure measurements (Ref. 10).

¹⁰E. Fawcett, *Phys. Rev. Letters* **26**, 829 (1971).