TABLE II. Observed and calculated values of $\partial T_c/\partial P$.

Element	T_c °K	Atomic volume cm³	$(C_s-C_n)_{T=T_c}$ mJ deg⁻¹ mole⁻¹	$\left(\frac{\partial H_c}{\partial T}\right)_{P=0,\,T=T_c}$ Oe deg⁻¹	H_0 Oe	$\left(\frac{\partial H_c}{\partial P}\right)_{T=T_c}$ 10^{-3} Oe bar⁻¹	$\left(\frac{\partial T_c}{\partial P}\right)^{\text{calc}}_{H=0}$ 10^{-6} deg bar⁻¹	$\left(\frac{\partial T_c}{\partial P}\right)^{\text{obs}}_{H=0}$ 10^{-6} deg bar⁻¹
V	5.03[a]	8.34	69.4[a]	−455	1310[a]	4.1±0.3[b]	9.0	11±3
						2.0±0.2[c]	4.4	
Nb	9.17[d]	10.80	140[d]	−421±4	1944[d]	−1.2±0.3[c]	−2.85	0±3
Ta	4.39[e]	10.83	42.2[e]	−334±2	825[f]	−0.8±0.3[c]	−2.4	−2.6±1.0[f]

[a] Reference 5. [b] Reference 10. [c] Reference 8. [d] Reference 7. [e] Reference 6. [f] Reference 9.

in Table II. In order to calculate values of $\partial T_c/\partial P$ using the Maxwell thermodynamic relationship,[4]

$$\left(\frac{\partial T_c}{\partial P}\right)_{H=0}=-\left(\frac{\partial H_c}{\partial P}\right)_{T=T_c}\left(\frac{\partial H_c}{\partial T}\right)_{P=0}^{-1}, \qquad (3)$$

we express the measured values[5–7] of C_s-C_n in terms of $(\partial H_c/\partial T)_{T=T_c}$ using the Rutgers relationship,[4]

$$(C_s-C_n)_{T=T_c}=\frac{VT_c}{4\pi}\left(\frac{\partial H_c}{\partial T}\right)^2_{P=0}. \qquad (4)$$

The values of $\partial H_c/\partial T$, given in Table II, derived in this manner are in good agreement with values obtained from directly measured critical-field curves for vanadium[5] and tantalum,[6] but not for niobium.[7]

Using the thermodynamic relationship (4) we have calculated values of $(\partial T_c/\partial P)_{H=0}$, and these are compared in Table II with our observed values. Table II also includes the results for tantalum; $(\partial T_c/\partial P)_{H=0}$ was determined for this element by Hinrichs and Swenson.[9] The sign of $(\partial T_c/\partial P)_{H=0}$ obtained for vanadium agrees with that predicted from the thermal-expansion data. The observed magnitude is in better agreement with the value calculated from the thermal-expansion data of Müller and Rohrer,[10] rather than the value determined from the data of White.[8] The calculated value of $(\partial T_c/\partial P)_{H=0}$ for niobium is about the limit of our experimental sensitivity and is, therefore, not inconsistent with the zero pressure dependence observed. The experimental results of Hinrichs and Swenson[9] are also in good agreement with the calculated value.

The effect of applying pressure to a superconductor, until recently, had always been associated with an observed decrease in the superconducting transition temperature.[11] However, a number of superconductors (Zr,[12] La,[13] U,[14] and V[15]) have now been found to exhibit a positive $\partial T_c/\partial P$. We may attempt to understand this difference in sign of the pressure dependence of the superconducting transition temperature by considering the volume derivative of the BCS[16] relationship,

$$T_c=0.85\Theta_D\exp(-1/A), \qquad (5)$$

with $A=N(0)V$, where $N(0)$ is the density of electron states at the Fermi surface and V is the attractive electron-electron interaction parameter. Differentiation of (5) with respect to volume gives

$$\frac{\partial\ln T_c}{\partial\ln v}=\varphi\ln\left(\frac{0.85\Theta_D}{T_c}\right)-\gamma_G, \qquad (6)$$

where $\varphi=\partial\ln A/\partial\ln v$ and γ_G, the Grüneisen constant, represents the volume dependence of the phonon spectrum. Rewriting $\partial\ln T_c/\partial\ln v$ in terms of $\partial T_c/\partial P$ we have

$$\frac{\partial T_c}{\partial P}=-|K|T_c\left\{\varphi\ln\left(\frac{0.85\Theta_D}{T_c}\right)-\gamma_G\right\}, \qquad (7)$$

where K is the compressibility.

The pressure dependence of the phonon spectrum is such as to increase T_c and will be roughly the same for all elements since γ_G has, in general, values between 1 and 3. Since $\ln(0.85\Theta_D/T_c)$ lies in the range 2.5 to 6.5 for most superconductors the sign and magnitude of $\partial T_c/\partial P$ is determined by φ. Rohrer[17] has pointed out that for nontransition metal superconductors φ is roughly constant and equal to 2.5±0.5. However, when we consider the behavior of the transition metal superconductors there is considerable variation both in the magnitude and the sign of φ.[18,19] Olsen and his co-

[9] C. H. Hinrichs and C. A. Swenson, Phys. Rev. 123, 1106 (1961).

[10] J. Müller and H. Rohrer, Helv. Phys. Acta. 31, 289 (1958).

[11] An exception to this generalization is thallium which shows a slight increase in T_c for applied pressures up to 2 kbar [Ref. 1; J. Hatton, Phys. Rev. 103, 1167 (1956); and I. D. Jennings and C. A. Swenson, Phys. Rev. 112, 31 (1958)]. Further application of pressure then causes T_c to decrease. Jennings and Swenson have explained this behavior as a consequence of the highly anisotropic nature of the physical properties of thallium.

[12] N. B. Brandt and N. I. Ginzburg, Zh. Eksperim. i Teor. Fiz. 46, 1212 (1964) [English transl.: Soviet Phys.—JETP 19, 823 (1964)].

[13] W. E. Gardner and T. F. Smith, Phys. Rev. 138, A484 (1965).

[14] T. F. Smith and W. E. Gardner, Phys. Rev. 140, A1620 (1965).

[15] Present work.

[16] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

[17] H. Rohrer, Helv. Phys. Acta 33, 675 (1960).

[18] J. L. Olsen, E. Bucher, M. Levy, J. Müller, E. Corenzwit, and T. Geballe, Rev. Mod. Phys. 36, 168 (1964).

[19] E. Bucher, J. Müller, J. L. Olsen, and G. Palmy, Phys. Letters 15, 303 (1965).