

Pressure Dependence of the Superconducting Transition Temperature of Vanadium and Niobium

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The pressure dependence of the superconducting transition temperature T_c of vanadium ($\partial T_c/\partial P = 11 \pm 3 \times 10^{-6}$ °K bar⁻¹) and niobium ($\partial T_c/\partial P = 0 \pm 3 \times 10^{-6}$ °K bar⁻¹) has been studied up to a maximum pressure of 10 kbar. The observed values are compared with values calculated from calorimetric and thermal-expansion data. A possible explanation of the observed variation in the sign of the pressure dependence of T_c in the transition-metal superconductors is offered.

OBSERVATIONS of the pressure dependence of the superconducting transition temperature T_c of vanadium and niobium have been made up to a maximum pressure of 10 kbar. Three samples of vanadium and two of niobium, obtained from various sources and of differing, but high, purities were examined. The analyses, as supplied by the manufacturers, of the samples are given in Table I. The cylindrical samples, ($\frac{1}{4}$ in. diam \times $\frac{3}{8}$ in. long) were prepared from the "as received" material with the exception of sample V3, which was cut from an ingot which we cast in an argon arc furnace. In order to minimize the introduction of strain into the samples during preparation all were cut using spark erosion.

Measurements were made in a Be-Cu alloy pressure capsule similar to that of Bowen and Jones.¹ Superconducting transitions were detected by a standard ac bridge technique with a signal frequency of 1 kc/sec. Temperatures were measured with a Honeywell germanium resistance thermometer, model MHSP 2401, which was calibrated against the vapor pressure of liquid helium 4 at temperatures below 4.2°K using the 1958 helium-4 vapor-pressure-temperature scale. The calibration points were fitted, with no significant deviation, to a function of the form, $\log R = \text{constant} - \log T$. This relationship was used for extrapolation of the calibration to temperatures above 4.2°K. The

superconducting transition temperature of pure lead, as determined in the pressure capsule at atmospheric pressure, using the extrapolated temperature calibration was 7.24 ± 0.02 °K, as against the accepted value of 7.19°K. The superconducting transition temperature of the vanadium sample V2, determined as 5.00 ± 0.01 °K at atmospheric pressure, was independently checked in another laboratory,² a value of 4.97 ± 0.01 °K being obtained. From these measurements it is concluded that the uncertainty in the absolute temperature, as determined with this thermometer, is ± 0.05 °K between 4.2 and 7°K and that it may be as high as ± 0.1 °K for temperatures between 7 and 10°K. However, in the present measurements we are primarily concerned with the variation of the transition temperature and this can be determined to ± 0.01 °K.

Superconducting transition curves were continuously recorded on a Moseley Autograf recorder. The X and Y fixes of the recorder were driven, after suitable amplification, by the voltage developed across the thermometer and by the rectified off-balance voltage from the detector bridge. The latter changed appreciably only during the superconducting transition.

Typical superconducting transition curves, which have been taken directly from the recorder trace, are shown in Fig. 1 for a sample of each element. All of the vanadium and niobium samples examined showed struc-

TABLE I. Sample analysis; all impurities are in ppm by weight.

Sample	Source	Purity (wt%)	O	N	H	C	Fe	Ni	Mg	Si	Mn	Mo	Ta	Cr	Ti
V2	Materials Research Corporation	>99.97	100	30	0.7	65	20	<10	<5	25	...	15
V3	Ames, Iowa	>99.9	345	35	10	150	330	40	<20	<40	<20	<80	45
V4	U. S. Bureau of Mines	>99.8	830	30	900	30
Nb2	Wah Chang Corporation	>99.9	<50	46	3.8	30	<100	<20	<20	<100	<20	<20	<500	<20	...
Nb3	Materials Research Corporation	>99.99	10	10	...	8	<10	<5	...	20	20	<10	...

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¹ D. H. Bowen and G. O. Jones, Proc. Roy. Soc. (London) A254, 522 (1960).

² We are indebted to Dr. T. Geballe of the Bell Telephone Laboratories, Murray Hill, New Jersey for this measurement.

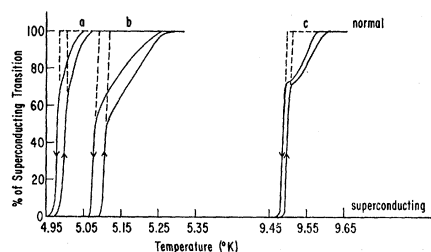


FIG. 1. The recorder traces of three typical superconducting transitions. (a) sample V2 at atmospheric pressure; (b) sample V2 at 8.5 kbar; (c) sample Nb2 at atmospheric pressure.

ture, similar to that shown in Fig. 1, in the initial stages of the superconducting transition. This structure is presumably associated with the presence of impurities or strains in the samples although it is also possible that it is a surface effect. Curves (a) and (b) are taken from measurements on the vanadium sample V2; curve (b) taken at 8.5 kbar exhibits the most extensive structure observed. Curve (c), on the niobium sample Nb2, was taken at atmospheric pressure and the transition remained essentially unchanged up to the highest pressure applied. In all cases the sharp, linear region of the transition curve was used to determine the superconducting transition temperature. This was taken, for both the warming and cooling cycles through the transition, as the temperature given by the intersection of the extrapolated normal trace and the extrapolation of the linear portion of the transition curve (see the dashed lines in Fig. 1). The mean of the two temperatures thus obtained has been taken as T_c .

Values of T_c for vanadium and niobium, as functions of pressure, are shown graphically in Figs. 2 and 3, respectively. The values of $\partial T_c/\partial P$ deduced from these plots for the different samples of each element agree within the limits of experimental accuracy. The mean value of $\partial T_c/\partial P$ for each element is given in Table II. The atmospheric pressure value of T_c , on the other hand, varies appreciably for the different samples of vanadium and niobium. This variation is again a

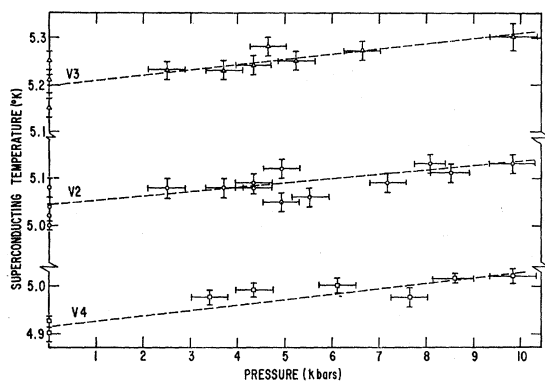


FIG. 2. The variation of the superconducting transition temperature of vanadium with applied pressure.

reflection of the difference in purity and the state of strain of the various samples. A similar insensitivity of the value of $\partial T_c/\partial P$ to the purity of the sample was also observed for tantalum, the remaining group VB element, by Swenson.³

It would be of interest to compare our observed values of $\partial T_c/\partial P$ for each element with the values determined from Ehrenfest's thermodynamic relationship for a phase change of the second kind,⁴

$$\left(\frac{\partial T_c}{\partial P}\right)_{H=0} = \frac{VT_c(\alpha_n - \alpha_s)}{C_n - C_s}, \quad (1)$$

where α and C are the volume thermal expansion coefficient and the specific heat in the normal (n) and the superconducting (s) states, respectively, measured at the superconducting transition temperature in zero magnetic field. Unfortunately, though experimental values of $C_s - C_n$ are readily available,⁵⁻⁷ there are no data for $\alpha_s - \alpha_n$. White⁸ expressed his thermal expansion data on vanadium, niobium, and tantalum in the nor-

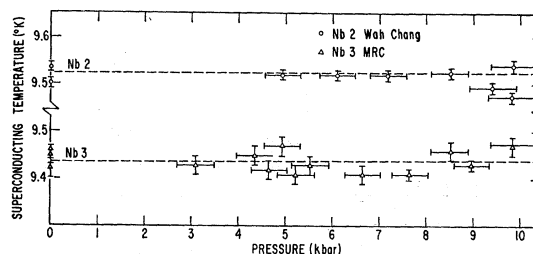


FIG. 3. The variation of the superconducting transition temperature of niobium with applied pressure.

mal and superconducting states in terms of $(\partial H_c/\partial P)$ calculated from the relationship,⁴

$$V_n - V_s = V_s \frac{H_c}{4\pi} \left(\frac{\partial H_c}{\partial P}\right)_T + \frac{H_c^2}{8\pi} \left(\frac{\partial V_s}{\partial P}\right)_T, \quad (2)$$

where $V_n - V_s$ is the difference in the volume between the normal (n) and superconducting (s) states. Unfortunately, due to a lack of reproducibility and to hysteresis effects, the volume change, $V_n - V_s$, could not be measured directly and, therefore, had to be estimated. He used calorimetric values of H_c in his calculations (except for tantalum) and his results are given

³ C. A. Swenson, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 11, p. 119.

⁴ See D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, England, 1960) for derivations of the necessary thermodynamic relationships.

⁵ W. S. Corak, B. B. Goodman, C. B. Satterthwaite, and A. Wexler, *Phys. Rev.* **102**, 656 (1956).

⁶ D. White, C. Chou, and H. L. Johnston, *Phys. Rev.* **109**, 797 (1958).

⁷ C. Chou, D. White, and H. L. Johnston, *Phys. Rev.* **109**, 788 (1958).

⁸ G. K. White, *Cryogenics* **2**, 292 (1962).

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

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

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

we express the measured values⁵⁻⁷ of $C_s - C_n$ in terms of $(\partial H_c/\partial T)_{T=T_c}$ using the Rutgers relationship,⁴

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

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 vanadium⁵ 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 Swenson⁹ 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 V¹⁵) 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 BCS¹⁶ relationship,

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

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

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

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

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

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 . Rohrer¹⁷ 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).

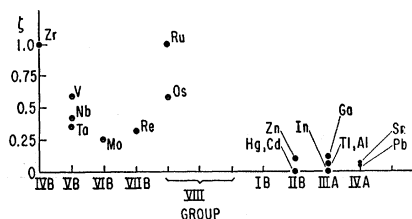


FIG. 4. The variation of ζ with position in the periodic system.

workers¹⁸⁻²¹ have made extensive studies of the correlation between φ and the isotopic mass dependence of T_c . In the BCS formalism the role of the phonon spectrum in the attractive interaction leads to a mass dependence of $M^{-0.5}$. This has been termed the "normal isotope effect." Now deviations from a coefficient of 0.5 may be written as $0.5(1-\zeta)$, where ζ is taken as a measure of the departure from the "normal isotope effect." The largest values of ζ have been observed in the transition metal superconductors.²² Swihart,²³ Morel and Anderson²⁴ and Garland²² have been able to explain these deviations by using a more realistic value for the cutoff energy of the Coulomb interaction than that employed in the BCS formalism.

The theory of Morel and Anderson²⁴ leads to the simple expression,

$$\zeta = (K_c^*/(K_p - K_c^*))^2, \quad (8)$$

where $K_p - K_c^*$ replaces the $N(0)V$ of the BCS rela-

tionship; K_p and K_c^* representing the phonon and screened Coulomb interactions, respectively. For the nontransition metal superconductors ζ is almost zero and it follows, therefore, from (8) that K_c^* must be very small compared to K_p . The importance of K_c^* in the transition metal superconductors may be inferred from the larger values of ζ observed.²² It has been suggested by Bucher, Müller, Olsen, and Palmy¹⁹ that the disappearance of superconductivity at each end of the transition series is due to the rapid increase in K_c^* . Values of ζ for all of the superconducting elements, shown plotted in Fig. 4 as a function of position in the periodic table, support this suggestion. Estimates of ζ for V, Ta, Nb, Re, Ga, and Al, for which no direct isotope measurements are available, were made from φ using the empirical relationship of Bucher *et al.*¹⁹ It is concluded, therefore, that the increased influence of K_c^* upon the superconducting transition temperatures of Zr and V results in the observed sign of the pressure dependence of T_c . Such an explanation is also undoubtedly applicable for the dramatic pressure dependence of T_c observed for La¹³ and U,¹⁴ but here the situation is complicated by the presence of f character in the electron wave functions at the Fermi surface.

It is interesting to make a comparison, in Fig. 4, of ζ for V, Nb, and Ta in group VB and Ru and Os in group VIII. This would indicate a decrease in the influence of K_c^* in going from the $3d$ to the $5d$ elements. This may be associated with the increasing width of the d band of the later transition metals.

We can see a definite need for further investigation of the pressure dependence and the isotope effect on the superconducting transition temperature of the remaining transition metal superconductors. Unfortunately, the experimental difficulties involved are quite considerable.

We should like to thank H. London, K. Andres, and M. A. Jensen for a number of informative discussions.

²⁰ K. Andres, J. L. Olsen, and H. Rohrer, IBM J. Res. Develop. **6**, 84 (1962).

²¹ E. Bucher, F. Heiniger, J. Müller, and J. L. Olsen, in *Proceedings of The Ninth International Conference on Low Temperature Physics, Columbus, Ohio 1964*, edited by J. G. Daunt, D. V. Edwards, F. J. Milford, and M. Yaqub (Plenum Press, Inc., New York, 1965).

²² J. W. Garland, Phys. Rev. Letters **11**, 114 (1963).

²³ J. C. Swihart, IBM J. Res. Develop. **6**, 14 (1962).

²⁴ P. Morel and P. W. Anderson, Phys. Rev. **125**, 1263 (1962).