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DEBYE TEMPERATURE IN THE HIGH-TEMPERATURE LIMIT AND
ANHARMONIC COMPONENT OF THE HEAT CAPACITY OF VANADIUM

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Values are presented for the Debye temperature in the high-temperature limit and the anharmonic component of the specific heat of vanadium at constant volume, based on heat-capacity measurements over the range 77-300°K.

In the high-temperature limit the Debye temperature characterizes the mean frequency $\langle \omega \rangle$ of the phonon spectrum [1] and is defined by the expression

$$\Theta_{\infty}^2 = \frac{5\hbar^2}{3k^2} \langle \omega^2 \rangle. \quad (1)$$

To determine Θ_{∞} by the absolute adiabatic method, the heat capacity of single-crystal vanadium was measured over the temperature range 77-300°K. Measurements were performed by a method similar to that used for study of the heat capacity of scandium, yttrium, and lanthanum [2], to an accuracy of 2% over the indicated temperature range. The specimen studied had a ratio of resistances at $T = 300^{\circ}\text{K}$ and $T = 6^{\circ}\text{K}$ (ρ_{300}/ρ_6) equal to 30.

The curve of the temperature dependence of heat capacity of vanadium showed anomalies in the form of a peak at a temperature of 210°K with $\Delta C_p = 2.5 \text{ J/}^{\circ}\text{K}\cdot\text{mole}$ and an increase in C_p by 3-4% at 240°K.

The specific heat of vanadium at constant volume C_v was calculated from the mean values of specific heat at constant pressure C_p . In calculating C_v the temperature dependence of the volume expansion coefficient β of vanadium given in [3] was used with the electronic component of the specific heat C_{el} with consideration of electron-phonon interaction from [4]. Using the values of the lattice component of specific heat thus obtained ($C_{lat} = C_v - C_{el}$) the temperature dependence of the Debye temperature of vanadium $\Theta(T)$ (Fig. 1, curve 1) was calculated from the relationship

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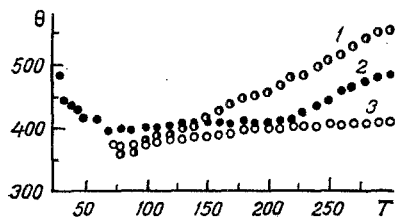


Fig. 1

Fig. 1. Debye temperature of vanadium vs temperature $\Theta(T)$ with consideration (1) and without consideration (3) of electron-phonon interaction, and from results of [5] (2). $\Theta(T)$, T, °K.

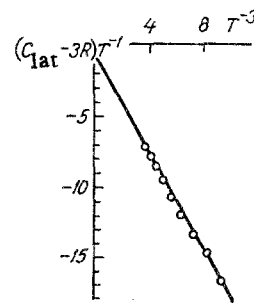


Fig. 2

Fig. 2. Quantity $(C_{\text{lat}} - 3R)T^{-1}$ ($\text{mJ} \cdot \text{°K}^{-2} \cdot \text{mole}^{-1}$) vs T^{-3} ($10^{-8} \cdot \text{°K}^{-3}$) for vanadium.

$$C_{\text{lat}}(T) = C_v^D [\Theta(T)/T]. \quad (2)$$

Figure 1 (curve 2) also shows the function $\Theta(T)$ for vanadium, obtained from the results of [5], with the assumption that the electronic component of the specific heat γ is equal to $9.26 \text{ mJ}/(\text{°K}^2 \cdot \text{mole})$ over the entire temperature interval $77\text{--}300\text{°K}$.

Curve 3 of Fig. 1 was calculated with the present data using the approximation that the electronic specific heat $C_{e1} = 9.26 \text{ mJ}/(\text{°K} \cdot \text{mole})$. As is evident from Fig. 1, consideration of electron-phonon interaction in defining the electronic specific heat of vanadium significantly reduces the value of $\Theta(T)$ in the temperature range $160\text{--}300\text{°K}$.

At temperature $T < \Theta$ the lattice specific heat is defined in the following manner [1, 6]:

$$C_{\text{lat}} = C_{v,h} + C_{v,anh} = 3R \left(1 - \frac{\hbar^2 \langle \omega^2 \rangle}{12k^2 T^2} - \dots \right) + A'T. \quad (3)$$

The anharmonic component of the specific heat $C_{v,anh}$ of the crystalline lattice is proportional to temperature in the first approximation [1]. Equation (3) was analyzed graphically in the coordinates $(C_{\text{lat}} - 3R)T^{-1}$, T^{-3} . The Debye temperature of vanadium in the high-temperature limit Θ_∞ can be defined from the slope of the straight-line curve of $(C_{\text{lat}} - 3R)T^{-1}$ vs T^{-3} over the temperature range $0.7 < T/\Theta < 1.3$. The slope of the straight line shown in Fig. 2 is $-1.76 \cdot 10^5 \text{ J}/\text{°K} \cdot \text{mole}$, which corresponds to $\Theta_\infty = 375\text{°K}$.

The value of the coefficient A' for the anharmonic component of the vanadium specific heat at constant volume can be determined from Fig. 2 using the size of the segment cut off by the straight line on the ordinate axis. The value of A' for vanadium comprised $-0.8 \text{ mJ}/(\text{°K}^2 \cdot \text{mole})$.

It has been established that consideration of electron-phonon interaction in determining the electronic component of vanadium specific heat [4] by the method of [7] leads to a smoother change in the curve $\Theta(T)$ in the temperature region $160\text{--}300\text{°K}$.

Thus, the experimental study of specific heat of vanadium in the temperature range $77\text{--}300\text{°K}$ has produced the value $\Theta_\infty = 375\text{°K}$, which is lower than the Debye temperature determined in the helium temperature range, $\Theta_0 = 425\text{°K}$ [8].

NOTATION

T, absolute temperature; Θ , Debye temperature; Θ_∞ , Debye temperature in high-temperature limit; Θ_0 , Debye temperature at $T = 0\text{°K}$; $\langle \omega \rangle$, mean frequency of phonon spectrum; $\langle \omega^2 \rangle$, second moment of frequency distribution function; ρ_{300} , resistivity at temperature $T = 300\text{°K}$; ρ_6 , resistivity at $T = 6\text{°K}$; C_p , specific heat at constant pressure; C_v , specific heat at constant volume; C_{e1} , electronic component of specific heat; C_{lat} , lattice component of specific heat; C_v^D , specific heat according to Debye model; $C_{v,h}$, specific heat at constant volume in harmonic approximation; $C_{v,anh}$, anharmonic component of specific heat at constant volume; \hbar , Planck's constant; k , Boltzmann's constant; A' , coefficient of anharmonic contribution to specific heat at constant volume.

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EFFECT OF HEAT TRANSFER IN THE IMPULSE METHOD ON THE MEASUREMENT OF THERMOPHYSICAL PROPERTIES

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The paper considers the effect of heat transfer in the impulse method of measurement on the value of the maximum temperature and on the time for achieving its half-value. Taking this heat transfer effect into account increases the accuracy of measuring the thermophysical properties.

The impulse method of determining thermophysical properties using lasers [1, 2] is the most effective of all the known methods. It can be used for determining the thermophysical properties directly in products without the preparation of special samples or setting up laboratory conditions. In this case, however, heat transfer from the free surfaces to the surroundings can have a considerable effect on the results of the measurements, and taking this into account makes possible an improvement in the accuracy of the measurements.

In the measurement of temperature conductivities under laboratory conditions, when heat exchange can be neglected, the essence of the method is as follows [2]. The interaction of a pulsed, focused laser beam with the solid surface can be regarded as the action of an instantaneous point source of heat of intensity q . In this case a temperature field of the following form is set up in a semiinfinite sample [3]:

$$T = \frac{2q}{c_p \rho (4\pi at)^{3/2}} \exp\left(-\frac{R^2}{4at}\right), \quad (1)$$

where $R^2 = x^2 + y^2 + z^2$.

If a thermocouple is placed at some distance y from the point of heat liberation, then after some time it will record a heat pulse which can be described by the dimensionless equation

$$\Theta = Fo^{-3/2} \exp\left(-\frac{1}{4Fo}\right), \quad (2)$$

where $\Theta = 4\pi^{3/2} y^3 c_p \rho T / q$ is the relative excess temperature.