Molybdenum lattice properties at high pressure

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A B S T R A C T

Proceeding from the pair interatomic interaction potential of Mie-Lenard-Jones type and the Einstein crystal model, the thermal equation of state and baric dependencies of the molybdenum lattice properties were obtained. The parameters of the pair potential were determined by self-consistent fitting to the values of the coefficient of thermal expansion and the bulk modulus under normal conditions. On the basis of the obtained parameters baric dependencies of the following properties were calculated: the Debye temperature, the first, second and third Grüneisen parameters, coefficient of thermal expansion and its pressure derivative, isochoric and isobaric heat capacities and their pressure derivatives, product of the thermal expansion coefficient and the isothermal bulk modulus, the surface energy. Calculations made along two isotherms 300 K and 3000 K, showed good agreement with the experimental data.

1. Introduction

The solid phase of molybdenum (Mo) has been studied for a long time, but, due to its high hardness and heat resistance, many of its properties have not yet been determined accurately even at room temperatures and zero pressure (P). In particular, the Debye temperature for $T = 0$ K and $P = 0$ is in wide range of values according to different authors: $\Theta_0 = 259$ K [1] and $\Theta_0 = 472.38$ K [2]. Also, the bulk modulus and other associated parameters are distinguished (for example, the first Grüneisen parameter). This resulted in difficulty of defining the parameters of the pair interatomic interaction potential for molybdenum proceeding from the Θ_0, γ_0 and the sublimation energy for $T = 0$ K and $P = 0$ (as it was made in Ref. [3]). In connection with this, we have developed a method for determining three parameters of the pair potential by self-consistent fitting of the calculated values of the coefficient of thermal expansion $\alpha_p = (\partial \ln V/\partial T)_P$, isothermal bulk modulus B_T for $T = 300$ K and $P = 0$ and thermal equation of state for $T = 300$ K to the experimental data known from the literature. This made it possible to obtain the parameters of the interatomic potential for Mo and further calculate correct values of the Θ_0, γ_0 and baric dependencies of the Mo lattice properties along different isotherms.

Let us note that techniques (both numerical and analytical) that are used for modeling the crystal state equation at high pressures contain in their formalism a lot of adjustable parameters that have no physics sense. That's why it is difficult to define the model from experimental data and predict its baric dependence along particular isotherm. That makes the results obtained by such methods inappropriate for further

applications. Approach proposed in present work allows to calculate by relatively simple technique both the state equation and the change in the molybdenum lattice properties for different $P - T$ -conditions. Calculations made along two isotherms showed good agreement with the experimental estimates.

2. Thermodynamic properties calculation method

To represent interatomic interaction, we have chosen the Mie-Lenard-Jones potential that recently shows good results with correctly defined parameters [4]:

$$\phi(r) = \frac{D}{(b-a)}\left[a\left(\frac{r_0}{r}\right)^b - b\left(\frac{r_0}{r}\right)^a\right], \tag{1}$$

where D and r_0 are the depth and the coordinate of the potential minimum, respectively, and $b > a \geq 1$ are parameters. Then the Debye temperature can be defined as follows [3,5]:

$$\Theta = A_w\xi\left[-1 + \left(1 + \frac{8D}{k_B A_w \xi^2}\right)^{\frac{1}{2}}\right], \tag{2}$$

where k_B is the Boltzmann constant, A_w is the function that arises due to the accounting of energy of atoms zero-point oscillations:

$$A_w = K_R \frac{5k_n ab(b+1)}{144(b-a)} \left(\frac{r_0}{c}\right)^{b+2},$$

$$K_R = \frac{\hbar^2}{k_B r_0^2 m},$$

$$\xi = \frac{9}{k_n}. \tag{3}$$

Here m is the atomic mass, $\hbar$ is reduced Planck constant, k_n is the first coordination number, $c = [6k_p V/(\pi N)]^{\frac{1}{3}}$ is the distance between centers of nearest-neighbor atoms, k_p is the structure packing factor, V is the volume, N is the number of atoms in the crystal.

Using the Einstein model for vibrational spectrum of monatomic crystal and the approximation "interaction between nearest neighbors only" for the specific Helmholtz free energy we can assume:

$$\frac{F}{N} = \left(\frac{k_n}{2}\right)DU(R) + 3k_B\Theta_E\left\{\left(\frac{1}{2}\right) + \left(\frac{T}{\Theta_E}\right)\ln\left[1 - \exp\left(-\frac{\Theta_E}{T}\right)\right]\right\}, \tag{4}$$

where Θ_E is the Einstein temperature, which is related to Debye temperature by the ratio [6]: $\Theta = (4/3)\Theta_E$, $R = r_0/c$ is the linear density of the crystal,

$$U(R) = \frac{aR^b + bR^a}{b-a}.$$

Proceeding from (2)–(4) we can calculate lattice properties of the crystal for particular values of V/N and T, if we know parameters of the interatomic potential (1) and the structure of the crystal. For the equation of state P and isothermal bulk modulus B_T we get:

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \left[\frac{k_n}{6}DU'(R) + 3k_B\Theta_E\gamma E_w(y)\right]\frac{N}{V}, \tag{5}$$

$$B_T = -V\left(\frac{\partial P}{\partial V}\right)_T = P + \left[\frac{k_n}{18}DU''(R) + 3k_B\Theta_E\gamma(\gamma - q)E_w(y)\right.$$
$$\left. - \gamma^2 T\frac{C_v(y)}{n}\right]\frac{N}{V}. \tag{6}$$

Here γ and q are the first and the second Grüneisen parameters,

$$C_v = 3Nk_B\frac{y^2\exp(y)}{[\exp(y)-1]^2},$$

$$E_w = 0.5 + \frac{1}{[\exp(y)-1]^2},$$

$$y = \frac{\Theta_E}{T} = \frac{3\Theta}{4T},$$

$$U'(R) = R\left[\frac{\partial U(R)}{\partial R}\right] = \frac{ab(R^b - R^a)}{b-a},$$

$$U''(R) = R\left[\frac{\partial U'(R)}{\partial R}\right] = \frac{ab(bR^b - aR^a)}{b-a}, \tag{7}$$

where C_v is the isochoric heat capacity of the Einstein crystal [6]. In accordance with (2) the first, second and third Grüneisen parameters have the forms:

$$\gamma = -\left(\frac{\partial\ln\Theta}{\partial\ln V}\right)_T = \frac{b+2}{6(1+X_w)},$$

$$X_w = \frac{A_w\xi}{\Theta}, \quad q = \left(\frac{\partial\ln\gamma}{\partial\ln V}\right)_T = \gamma\frac{X_w(1+2X_w)}{(1+X_w)},$$

$$z = -\left(\frac{\partial\ln q}{\partial\ln V}\right)_T = \gamma(1 + 4X_w) - 2q = \gamma\left(\frac{1+3X_w}{1+X_w}\right) = \frac{(b+2)}{6}\frac{(1+3X_w)}{(1+X_w)^2}. \tag{8}$$

Isobaric thermal coefficient of volume expansion can be calculated from the Grüneisen equation [6]:

$$\alpha_p = \frac{\gamma C_v}{V B_T} = \frac{\gamma C_v}{N B_T [\pi r_0^3/(6k_p)]}\left(\frac{V_0}{V}\right),$$

$$V_0 = N\frac{\pi r_0^3}{6k_p}. \tag{9}$$

Isobaric heat capacity is determined by the well-known expression [6]: $C_p = C_v(1 + \gamma\alpha_p T)$, isochoric heat capacity is determined from (7). Specific (per unit area) surface energy of the face (100) in [J/m²] is determined by formula [3]:

$$\sigma = -\frac{k_n D R^2}{12\alpha^{2/3}r_0^2}L_E(\infty). \tag{10}$$

Here $\alpha = \pi/(6k_p)$ is the structure parameter,

$$L_E(\infty) = U(R) + \frac{18\gamma k_B\Theta_E}{(b+2)Dk_n}E_w\left(\frac{\Theta_E}{T}\right),$$

$$F_E(y) = \frac{y^2\exp(y)}{[\exp(y)-1]^2} \tag{11}$$

These formulas were validated at $P = 0$ and temperatures from $T = 0$ K to the melting point (T_m) and showed good agreement with the experimental data for many crystals of simple (single-component) substances [3].

Obtained expressions (2)–(11) allow us to calculate the dependence of state equation and lattice properties on arguments $V/V_0 = (c/r_0)^3 = R^{-3}$ and temperature T for the given monatomic crystal structure (ie for particular k_n and k_p), if we know all the four parameters of the interatomic potential (1). This formalism was used to study the thermodynamic properties of bcc iron [7,8], fcc iron [9], diamond [10] and three polymorphous modifications of silicon and germanium [11]. Comparison of the calculations with the experimental data for all these substances showed good results. That's why we have applied this formalism for the calculation of the molybdenum properties.

3. Molybdenum interatomic potential parameters

Molybdenum crystal ($m = 95.94$ amu) has a body-centered cubic (bcc) structure: $k_n = 8$, $k_p = 0.6802$. Molybdenum is one of the hardest crystals that makes difficult to study its thermodynamic properties for high $P - T$ conditions. Thats why there is no published experimental data for the baric dependence of the specific heat and the coefficient of thermal expansion.

The parameters of the Mie-Lenard-Jones pair interatomic potential (1) for Mo that were determined by the method described in Refs. [3,12] are

$$r_0 = 2.72\cdot10^{-10} \text{ m}, \quad D/k_B = 19776.91 \text{ K},$$
$$a = 1.93, \quad b = 7.68. \tag{12}$$

Note that all four parameters of potential (1) were primarily determined from a closed set of four equations [3,12]. This set included the following four quantities determined experimentally at $T = 0$ K and $P = 0$ GPa: V_0 is the molar volume, L_0 is the specific atomization energy, Θ_0 is the Debye temperature, and γ_0 is the first Grüneisen parameter. This technique was used to obtain the set of parameters (12). But, as it was noticed in Refs. [3,5,8], values Θ_0 and γ_0 are defined from the experimental data not quite accurate. Since we have $k_B\Theta_0/D \ll 1$ for molybdenum, the uncertainty of Θ_0 and γ_0 weakly influences the calculation of the parameters r_0 but significantly changes the D value and the potential powers. Therefore, we have corrected a, b and D/k_B using both isotherm $T = 300$ K of the thermal state equation $P(V/V_0, 300$ K$)$, $\alpha_p(P, T)$ and $B_T(P, T)$ measured under normal conditions, i.e., when $P = 0$ and $T = 300$ K. For molybdenum the average value of $\alpha_p = 15.0\cdot10^{-6}$K^{-1} [13], $B_T = 243$ GPa [14]. Such fitting for powers of attraction of the bcc Mo resulted in the following values:

$$a = 1.87, \quad b = 6.82, \quad D/k_B = 48950 \text{ K}.$$

Proceeding from obtained values of interatomic potential parameters, we have calculated the following lattice properties for $P = 0$ presented in Table 1:

It is seen from the expressions (2), (3) and (8) that the following limiting relations hold true for $P \to \infty$ (i.e., when $V/V_0 \to 0$ or $X_w \to \infty$) [8]:

$$\lim_{V/V_0\to0} \Theta = \Theta_{\max} = \frac{4k_n D}{9k_B} = 70317.9 \text{ K},$$

$$\lim_{V/V_0\to0} \gamma = \gamma_{\min} = 0,$$