Heat capacity of technetium*

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(Received 30 June 1975)

The heat capacity of technetium has been measured in zero field between 3 and 15 K. A superconducting transition temperature $T_c = 7.86$ K is found. The electronic heat-capacity coefficient and zero-degree Debye temperature are 4.30 mJ/moleK^2 and 454 K, respectively. An electron-phonon enhancement factor of 0.65 is found from the McMillan equation. The thermodynamic properties of the superconducting state also indicate that technetium is an intermediate-coupling superconductor.

Technetium has the second-highest superconducting transition temperature of any element at zero pressure. However, extensive physical-property measurements have been made possible only in recent years, with the availability of ^{99}Tc from nuclear fuel element reprocessing. The decay of ^{99}Tc by soft β^- emission results in a self-heating power of $\simeq 15\ \mu W/g$, which is sufficiently large to preclude low-temperature calorimetric studies by conventional dc methods. In this paper we report the first heat-capacity measurements on technetium, made in zero-field between 3 and 15 K using a new heat-pulse method[1] designed for use with self-heating samples.

The sample, spark cut from a 6-mm-diam polycrystalline rod, was annealed in high vacuum ($\leq 10^{-6}$ Torr) for 5 h at 1200 °C, followed by 16 h at 950 °C. The resistance ratio, $\rho(300\,\mathrm{K})/\rho(8\,\mathrm{K})$, was 420 after annealing. This compares to ratios of 97 and 70 reported for the samples used in previous magnetic[2] and resistivity[3] studies. Because of the radioactivity, both the sample preparation and the heat-capacity measurements were conducted inside a glovebox. The calorimeter has been described in detail elsewhere.[1] The accuracy of the data is about 1%.

The heat-capacity data are shown in Fig. 1, plotted as C/T vs T^2. A superconducting transition was observed at $T_c = 7.86$ K (as determined below). The finite width of the transition shown in Fig. 1 (~ 0.5 K) is associated with the finite temperature increment used in the heat-pulse measurements (typically $\simeq 0.1\ T$) and not with an intrinsic property of the sample.[4] The precise value of T_c was found by examining those data points for which the temperature pulse overlaps T_c and utilizing the expression

$$\Delta Q = \int_{T_1}^{T_2} C(T)\,dT = \int_{T_1}^{T_c} C_s(T)\,dT + \int_{T_c}^{T_2} C_n(T)\,dT$$

to solve for T_c. In this expression ΔQ is the measured amount of heat delivered to the sample to cause the temperature to increase from T_1 to T_2. $C_s(T)$ and $C_n(T)$ are the heat capacities of the superconducting and normal states, respectively. $C_s(T)$ near T_c was determined from an extrapolation of a polynomial fit to the data below T_c; $C_n(T) = \gamma T + \beta T^3$ was calculated using the values for γ and β as determined below. The uncertainty in the value of T_c determined this way is less than ± 0.01 K. The T_c for this sample is close to the value found by Sekula *et al.*[2] (7.77 K), but is somewhat higher than that reported for a less-pure sample (7.46 K).[5]

Because of expected deviations from the simple T^3 lattice law at temperatures only slightly above T_c, it was not certain that the electronic heat-capacity coefficient γ and the zero-degree Debye temperature Θ_0 could be reliably extracted from a plot of C/T vs T^2 using only the data above 7.86 K. Therefore, these parameters were determined us-

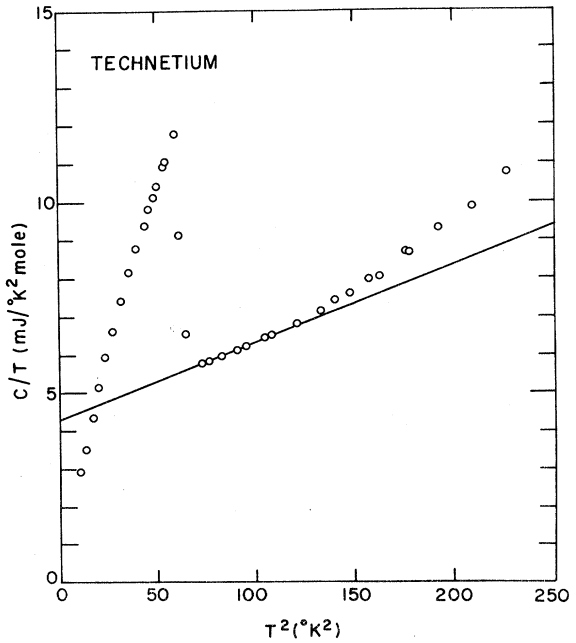

FIG. 1. C/T vs T^2 between 3 and 15 K for technetium. The solid line corresponds to $C = 4.30T + 0.0219T^3$ mJ/moleK, as discussed in the text.

ing a different method, which utilizes the constraint that at T_c the entropies S_s and S_n of the superconducting and normal states are equal. We assume that at T_c the normal-state heat capacity is given by

$$C_n(T_c) = \gamma T_c + \beta T_c^3.$$

Then,

$$S_s(T_c) = \int_0^{T_c} \frac{C_s(T)}{T}\, dT = S_n(T_c) = \gamma T_c + \tfrac{1}{3}\beta T_c^3.$$

Knowing $C_n(T_c)$ and $S_s(T_c)$, we can determine γ and β. $S_s(T_c)$ was determined by a graphical integration of $C_s(T)/T$ between zero temperature and T_c. We find $\gamma = 4.30 \pm 0.05$ mJ/mole K^2 and $\beta = 0.0211 \pm 0.006$ mJ/mole K^4, which corresponds to $\Theta_0 = 454 \pm 4$ K. The principal source of the stated uncertainties in the γ and β values is due to the extrapolation of the $C_s(T)/T$ curve to zero temperature required for the entropy determination. The value for Θ_0 is in excellent agreement with the result from low-temperature ultrasonic measurements,[6] which also yield $\Theta_0 = 454$ K.

As a check of the above analysis, a separate determination of γ and β was made by fitting the normal state data (7.9 – 15 K) to a series in odd powers of T. Terms up to T^7 were needed to characterize the data over the entire range; the use of additional higher-order terms resulted in an increase of the rms deviation of the fit. Accordingly, the normal state data is best described by

$$C_n(T) = \gamma T + \beta T^3 + \delta T^5 + \mu T^7. \qquad (1)$$

When $C_n(T)$ is expressed in units of mJ/mole K, the coefficients in (1) and their standard deviations are $\gamma = 4.29 \pm 0.1$, $\beta = 0.0227 \pm 0.003$, $\delta = (-6.5 \pm 2) \times 10^{-5}$, and $\mu = (4.3 \pm 0.7) \times 10^{-6}$. The values obtained for γ and β (corresponding to $\Theta_0 = 441 \pm 18$ K) are consistent with those determined above; however, the relatively large standard deviations of the coefficients in (1) indicate that this analysis is somewhat less reliable than that using the entropy constraint. The curve $C/T = \gamma + \beta T^2$ is shown in Fig. 1 as the solid line, and we note that it nicely describes the data up to about 11 K $\approx \frac{1}{40}\Theta_0$.

An electron-phonon enhancement factor $\lambda = 0.65$ is obtained from the McMillan equation,[7] using the measured values of Θ_0 and T_c and assuming $\mu^* = 0.13$. The bare density of electronic states is given by $N(0) = 3\gamma/2\pi^2 k_B^2(1+\lambda) = 1.10$ eV^{-1}.

The heat-capacity jump at T_c is $\Delta C \equiv C_s(T_c) - C_n(T_c) = 1.57\, \gamma T_c$, close to the BCS prediction of 1.52. The thermodynamic critical field $H_c(T)$ was determined in the usual way from the differences between the free energies of the normal and superconducting states. The free energies were calculated by graphically integrating the entropies as functions of temperature between T and T_c. For zero temperature a value of $H_c(0) = 1331 \pm 10$ Oe was obtained. The uncertainty reflects the maximum error that could have been introduced from the extrapolation of the S vs T curves to $T = 0$. An upper limit to $H_c(0)$ of 1410 Oe had been determined from magnetization measurements.[2] For weak-coupling superconductors ($\lambda \ll 1$) the BCS theory predicts $\gamma T_c^2 / V H_c^2(0) = 0.170$, where V is the molar volume. For technetium this predicts $H_c(0) = 1336$ Oe, in excellent agreement with the present calorimetric determination, even though the magnitude of λ shows that technetium cannot be considered a weakly coupled superconductor. The deviation of $H_c(T)$ from the parabolic temperature dependence predicted by the two-fluid model is shown in Fig. 2 where the function $D(t) = H_c(t)/H_c(0) - (1 - t^2)$ is plotted versus reduced temperature squared, $t^2 = T^2/T_c^2$. Also shown are the BCS prediction for weakly coupled superconductors, as well as the $D(t)$ curve for Nb.[8] These data are consistent with the magnitude of the λ value, since they indicate that Tc is not as strongly coupled as Nb. This also explains why the quantities ΔC and $H_c(0)$ are more precisely predicted from the BCS theory for Tc than they are for Nb.

From the Rutgers relation

$$\left(\frac{dH_c}{dT}\right)^2_{T_c} = \frac{4\pi \Delta C}{V T_c},$$

we obtain $(dH_c/dT)_{T=T_c} = 316$ Oe/K. This compares to the value 322 Oe/K obtained from direct magnetic measurements.[2]

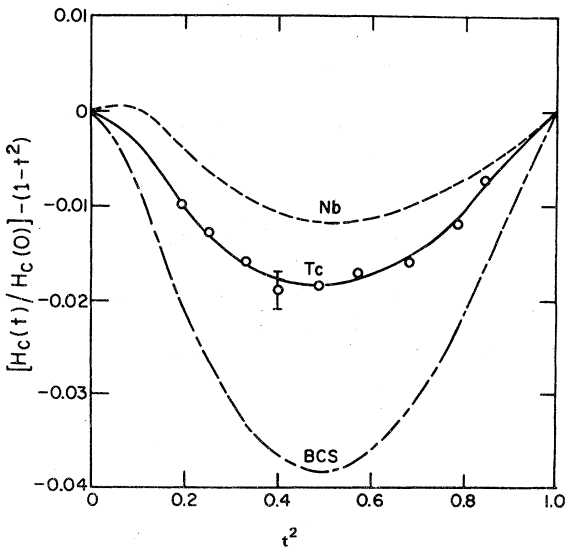

FIG. 2. Deviation of $H_c(T)$ from the two-fluid model prediction. The function $H_c(t)/H_c(0) - (1 - t^2)$ is plotted versus $t^2 = (T/T_c)^2$. Also shown are the BCS prediction and data for Nb (taken from Ref. 8). The error bar represents the approximate uncertainty in the curve for Tc.

TABLE I. Normal- and superconducting-state parameters for technetium, determined from heat-capacity measurements. See text for meaning of symbols.

T_c (K)	7.86
γ (mJ/mole K^2)	4.30 ± 0.05
Θ_0 (K)	454 ± 4
λ	0.65
$\Delta C/\gamma T_c$	1.57
$H_c(0)$ (Oe)	1331 ± 10
$(dH_c/dT)_{T=T_c}$ (Oe/K)	316

The electronic heat capacity of the superconducting state C_{es} was analyzed by plotting $\log(C_{es}/\gamma T_c)$ vs T_c/T. For $T_c/T > 1.5$, C_{es} is well described by $C_{es} = a\gamma T_c e^{-bT_c/T}$, where $a = 8.4$ and $b = 1.53$, compared to the BCS values 8.5 and 1.44, respectively. No deviations from this dependence are observed; however, previously observed deviations from exponential behavior in V and Nb occurred at higher values of T_c/T than could be attained in these measurements. Previous magnetization measurements[2] have indicated that, at lower temperatures, effects due to energy-gap anisotropy might be present in Tc.

The calorimetrically determined superconducting and normal state parameters for technetium are summarized in Table I.

Finally, it is interesting to compare technetium (which has a $4d^7$ configuration) with its $5d^7$ counterpart, rhenium ($\lambda = 0.45$, $T_c = 1.69$ K) because of the large difference between their transition temperatures. Both elements have the hcp structure. According to McMillan,[7] $\lambda = N(0)I/M\langle\omega^2\rangle$, where M is the atomic mass, I is an average-squared electronic matrix element, and $\langle\omega^2\rangle$ is an average-squared phonon frequency. In the absence of detailed information about the phonon spectrum of Tc, we assume $\langle\omega^2\rangle \approx \Theta_0^2$. It is then found that the difference between the quantity $N(0)I \approx \lambda M\Theta_0^2$ for Tc and Re is less than 5%, indicating that the difference in λ-values is determined by the phonon factor $M\langle\omega^2\rangle$. This is not surprising, since a similar result for bcc transition metals is well known.[7] Thus, the explanation of the different T_c values for these two elements appears to require an understanding of why the Re lattice is harder than predicted from the simple $M^{-1/2}$ variation of Θ_0 expected for isostructural systems. Although preliminary de Haas–van Alphen work indicates that the band structures of Re and Tc are probably very similar,[9] it is likely that the relatively broad $5d$ orbitals in Re participate in bonding to a greater extent than the narrower $4d$ orbitals in Tc.

ACKNOWLEDGMENTS

We would like to thank G. J. Pokorny for experimental assistance and A. J. Arko for several helpful discussions.

*Research supported by the U. S. Energy Research and Development Administration.

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[4]With our technique (see Ref. 1) the temperature difference between the sample and its environment is measured continuously. During a heat pulse this temperature difference increases by an amount δT due to the finite response time of the temperature controller used with this method. As shown in Ref. 1, $\delta T \propto C^{-1}$, and is therefore sensitive to sharp changes in C. For technetium δT exhibits a sharp jump at T_c for temperature pulses overlapping T_c. The width of this discontinuity, which measures the width of the superconducting transition, is ≤ 0.05 K. Resistivity measurements on the same sample indicated $T_c = 8.0$ K with a transition width of < 0.07 K. Since the temperature control was not ideal, and the measurements were made in the presence of moderate drifts, this value for the width represents an upper limit.

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