

High-pressure high-temperature equations of state of shocked bcc vanadium

A M Molodets, A A Golyshev and D V Shakhrai

Institute of Problems of Chemical Physics of the Russian Academy of Sciences, Academician
Semenov Avenue 1, Chernogolovka, Moscow Region 142432, Russia

E-mail: molodets@icp.ac.ru

Abstract. The semiempirical free-energy relation for hydrostatically compressed isotropic solid was written for body-centered-cubic (bcc) vanadium as a function of the specific volume and temperature with the phonon component and the contribution of the electronic subsystem. According to the thermodynamic rules the thermal as well as caloric equations of state are defined through the partial derivatives of free energy. A thermal equation of state gives the pressure as a function of volume and temperature. Caloric equation of state specifies the energy as a function of volume and temperature also. The proposed equations of state of bcc vanadium have been verified by comparison of calculated high-pressure isotherms, heat capacity, volume thermal expansion coefficient and Hugoniot with experimental data. The developed equations of state allow to calculate thermal properties of compressed bcc vanadium under static pressure and shock pressures 0–70 GPa and temperatures 100–1000 K.

1. Introduction

The studying of physical properties of vanadium at high dynamic and high static pressure is conducted since 1970. In [1] the possibility of electronic transitions in vanadium was investigated at strong shock compression. In [2] the experimental isotherm up to pressure 80 GPa is received. In the same work structural phase transition of vanadium under pressure 69 GPa without change of number of atoms in an elementary cell (elastic phase transition) is found. Elastic phase transition of vanadium is structural phase transformation of body-centered-cubic (bcc) to rhombohedral structure. Recently this phenomenon involves special attention of researchers.

In [3] investigations of vanadium are undertaken at shock compression for the purpose of detection of its elastic phase transition in shock waves. Authors have found the discontinuity of the sound velocity against shock pressure at 60 GPa. They have connected this feature with transition of vanadium from bcc to rhombohedral structure under shock compression.

Authors [4] have shown that pressure of elastic phase transition in vanadium depends on a state of stress of the sample. They have confirmed the bcc to rhombohedral phase transition at 61.5 GPa under quasihydrostatic compression in the Ne pressure medium. Under the nonhydrostatic condition authors have found the phase transition occurring at 30 GPa at ambient temperature and 37 GPa at 425 K. That is the transition under the hydrostatic condition is hindered and it can occur at much lower pressure under the nonhydrostatic condition.

The pressure dependence of the quasistatic yield strength of vanadium in polycrystalline foils and powders has been measured up to 90 GPa at room temperature [5]. Following an initial increase in the strength with pressure, a decrease in the strength of vanadium was observed



starting at 40–50 GPa. The softening of the yield strength of vanadium at high pressure is associated with a subtle phase transition from bcc to rhombohedral structure.

Thus, in the phase diagram of vanadium at 30–70 GPa the transformations bcc of vanadium occur both at static, and at shock compression. Thereupon construction of the equation of state of the starting bcc-phase vanadium at high pressures and temperatures is an actual problem. It is necessary to notice the equations of state should not only give the adequate description of thermal properties but also to be suitable for modeling of shocked metal with help of mechanics of continua. In many cases the semiempirical equations [6] of state meet these requirements.

The results of semiempirical calculation of thermodynamic characteristics were presented in [7] for twenty seven metals including vanadium. The vanadium results [7] were presented only in pressure-volume curves and shock velocity-mass velocity curve without the numerical values of fitting parameters for semiempirical equation of state. The semiempirical equation of state of vanadium with 9 fitting parameters and their values were presented in [8]. It is necessary to notice, that the high pressure room temperature isotherm [2] and the high-pressure high-temperature isotherms [9] have not been considered in [7, 8]. So the purpose of the given work consisted in development of the semiempirical equation of state for bcc phase vanadium which integrates the available shock and static high-pressure high-temperature experimental data.

2. Analytical form for equations of state

The semiempirical free-energy relation $\Phi(V, T)$ for hydrostatically compressed isotropic solid was written as a function of the specific volume V and temperature T with the phonon component $F(V, T)$ and the contribution of the electronic subsystem $F_e(V, T)$:

$$\Phi(V, T) = F(V, T) + F_e(V, T). \quad (1)$$

The phonon component $F = F(V, T)$ is based on the Einstein oscillators model and was taken as

$$F = E_x + 3R \left[\frac{\Theta}{2} + T \ln \left(1 - \exp \left(-\frac{\Theta}{T} \right) \right) \right]. \quad (2)$$

In equation (2) all designations are traditional, but the such key functions as characteristic temperature Θ and the potential energy E_x are defined by formulas [10]. According with reference [10] the expression for characteristic temperature $\Theta = \Theta(V)$ depending only from volume V , is defined as

$$\Theta = \Theta_0 \left(\frac{v_0 - V}{v_0 - V_0} \right)^2 \left(\frac{V_0}{V} \right)^{2/3}, \quad (3)$$

$$v_0 = V_0 \left(1 + \frac{2}{\gamma_0 - 2/3} \right), \quad (4)$$

where $\Theta_0 = \Theta(V_0)$, $\gamma_0 = \gamma_0(V_0, T_0)$ is the Grüneisen parameter at initial volume V_0 and initial temperature T_0 .

The expression for $E_x = E_x(V)$ is defined as

$$E_x = -v_x (C_1 H_x + C_2 x) + C_3, \quad (5)$$

where

$$H_x = 9 \left(\frac{1}{10} x^{-2/3} + 2x^{1/3} + \frac{3}{2} x^{4/3} - \frac{1}{7} x^{7/3} + \frac{1}{70} x^{10/3} \right), \quad (6)$$

$$x = \frac{V}{v_x}. \quad (7)$$

Table 1. The coefficients for relation $\Phi(V, T)$ (1).

$T_0,$	$V_0,$	$\Theta_0,$	$v_0,$	$v_x,$	$C_1,$	$C_2,$	$C_3,$	$\beta_0,$
K	cm ³ /mol	K	cm ³ /mol	cm ³ /mol	GPa	GPa	kJ/g	mJ/mol K ²
300	8.35	303	29.507	25.467	-124.003	2545.0373	-653.1517	5.0

In equations (5)–(7) the parameter v_x represent the fitting parameters, but the coefficients C_1 , C_2 , C_3 are integration constants. The constants C_1 , C_2 , C_3 are expressed analytically through the handbook thermophysical properties at normal conditions. The optimum value of v_x is defined from a coincidence condition between experimental and computational maximum pressure of a room temperature high pressure isotherm.

The electron component $F_e = F_e(V, T)$ in accord with reference [11] is

$$F_e = -\frac{1}{2}\beta_0 T^2 \left(\frac{V}{V_0} \right)^{1/2}. \quad (8)$$

In line with reference [11], the value of β_0 for solids is taken from experimental data on the heat capacity at low temperatures or it is considered to be an adjusting parameter. In this study we select this coefficient so as to match the calculated temperature dependence of heat capacity to the experimental one.

According to the thermodynamic rules the caloric equation of state (internal energy (E)–volume (V)–temperature (T) relation) is defined through partial derivative of free energy $E = \Phi - T(\partial\Phi/\partial T)_V$. Usage of (1) gives

$$E = E_x + 3R\Theta \left(\frac{1}{2} + \frac{1}{\exp(\Theta/T) - 1} \right) + \frac{1}{2}\beta_0 \left(\frac{V}{V_0} \right)^{1/2} T^2. \quad (9)$$

Similarly thermal equation of state (relation of the pressure, P , the volume, V , and the temperature, T) $P = P(V, T) = -(\partial\Phi/\partial V)_T$ is

$$P = C_1 F(x) + C_2 + 3R\frac{\gamma}{V}\Theta \left(\frac{1}{2} + \frac{1}{\exp(\Theta/T) - 1} \right) + P_e, \quad (10)$$

$$F(x) = 3 \left(-\frac{1}{5}x^{-5/3} + 2x^{-2/3} + 6x^{1/3} - x^{4/3} + \frac{1}{7}x^{7/3} \right), \quad (11)$$

$$\gamma = -\frac{\partial \ln \Theta}{\partial \ln V} = \frac{2}{3} + \frac{2V}{v_0 - V}, \quad (12)$$

$$P_e = \frac{\beta_0}{V_0} \left(\frac{T}{2} \right)^2 \left(\frac{V_0}{V} \right)^{1/2}. \quad (13)$$

3. Equations of state of bcc vanadium and its verification

The coefficients of (1) and hence of (9) and (10) for bcc vanadium are listed in table 1.

Let us verify the proposed equations of state of vanadium. For this purpose we will calculate the room temperature isotherm, high temperature isotherm, heat capacity, volume thermal expansion coefficient and Hugoniot. Then we will compare the received results with experiments.

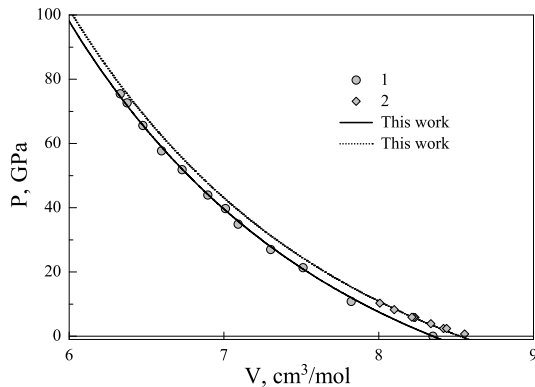


Figure 1. Volume–pressure dependences of the bcc-phase vanadium: 1 is the experimental room temperature (300 K) isotherm [2], 2 is the experimental high temperature (1000 K) isotherm [9], solid line is calculated isotherm at $T_{0i} = 300$ K, dotted line is calculated isotherm at $T_{0i} = 1000$ K. Isotherm were calculated as $P = P(V, T_{0i})$ with help of (10).

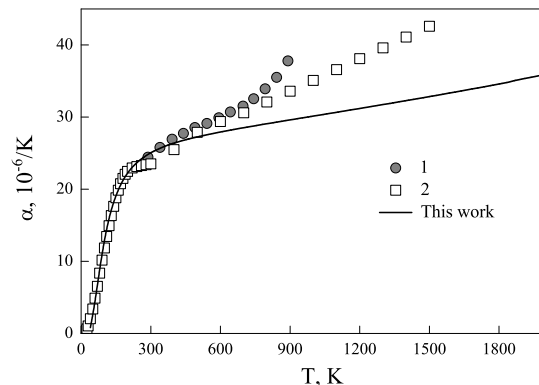


Figure 2. Thermal expansion coefficient α as the function of temperature T at atmospheric pressure for bcc-phase vanadium: 1 is the experimental data [12], 2 is the experimental data from [13], solid line is the calculated $\alpha(T)$ at atmospheric pressure according to (14) and (10).

Calculated and experimental isotherms of bcc phase of vanadium are demonstrated in the figure 1. Here the calculation coincides with experiment [2] under volume decreasing from V_0 to $V = 0.74 V_0$ for the room temperature isotherm. Corresponding to experimental data [9] is satisfactory at $0.95 V_0 < V < V_0$ for the high-temperature isotherm. But in the range of $V \approx 1.03 V_0$ the mismatch begins. So the accordance of calculation with experiment worsens in the range of stretching.

Comparison of calculation and experiment for thermal expansion testifies about same. Experimental data $\alpha(T)$ [12,13] are shown in the figure 2. The result of calculation is presented also in the figure 2. The calculating of $\alpha(T)$ was fulfilled as

$$\alpha = -\frac{(\partial P/\partial T)_V}{V(\partial P/\partial V)_T}. \quad (14)$$

Apparently calculation with the experimental data in a range of temperatures 100–500 K. The mismatch increases with temperature. But the errors on volume on the isotherm (see the figure 1) are insignificant and make about 0.5%. The calculation of α gives understating on 25% at temperature 1000 K.

The figure 3 shows the satisfactory matching between experimental data [12, 14] and calculation of a heat capacity according the formula

$$C_p = -T \left(\left(\frac{\partial^2 \Phi}{\partial T^2} \right)_V + \frac{((\partial P/\partial T)_V)^2}{(\partial P/\partial V)_T} \right). \quad (15)$$

At last, the figure 4 shows the satisfactory matching of calculated and experimental Hugoniot of vanadium. Calculation was carried out on standard procedure. This procedure uses the caloric equation of state (9) and the conservation law for energy that connect the initial pressure–volume–energy (P_0, V_0, E_0) and final shocked pressure–volume–energy (P, V, E) states through

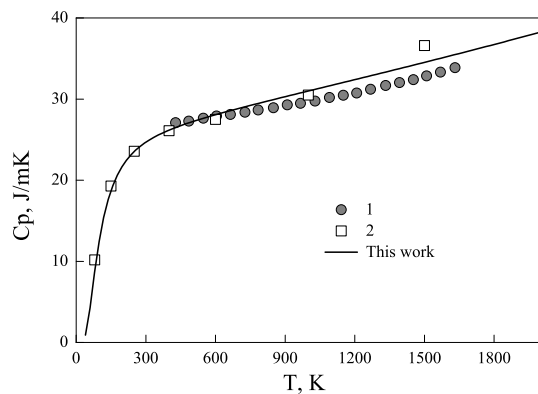


Figure 3. Specific heat capacity at constant pressure C_p as the function of temperature T at atmospheric pressure for bcc-phase vanadium. 1 is the experimental data [12], 2 is the experimental data from [14], line is the calculated $C_p(T)$ at atmospheric pressure according to (15), (1) and (10).

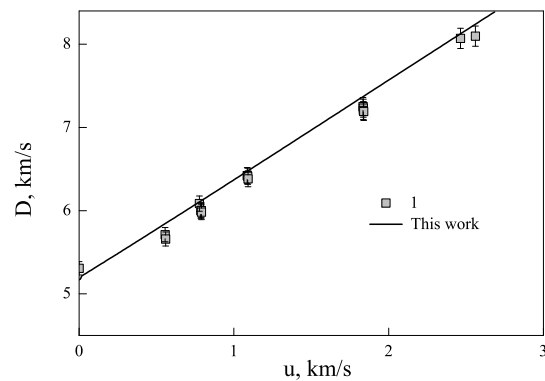


Figure 4. High pressure Hugoniot of the bcc-phase vanadium in mass velocity (u)—shock velocity (D) of bcc-phase vanadium. 1 is the experimental data [15], line is the calculation with help of (9) and (16).

the following equation:

$$E - E_0 = \frac{1}{2}(P + P_0)(V_0 - V). \quad (16)$$

Calculated shock temperature of bcc vanadium in the range of pressure up to ≈ 70 GPa reached ≈ 930 K.

Thus the accordance between the calculations and experimental data in the figures 1–4 corroborated the thermal equation of state $P = P(V, T)$ (10) and the caloric equation of state $E = E(V, T)$ (9) for the bcc-phase vanadium.

4. Conclusion

The semiempirical free-energy relation for hydrostatically compressed bcc-phase vanadium is defined. The equations of state of this metal are obtained as the explicit volume-temperature-pressure function and volume-temperature-energy function. The developed equations of state allow to calculate thermal properties of compressed vanadium under static pressure and shock pressure 0–70 GPa and temperature 100–1000 K.

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