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LETTER TO THE EDITOR

A simple model for calculating the P – T phase diagram of Ti

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Abstract. The FP-LMTO method is used to calculate the total energy and equilibrium lattice properties for the observed phases of Ti. The temperature dependences of the free energy, specific volume, bulk modulus, Debye temperature, and Grüneisen constant are found for these structures within the Debye model. For most quantities a good quantitative agreement with experiment is obtained. The P – T phase diagram constructed from the calculated thermodynamical Gibbs potentials fits well the available room-temperature data on the $\alpha \rightarrow \omega$ transition. The model suggested predicts the formation of a high-pressure β -phase in Ti at $P_{T=300\text{ K}}^{\omega \rightarrow \beta} = 950$ kbar, a pressure which nowadays may be reached experimentally.

The theoretical first-principles investigation of the phase stability of crystals generally consists in analysing the calculated binding curves for given lattices [1]. These curves are used to calculate the ground-state properties: the equilibrium volume, cohesive energy, and bulk modulus [2]. For the high-pressure phases, the quantitative agreement of the lattice properties calculated at $T = 0$ with room-temperature experiments is usually unsatisfactory. The central problem of the microscopic description of structural transformations occurring in metals under pressure is the development of a consistent model for finite temperatures. The simplest way to investigate the structural phase transitions on the basis of first-principles binding curves is to use the Debye–Grüneisen theory. In such a model, the characteristic Debye temperature Θ_D is calculated in terms of the bulk modulus B , and then the free energy $F(T, V)$ is found as a function of Θ_D and the volume V . The applicability of this method to the study of particular metals is restricted by the isotropic Debye model and the assumption of a mean sound velocity v .

Earlier, using for cubic metals the expression for the mean sound velocity [3], the authors of the paper [4] calculated the temperature properties of 14 bcc and fcc metals within the Debye model. The temperature dependence of the lattice constant and the linear thermal expansion coefficient calculated by minimizing the free energy with respect to the volume agree quite well with the experimental data. Thus the method mentioned seems to be appropriate for cubic metals. Similar investigations for transition metals, in which the ground state has a noncubic lattice and the cubic-type structures are high-pressure and/or high-temperature phases, were not performed.

The interfaces of the group-IVa metals (Ti, Zr, Hf) in the case of simultaneously high temperature and pressure are not clearly defined as yet. The aim of this article is to calculate from first principles the band structure of Ti, and to construct the P – T phase diagram within the Debye model. The temperature dependences of the lattice properties calculated for all observed phases of Ti may be useful, especially when compared with

experimental data. Previously, we have performed similar investigations for Zr [5]. The study of the phase stability of group-IVa d metals has been stimulated by the breaking of the hcp \rightarrow ω \rightarrow bcc sequence of structural transformations observed with increasing pressure at room temperatures. In Ti the pressure stabilizing the bcc phase at room temperature has not yet been attained, whereas the ω \rightarrow bcc transition has been detected in Zr and Hf at 350 kbar and 710 kbar, respectively [6]. At ambient pressure, with temperature elevation all metals of this group transform from the stable room-temperature hcp structure (the α -phase) to the bcc one (the β -phase) which persists up to the melting temperature. For Ti, $T^{\alpha\rightarrow\beta} = 1155$ K at ambient pressure, decreasing as $dT/dP \approx -2.6$ K kbar $^{-1}$ when the pressure increases [7].

We now consider the electronic structure calculation. In recent years, first-principles total-energy calculations within the local density approximation (LDA) have been repeatedly performed for different crystalline modifications of Ti [8, 9]. The authors who performed the most careful calculation [9] have found the high-pressure β -phase to arise in this metal at 575 kbar. Using the LDA within the framework of density functional theory for the exchange–correlation energy calculation results, as a rule, in underestimation of the equilibrium volume value. The generalized gradient approximation (GGA) [10] considerably improves the quantitative agreement of the calculated equilibrium volume with the observed one. It is by using the GGA that we succeeded in obtaining the total energies for Zr, which allowed a realistic P – T phase diagram to be constructed [5].

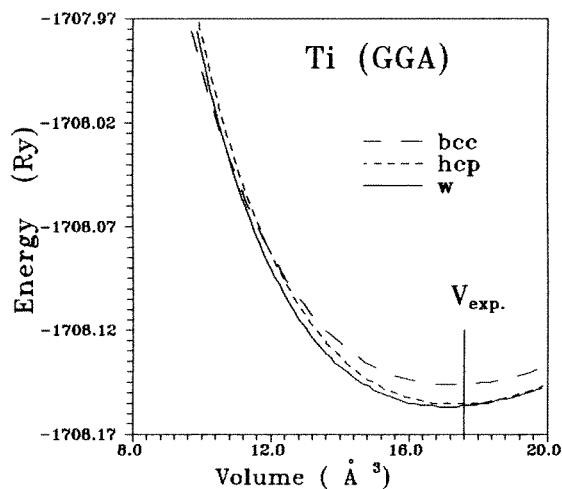


Figure 1. The total energy versus volume for three phases of Ti. The solid vertical line corresponds to the experimental volume for α -Ti.

To calculate the band structure, we used the FP-LMTO method [11]. When expanding the basis functions in spherical harmonics inside the MT spheres, re-expanding the MT orbitals outside the MT spheres, and expanding the crystalline potential and charge density, the maximum values of the angular momentum l were taken to be 2, 4, and 8, respectively. Three values of the MT-orbital tail energy (two positive and one negative for 3p states) were chosen to describe the conduction band. In integrating over the irreducible part of the Brillouin zone, we used 145, 165, and 792 k -points for β -, ω -, and α -Ti, respectively. In all of the calculation variants, the MT-sphere radii were chosen to be equal and corresponding to one of the two types of ω -phase atom: $r_{MT} = 2.52$ au. The ratio c/a was taken to

be 0.617 for the ω -phase, and 1.588 for the α -phase, which corresponds to the available experimental data.

The binding curves for the three structures of Ti investigated are presented in figure 1. The calculated binding curves were analysed and the equilibrium properties were defined as in [4]. Comparing the total energies, one can conclude that the GGA calculation suggests only the $\omega \rightarrow \beta$ transformation. As to the volume obtained for the $\alpha \rightarrow \omega$ transition, it is found to exceed the experimental value of V_0 for the α -phase. This fact can be explained by the specific shapes of the GGA binding curves which are shifted towards larger volumes. In accordance with our calculations, the ground state of Ti corresponds to a rather open hexagonal ω -structure with three atoms per unit cell and the packing ratio of ~ 0.57 , which is unusual for d metals. For V_0 the difference in total energy between the α - and ω -phases is ~ 1.0 mRyd.

We now consider the Debye model formalism. Let us define the free energy of the system as a sum of the rigid-lattice total energy and the free vibrational energy. Then, neglecting the electron subsystem entropy, we have

$$F(V, T) = E_e(V) + E_D(V, T) - T S_D(V, T). \quad (1)$$

Here $E_e(V)$ is the total energy of the electron subsystem. In the Debye model, the vibrational lattice energy E_D and the entropy S_D are expressed as

$$E_D(V, T) = 3k_B T D(x_D) + E_0 \quad (2)$$

$$S_D(V, T) = 4k_B \left[D(x_D) - \frac{3}{4} \ln(1 - e^{-x_D}) \right] \quad (3)$$

where $x_D = \Theta_D/T$, $D(x_D)$ is the Debye function of the heat capacity normalized to unity in the high-temperature limit [12], and $E_0 = \frac{9}{8}k_B\Theta_D$ is the energy of zero-point lattice vibrations.

The final expression for the free energy has the form

$$F(V, T) = E_e(V) - k_B \left[D(x_D) - 3 \ln(1 - e^{-x_D}) - \frac{9}{8}x_D \right]. \quad (4)$$

As seen from (4), the Debye temperature should be estimated in order to calculate the free energy. Let us describe the technique for calculating Θ_D . Assuming a constant sound velocity, one can write down a simple relation between Θ_D and B [3, 4]:

$$\Theta_D = K(aB/M)^{0.5} \quad (5)$$

where a is the lattice constant in au, B is measured in kbar, a in amu, and $K = 42.172$. Using this value of K and the experimental bulk modulus results in overestimation of Θ_D as compared with the experimental Debye temperature. This is due to the assumption of a constant sound velocity which is proportional to \sqrt{B} . In [4] it was shown that for cubic nonmagnetic metals a good agreement with experiment can be obtained with the use of Anderson's average for the sound velocity [3]. This makes it possible to choose for cubic metals a universal K -value of 26.024, which relates the experimental Debye temperature and bulk modulus quite well. However, there is no reason to believe that the same K may be used for noncubic metals as well. The simplest way to define the numerical value of K for noncubic metals is to use relation (5) with the experimental values $(\Theta_D)_{exp}$ and B_{exp} . As a result, the particular K -values will differ for the two different metals and the crystalline structures of the same metal. Using the value of K obtained and the bulk modulus calculated from the total energy, one can find the theoretical value of Θ_D and then the free energy (4). Next, the equilibrium volume, bulk modulus, Debye temperature, and Grüneisen constant may be redefined by minimizing $F(V, T)$ for each fixed temperature. Also the

temperature dependences of the above quantities and the coefficient of volume expansion are readily calculated (see, e.g., [4]). Note that the Debye temperature in (4) was taken to be temperature independent.

Table 1. The equilibrium lattice parameters of α -Ti as compared to the experimental data (V_0 is the equilibrium volume, B_0 is the bulk modulus, γ_0 is the Grüneisen constant, and $(\Theta_D)_0$ is the Debye temperature).

	V_0 (\AA^3)	B_0 (Mbar)	γ_0	$(\Theta_D)_0$ (K)
Experimental	17.60	1.05	1.18	420.0
Calculated, at $T = 0$ K	17.36	1.14	1.275	369.0
Calculated, at $T = 300$ K	17.46	1.12	1.277	365.6

We have calculated the temperature dependences of the lattice properties for three structures observed in Ti. For the hexagonal α - and ω -phases, K was taken to be equal to 32.056, a value determined from the experimental values of Θ_D and B_0 for the equilibrium α -phase. The lattice properties of α -Ti calculated in the Debye model at $T = 0$, with allowance for zero-point vibrations, and at $T = 300$ K are given in table 1, in comparison with the experimental data [13] (the experimental value of Θ_D was derived from measurements of the low-temperature specific heat). As no experimental value of B for the bcc structure was available, Θ_D was calculated with a fitted K -value of 20.456. The fitting procedure will be described below.

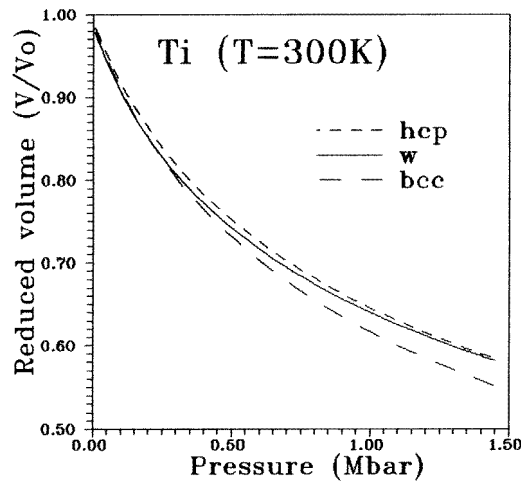


Figure 2. The equation of state for the α -, ω -, and β -phases of Ti at $T = 300$ K.

We now investigate the P - T phase diagram of Ti. To construct the phase diagram, the thermodynamical Gibbs potentials $G(P, T)$ should be calculated and compared for three structures on a fixed mesh of independent parameters (P, T):

$$G(P, T) = F(V, T) + PV. \quad (6)$$

The isothermal dependences $P(V)$ were calculated by direct differentiation of the free energy, $P = -(\partial F/\partial V)_T$, for each structure. The $P(V)$ curves obtained at $T = 300$ K are shown in figure 2. On the basis of the theoretical curves for the equation of state, the

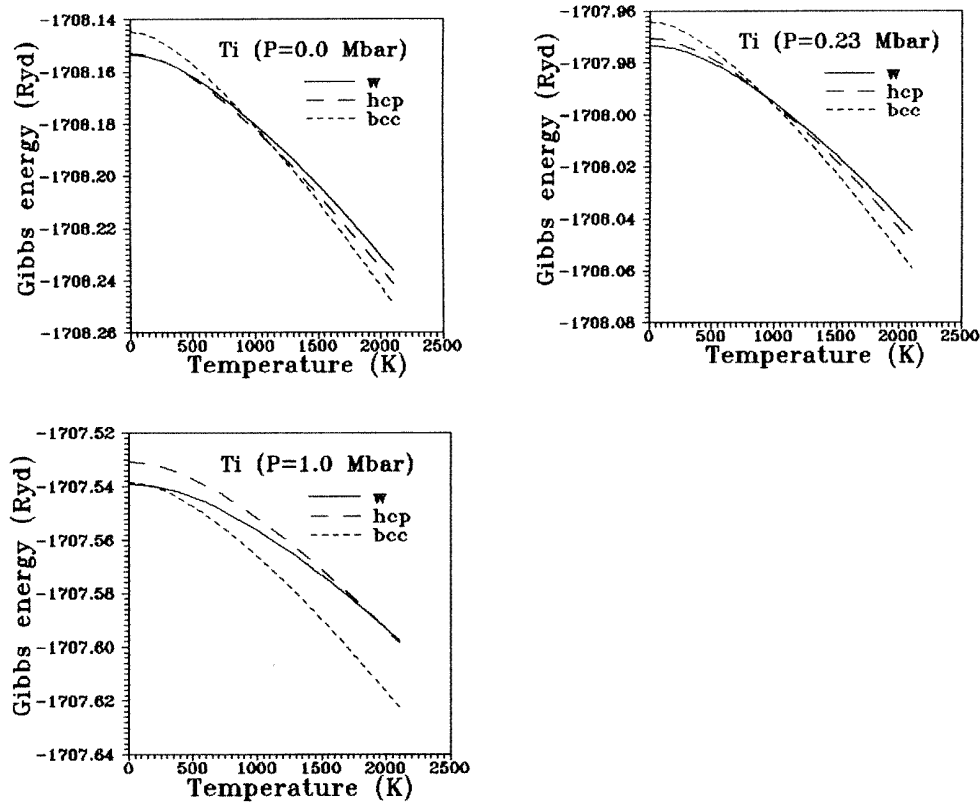


Figure 3. The temperature dependences of the Gibbs energy for different pressures.

specific volume was found at fixed values of temperature and pressure for each structure, and then used in calculating the Gibbs energies (6).

The procedure for defining the points of intersection is illustrated by figure 3, displaying the temperature dependences of the Gibbs energy for $P = 0$, $P = 0.23$ Mbar, and $P = 1$ Mbar. At $P = 0$, for the range $0 < T < 320$ K, the Gibbs potential is a minimum for the ω -phase; further on, up to $T = 1160$ K, the α -phase becomes preferred, while at $T > 1160$ K the β -phase is realized. The points of intersection of the curves in figure 3 determine the interfaces of the P - T diagram. The middle panel of figure 3, for $P = 0.23$ Mbar, corresponds to the triple point of the phase diagram. The bottom panel of figure 3, for $P = 1$ Mbar, demonstrates the formation of a high-pressure β -phase.

The calculated P - T phase diagram is presented in figure 4. The theoretical temperature of the $\alpha \rightarrow \beta$ transition at zero pressure differs from the experimental value by only 5 K due to the fitting of K for the bcc structure in (5). Using the universal K -value of 26.024 proposed in [4] for cubic metals results in an overestimated $\alpha \rightarrow \beta$ transition temperature at ambient pressure ($T_{P=0}^{\alpha \rightarrow \beta} \approx 2100$ K). Hence, in this work we had to vary the magnitude of K in order to get a good fit to the experimental data. Note that in a previous paper [5], a satisfactory agreement with experiment was obtained for the $\alpha \rightarrow \beta$ transition temperature for Zr with the universal K -value. The fitting procedure consisted in diminishing the coefficient K so that the point of intersection of the Gibbs energy curves for the hcp and bcc structures shifted toward lower temperatures (see figure 3). Also, the magnitude of K

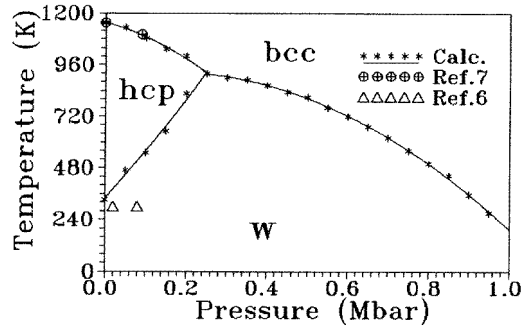


Figure 4. The P - T diagram of Ti.

in this work was assumed to be independent of temperature and pressure.

The P - T diagram suggested agrees qualitatively with the available data on the pressure-induced $\alpha \rightarrow \omega$ transition in Ti. The model temperature of this transition is overestimated by 100–150 K. The calculated triple point ($P_{\text{triple}} = 240$ kbar, $T_{\text{triple}} = 920$ K), though different in temperature and pressure from that determined on the basis of experimental data [7], belongs to the $\alpha \rightarrow \beta$ interface. Our model predicts the formation of a high-pressure β -phase in Ti at $P_{T=300\text{ K}}^{\omega \rightarrow \beta} = 950$ kbar. So far, the isothermal compressibility of the group-IVa metals has been experimentally studied at room temperatures only up to 710 kbar [6]. Most probably, in contrast to the case for Zr and Hf, a pressure sufficient for the $\omega \rightarrow \beta$ transition is still not attained for Ti.

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