Heat Capacity of Tantalum in the Normal and Superconducting States: Identification of the Contributions

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Abstract—Tantalum is used as an example to show that a statistical thermodynamic approach applied in the regions of the superconducting and normal states of the metal can estimate the reliable thermodynamic parameters that are related to the heat capacity of the metal (electronic heat capacity coefficient ζ, Debye temperature θ_D) and can estimate their errors statistically. The calculated heat capacity and the determined low-temperature values of the parameters agree satisfactorily with the data of self-consistent thermodynamic calculations performed in an extended temperature range.

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INTRODUCTION

Metallic tantalum is widely used due to a unique set of its physicochemical and technical properties [http://ru.wikipedia.org]. Tantalum is one of the refractory ($T_m \approx 3290$ K) and corrosion-resistant metals; as a result, it is applied to produce the parts of the equipment intended for operation at very high temperatures and in aggressive media. Tantalum is widely employed in ferrous metallurgy as an alloying element for the manufacture of special steels and alloys. Moreover, it is characterized by high biological compatibility with living tissues; therefore, it is widely used in medicine as a pin material.

The physical properties of tantalum are also unique, which provokes constant scientific interest in it as a convenient model object for testing various theories of formation of the thermophysical properties of condensed substances (see, e.g., [1–8]). The modern approaches to the calculation of thermodynamic properties include the ab initio calculations that are based on various concepts of the electronic structure of a metal and its "deformation" as a function of temperature and pressure. Computer programs for such calculations are well developed. Unfortunately, good agreement between the results of such calculations and experimental data was only obtained in a few cases for some properties in limited temperature and pressure ranges. In particular, it is difficult to calculate the heat capacity of tantalum $C(T)$ and the derivative properties, namely, Debye temperature $\theta_D(T)$ and electronic heat capacity coefficient ζ [9–20]. However, it is these properties that substantially determine the change in the thermodynamic properties of tantalum at intermediate and high temperatures.

According to various data, the low-temperature limit of the Debye temperature θ_D^0 of tantalum changes from 217 K [21] to 250 K [15]; moreover, there is no generally accepted opinion regarding both the value and character of the $\theta_D(T)$ dependence. For example, Debye temperature $\theta_D(T)$ found from calorimetric measurements first decreases from $\theta_D^0 = 236$ to 226 K at $T = 45$ K and then rapidly increases to 312 K at $T = 273$ K [12], whereas other authors (see, e.g., [7, 16]) point to a smooth change in function $\theta_D(T)$ from low-temperature value θ_D^0 to 220–230 K at room temperature. According to various authors, the electronic heat capacity coefficient of tantalum ζ (mJ mol^{-1} K^{-2}) falls in the range from 3.33 ± 0.05 [20] to 7.83 [19]; in most works, its values lie in the range $5 \leq \zeta \leq 7$. In other words, there is no generally accepted value of ζ.

The significant uncertainty in the values of the Debye temperature and the electronic heat capacity coefficient indicates that a number of the basic properties of tantalum are poorly understood. In turn, this results in certain difficulties for the development of models for the thermodynamic properties of tantalum that use parameters θ_D and ζ, such as the self-consistent thermodynamic model (SCTDM) of solids [22–25]. Therefore, the necessity of refinement of some thermodynamic parameters of tantalum is obvious, and this is the purpose of this work.

The study of the heat capacity of tantalum at low temperatures is of particular scientific interest due to the following reasons. First, tantalum is a superconductor with a rather high superconducting transition temperature $T_{sc} = 4.39$ K; from this standpoint, it is a
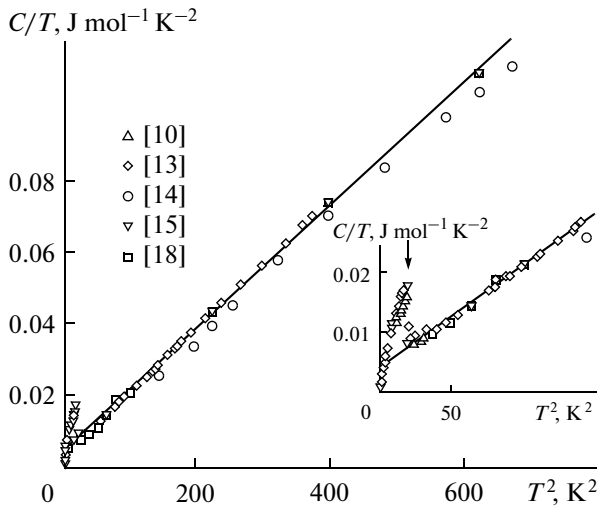
Fig. 1. C/T vs. T^2 for tantalum at low temperatures: (points) experimental (reference) calorimetric data [10, 13–15, 18] and (solid line) linear trend. (inset) C/T vs. T^2 for tantalum at below 12 K. The arrow indicates the superconducting transition temperature.

convenient model object (see, e.g., [17, 19, 20]). Tantalum is considered to be a simple superconductor, and a change in it thermodynamic properties is well described by the Bardeen−Cooper−Schrieffer (BCS) theory [26]. Nevertheless, there exist modern works disputing with this concept (see, e.g., [20]). Therefore, this problem requires an additional investigation.

Second, low-temperature data on the heat capacity of a metal make it possible to separate the contributions to the total heat capacity that are caused by the crystal lattice (Debye contribution), which is proportional to T^3, and by the conduction electron subsystem (electron contribution in the normal state), which is proportional to T,

$$C = \frac{12\pi^4}{5} R \left(\frac{T}{\theta_D^3}\right)^3 + \zeta T. \quad (1)$$

In practice, these contributions are separated by the dependence of C/T on T^2 and by a linear interpolation of this dependence by the least squares method (linear regression),

$$\frac{C}{T} = \zeta + \frac{12\pi^4 R}{5\theta_D^{0^3}} T^2. \quad (2)$$

In Eqs. (1) and (2), $R = 8.31441$ J mol^{-1} K^{-1} is the gas constant and θ_D^0 is the low-temperature limit of the Debye temperature. It should be noted that the described simple scheme is idealized and that it is complicated for real metals, in particular, because of the fact that the phonon spectra of substances are much more complex than in the Debye model. This behavior can be represented as a temperature depen-

dence of Debye temperature $\theta_D^0(T)$. For some metals, this dependence is rather strong, which is most pronounced at low temperatures. In turn, this finding leads to a nonlinear $C/T(T^2)$ dependence and to the problem of a correct choice of the temperature range ΔT in which the $C/T(T^2)$ dependence can be described by a linear trend. Even small errors in choosing range ΔT can result in noticeable errors for the linear regression parameters. In turn, these errors can be decisive for, e.g., estimating the electronic heat capacity of a solid metal in a wide temperature range.

RESULTS AND DISCUSSION

Figure 1 shows the low-temperature $C/T(T^2)$ dependence for tantalum. Allowing for the analysis made above, we analyze the $C/T(T^2)$ dependence for the ΔT_1 range $T_{sc} < T < \theta_D^0/10$, where $\theta_D^0/10 \approx 20$ K. With allowance for the standard errors, the linear trend (linear regression) coefficients found by the least squares method are $\zeta = 4.08 \pm 0.22$ mJ mol^{-1} K^{-2} and $12\pi^4 R/5\theta_D^{0^3} = 172.4 \pm 1.4$ μJ mol^{-1} K^{-5}. From the last coefficient, the low-temperature limit of the Debye temperature for tantalum can be estimated at $\theta_D^0 = 224.25 \pm 0.62$ K. The high linear correlation coefficient squared ($R^2 = 0.9963$) indicates good quality of the linear regression of the $C/T(T^2)$ dependence for tantalum.

To perform a crosscheck of the reliability of our results, we constructed a linear regression of the $C/T(T^2)$ dependence in the temperature range ΔT_2 $1 < T < 20$ K. The electronic heat capacity of tantalum at $T < T_{sc}$ was taken for the normal state of the superconductor; that is, it was measured in a magnetic field higher than the critical field. Although this is usual practice, the possible dependence of the heat capacity of the electron subsystem on the magnetic field should also be taken into account. The following parameters were calculated for range ΔT_2: $\zeta = 4.54 \pm 0.20$ mJ mol^{-1} K^{-2}, $12\pi^4 R/5\theta_D^{0^3} = 170.2 \pm 1.4$ μJ mol^{-1} K^{-5}, $\theta_D^0 = 225.21 \pm 0.60$ K. The linear correlation coefficient squared is $R^2 = 0.9958$. The agreement for both sets of the results is satisfactory for all parameters except for electronic heat capacity coefficient ζ: the relative difference in its values reaches 11%, whereas the difference in the values of θ_D^0 is slightly larger than 0.4%. The significant differences in the values of ζ again indicates the importance of careful justification of calculation temperature range ΔT. The detected differences can be explained by the dependence of the heat capacity of the electron subsystem in the superconductor on the magnetic field.
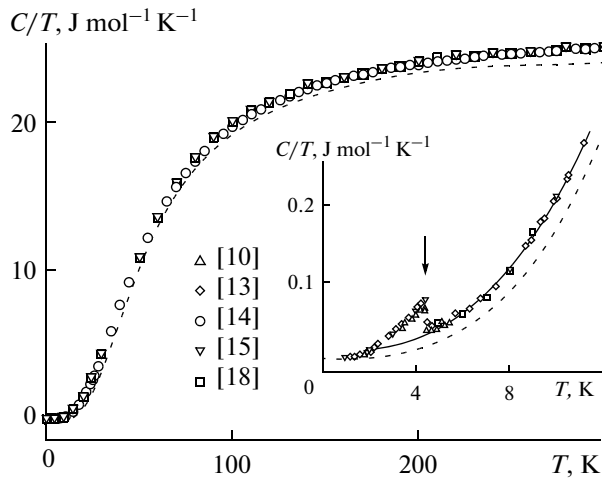
Fig. 2. Temperature dependence of the heat capacity $C(T)$ of tantalum at below 300 K: (lines) self-consistent calculation ((solid line) total heat capacity, (dotted line) lattice part of the heat capacity) and (points) experimental (reference) data [10, 13–15, 18]. The arrow indicates the superconducting transition temperature in the heat capacity curve $C(T)$ of tantalum below 12 K.

Fig. 3. Temperature dependence of the electronic heat capacity $C_e(T)$ of tantalum at low temperatures: (points) experimental (reference) data [10, 13, 15, 18], (lines) calculation results ((solid line) electronic heat capacity in the normal (Sommerfeld model) and superconducting (BCS model) states, (dashed line) quadratic interpolation of the heat capacity in the superconducting state, (dotted line) extrapolation of the normal electronic heat capacity to the superconducting state). The arrow indicates the superconducting transition temperature.

Figure 2 shows the heat capacity of tantalum over a wide temperature range ($0 < T \le 300$ K). The empirical data for the $C(T)$ dependence of various authors (Fig. 2, points) agree well with each other and with the heat capacity calculated in terms of SCTDM for solids [22–25]. The dotted line shows the calculated phonon (lattice) part of heat capacity $C_p(T)$, and the solid line illustrates total heat capacity $C(T) = C_p(T) + \zeta T$. Without analyzing the SCTDM calculation results (which requires a separate investigation), we note that the electronic heat capacity coefficient considered in the SCTDM model as a free parameter is $\zeta = 4.00$ mJ mol^{-1} K^{-2}, which agrees with the value of ζ obtained from an analysis of the low-temperature heat capacity of tantalum in temperature range ΔT_1 accurate to 2%.

The temperature dependence of the Debye temperature of tantalum calculated with the SCTDM model is weak, which is in conflict with the calorimetric data in [12]: $\theta_D^0(T)$ decreases monotonically from $\theta_D^0 = 236.0$ K at $T \to 0$ to 235.3 K at $T = 300$ K. The calculated value of θ_D agrees with θ_D^0 obtained from an analysis of the low-temperature heat capacity of tantalum accurate to ~5%. In other words, the heat capacity of metallic tantalum well follows a simple thermodynamic model with constant parameters ζ and θ_D^0 over a wide temperature range (up to 300 K or above; the discrepancy between the experimental and calculated values of $C(T)$ becomes significant above ~700 K).
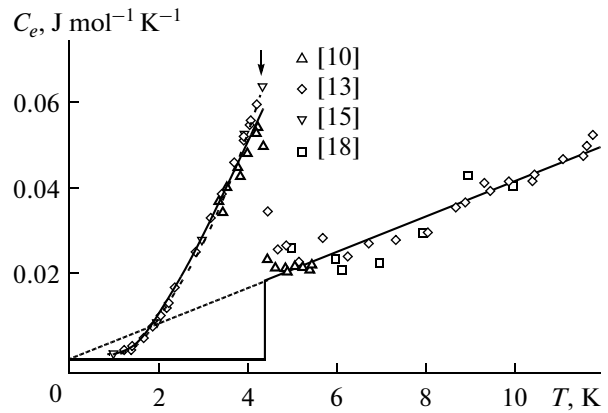
The electronic heat capacity of tantalum in the normal and superconducting phases can be separated as the difference between the total heat capacity and its phonon part,

$$C_e(T) = C(T) - C_p(T). \qquad (3)$$

Figure 3 shows the separated electronic part of the heat capacity of tantalum. The electronic heat capacity in the normal phase is linear in temperature and is satisfactorily described by the Sommerfeld model, $C_e(T > T_{sc}) = \zeta T$. In the superconducting state, the electronic heat capacity in terms of the BCS theory is described by an exponential function of temperature [17, 26],

$$C_e(T < T_{sc}) = A \exp\left[-\frac{\Delta(0)}{2k_B T}\right], \qquad (4)$$

where A is a constant dependent on the properties of the superconductor, k_B is the Boltzmann constant, and $\Delta(0)$ is the energy gap of the superconductor at $T \to 0$. The BCS model is generally accepted, at least for simple superconductors, including tantalum. However, as noted above, some authors state that the heat capacity of tantalum in the superconducting state follows a simple T^2 power law (see, e.g., [20]),

$$C_e(T < T_{sc}) = B_0 + B_2 T^2, \qquad (5)$$

where B_0 and B_2 are empirical coefficients having no clear physical meaning. To check the adequacy of the statements expressed by Eqs. (4) and (5) is one of the purposes of this work.

The correspondence of the detected electronic heat capacity of superconducting tantalum to the BCS
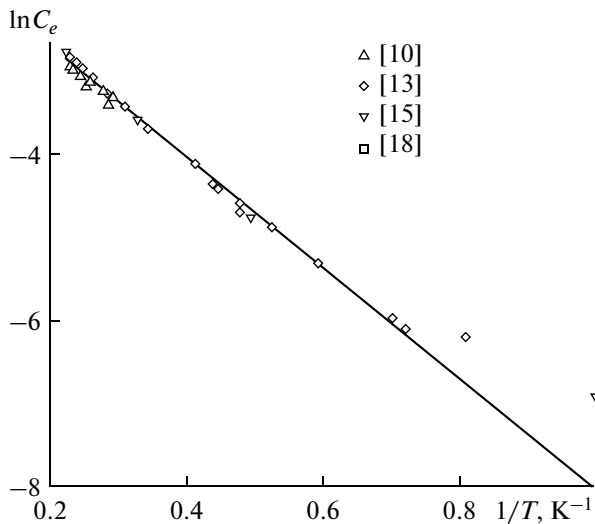
Fig. 4. Function $\ln C_e(1/T)$ for tantalum in the superconducting phase: (points) experimental (reference) data [10, 13, 15, 18] and (solid line) linear trend.
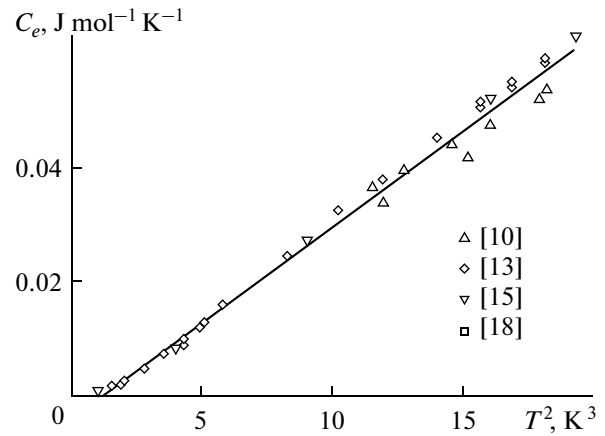

Fig. 5. Function $C_e(T^2)$ for tantalum in the superconducting phase: (points) experimental (reference) data [10, 13, 15, 18] and (solid line) linear trend.

model can be tested by the least squares method, i.e., by analyzing the dependence of $\ln C_e$ on reciprocal temperature $1/T$. This function should be linear,

$$\ln C_e = \ln A - \frac{\Delta(0)}{2k_B}\frac{1}{T}. \qquad (6)$$

Equation (6) for the logarithm of the electronic heat capacity of tantalum separated from the experimental data in [10, 13, 15] using Eq. (3) satisfactorily follows a linear trend ($R^2 = 0.9961$), which supports the correctness of the conclusions made using the BCS theory (Fig. 4). The energy gap of tantalum in the superconducting state that was obtained from a linear regression is $\Delta(0) = 3.09 \pm 0.04$ (expressed in energy units $k_B T_{sc}$, as is common). This value agrees rather well with the values of $\Delta(0)$ calculated by other methods, namely, 3.0 [27] (electron absorption in the far infrared region), 3.4 ± 0.2 [28] (ultrasonic measurements), 3.62 ± 0.06 [29] (ultrasound absorption in a high-purity tantalum single crystal), 3.55 ± 0.02 [30] (surface impedance measurements in the microwave region), and 3.5 [26] (BCS theory). The deviations from the BCS values become noticeable only at the lowest temperatures in the vicinity of the superconducting transition temperature $T_{sc} = 4.39$ K (Figs. 3, 4).

Figure 5 shows the dependence of the "experimental" electronic heat capacity of tantalum [10, 13, 15] on temperature squared given in [20]. This dependence also satisfactorily follows a linear trend ($R^2 = 0.9917$) but is slightly worse than in the case of the BCS theory. The authors of [20] used the data from only one work ([13]) to determine the coefficients in Eq. (5) and found that a function quadratic in T very well describes the empirical $C_e(T^2)$ data ($R^2 = 0.9995$) [13]. Using the least squares method, we found the

parameters in the linear $C_e(T^2)$ regression for tantalum in the superconducting phase, $B_0 = -0.00415 \pm 0.0007$ and $B_2 = 0.00344 \pm 0.00005$. As noted above, coefficients B_0 and B_2 in Eq. (5) have no clear physical meaning, in contrast to the parameters in the BCS theory. Moreover, the calculated $C_e(T)$ dependence with coefficients B_0 and B_2 becomes negative at temperatures $T < 1.1$ K, which obviously has no physical meaning. As noted in [20], this means that the behavior of the heat capacity of tantalum described by Eq. (5) at the lowest temperatures is wrong and should be changed into a more adequate one.

Thus, it should be admitted that there are no reasonable grounds to replace the electronic heat capacity $C_e(T)$ calculated by the BCS theory (see Eq. (4)) and quadratic in T by the $C_e(T)$ dependence (see Eq. (5)) proposed in [20]. In the case of tantalum, the BCS theory is adequate. The idea [20] that quadratic dependence (5) describes the experimental data better than exponential dependence (4) using the BCS model can be explained by the fact that the authors of [20] took into account a single set of experimental data [13], whereas statistical processing of the data from works apart from [13] leads to the converse conclusion. This conclusion emphasizes the importance of statistical processing of the entire experimental information, especially in the important cases of estimating the adequacy of a certain physical theory.

CONCLUSIONS

(1) Using tantalum as an example, we applied a statistical thermodynamic approach to determine the thermodynamic parameters in its superconducting and normal states that are related to the heat capacity of the metal (i.e, electronic heat capacity coefficient ζ, low-temperature limit of Debye temperature θ_D^0,

energy gap $\Delta(0)$). Reliable tabulated values of some of these parameters, e.g., ζ, were absent.

(2) It was shown that, in contrast to the calculations that take into account the results of only single studies, a statistical approach makes it possible to adequately estimate important thermodynamic parameters and to quantitatively describe the thermodynamic functions of metals over a wide temperature range.

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