

FIRST PRINCIPLES CALCULATIONS OF ALLOY PHASE DIAGRAMS BY COMBINED STATISTICAL MOMENT AND CLUSTER VARIATION METHODS: HIGH TEMPERATURE BCC TA-W AND MO-TA ALLOYS¹

K. Masuda-Jindo²
Vu Van Hung³
P.E.A. Turchi⁴

Abstract

The thermodynamic quantities of metals and alloys are studied using the moment method in the quantum statistical mechanics, going beyond the quasi-harmonic approximations. Including the power moments of the atomic displacements up to the fourth order, the free energies and the related thermodynamic quantities are derived explicitly in closed analytic forms. The configurational entropy term is taken into account by coupling the moment expansion scheme with the cluster variation method (CVM). The melting transitions of TaW alloys are also investigated within the framework of Statistical Moment Method. The energetics of the binary (Ta-W and Mo-Ta) alloys are treated within the framework of the first-principles TB-LMTO method coupled to CPA and GPM (generalized perturbation method). The equilibrium phase diagrams are calculated for the refractory Ta-W bcc alloys.

Key words: Statistical moment method; Cluster variation method; Tight-binding LMTO; Coherent potential approximation; Alloy phase diagram; Ta-W alloy

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² *Department of Materials Science and Engineering, Tokyo Institute of Technology Nagatsuta 4259, Midori-ku, Yokohama 226-8503, Japan*

³ *Hanoi National Pedagogic University, km8 Hanoi-Sontay Highway, Hanoi, Vietnam*

⁴ *Lawrence Livermore National Laboratory, PO Box 808, L-353 LLNL, Livermore CA 94551 U.S.A.*

1 INTRODUCTION

The explicit analytic calculations of the thermodynamic quantities of metals and alloys are of great importance for the fundamental understanding of phase stabilities and phase transitions and also for the purpose of the materials (alloy) designs.^(1,2) However, they have been calculated so far extensively by using the molecular dynamics methods and/or the Monte Carlo simulations.^(3,4) It is the purpose of the present article to study the thermodynamic quantities of metals and alloys using the moment method in the quantum statistical mechanics, hereafter referred to as the statistical moment method (SMM).^(5,6) We firstly derive the Helmholtz free energy formula, $\Psi(V,T)$, of metals and alloys using the fourth order moment approximation, and then calculate the thermodynamic quantities, i.e., thermal lattice expansions, root mean square atomic displacements, specific heats, Grüneisen constants and elastic moduli.

The application calculations using the SMM are performed for ordinary cubic metals and for the bcc alloys. Recently, much attention has been paid to alloy systems made of refractory metals of columns VB and VIB of the Periodic Table^(7,8) and in particular, Nb, Mo, Ta, and W that display high melting temperature space and nuclear applications. In view of this, we calculate the equilibrium phase diagram of Ta-W alloys including the effects of thermal lattice vibrations.

2 THEORY

We derive the thermodynamic quantities of metals and alloys, taking into account the higher (fourth) order anharmonic contributions in the thermal lattice vibrations going beyond the quasi-harmonic (QH) approximation. The basic equations for obtaining thermodynamic quantities are derived in a following manner: The equilibrium thermal lattice expansions are calculated by the force balance criterion and then the thermodynamic quantities are determined for the equilibrium lattice spacings. The anharmonic contributions to the thermodynamic quantities are given explicitly in terms of the power moments of the thermal atomic displacements.

We consider a quantum system, which is influenced by supplemental forces α_i in the space of the generalized coordinates q_i .^(5,6) The Hamiltonian of the crystalline system is then given by

$$\hat{H} = \hat{H}_0 - \sum_i \alpha_i \hat{q}_i, \quad (1)$$

where \hat{H}_0 denotes the crystalline Hamiltonian without the supplementary forces α_i and upper hats $\hat{\quad}$ represent operators. The supplementary forces α_i are acted in the direction of the generalized coordinates q_i . The thermodynamic quantities of the harmonic crystal (harmonic Hamiltonian) will be treated in the Einstein approximation. Within the fourth order moments approximation, the free energy of the system is given by

$$\Psi = U_0 + 3N\theta \left[X + \ln(1 - e^{-2X}) \right] + 3N \left\{ \frac{\theta^2}{k^2} \left[\gamma_2 X^2 \coth^2 X - \frac{2}{3} \gamma_1 \left(1 + \frac{X \coth X}{2} \right) \right] + \frac{2\theta^3}{k^4} \left[\frac{4}{3} \gamma_2^2 X \coth X \left(1 + \frac{X \coth X}{2} \right) - 2\gamma_1 (\gamma_1 + 2\gamma_2) \left(1 + \frac{X \coth X}{2} \right) (1 + X \coth X) \right] \right\} \quad (2)$$

where $X = \hbar\omega/2\theta$, θ being $k_B T$. k and γ_i are second and fourth order derivatives of E_{ci} (total energy per atom) and defined by the following formulae

$$k = \left[\frac{\partial^2 E_{ci}}{\partial u_{i\alpha}^2} \right]_{eq} \equiv m\omega^2, \quad (3)$$

and

$$\gamma_i = \frac{1}{6} \left[\left(\frac{\partial^4 E_{ci}}{\partial u_{i\alpha}^4} \right)_{eq} + 6 \left(\frac{\partial^4 E_{ci}}{\partial u_{i\beta}^2 \partial u_{i\gamma}^2} \right)_{eq} \right] \quad (4)$$

$$\equiv \frac{1}{6} [\gamma_{1i} + 6\gamma_{2i}],$$

respectively.

With the aid of the free energy formula $\Psi = E - TS$, one can find the thermodynamic quantities of metal systems. The specific heats and elastic moduli at temperature T are directly derived from the free energy Ψ of the system. For instance, the isothermal compressibility χ_T is given by

$$\chi_T = 3(a/a_0)^3 / \left[2P + \frac{1}{3N} \frac{\sqrt{2}}{a} \left(\frac{\partial^2 \Psi}{\partial r^2} \right)_T \right], \quad (5)$$

Where

$$\frac{\partial^2 \Psi}{\partial r^2} = 3N \left\{ \frac{1}{6} \frac{\partial^2 U_0}{\partial r^2} + \theta \left[\frac{X \coth X}{2k} \frac{\partial^2 k}{\partial r^2} - \frac{1}{4k^2} \left(\frac{\partial k}{\partial r} \right)^2 \left(X \coth X + \frac{X^2}{\sinh^2 X} \right) \right] \right\}. \quad (6)$$

On the other hand, the specific heats at constant volume C_v is

$$C_v = 3Nk_B \left\{ \frac{X^2}{\sinh^2 X} + \frac{2\theta}{k^2} \left[\left(2\gamma_2 + \frac{\gamma_1}{3} \right) \frac{X^3 \coth X}{\sinh^2 X} + \frac{\gamma_1}{3} \left(1 + \frac{X^2}{\sinh^2 X} \right) - \gamma_2 \left(\frac{X^4}{\sinh^4 X} + \frac{2X^4 \coth^2 X}{\sinh^2 X} \right) \right] \right\}. \quad (7)$$

The specific heat at constant pressure C_p is determined from the thermodynamic relations

$$C_p = C_v + \frac{9TV\alpha_T^2}{\chi_T}, \quad (8)$$

where α_T denotes the linear thermal expansion coefficient and χ_T the isothermal compressibility. In the above Eqs. (2), (6) and (7) the site indices i for the parameters k , γ_1 and γ_2 are omitted because each atomic site is equivalent when dealing with a monoatomic cubic crystal with primitive structure. The relationship between the isothermal and adiabatic compressibilities, χ_T and χ_s , is simply given by

$$\chi_s = \frac{C_v}{C_p} \chi_T. \quad (9)$$

One can also find "thermodynamic" Grüneisen constant as

$$\gamma_G = \frac{V}{C_v} \left[\frac{\partial S}{\partial V} \right]_T = \frac{\alpha_T B_s V}{C_p}, \quad (10)$$

where $B_s \equiv \chi_s^{-1}$ denotes the adiabatic bulk modulus.

3 RESULTS AND DISCUSSIONS

3.1 Thermodynamic Quantities of Metals

In Figure1 we show the thermal expansion coefficients, α_T , of bcc Ta crystal at zero pressure as a function of temperature T , together with those of the previous theoretical calculations,⁽¹⁶⁾ and the experimental results.^(17,18) The calculated thermal expansion coefficients of bcc Ta crystal are in good agreement with the experimental results expect for higher temperature region than $\sim 2000K$. For this higher

temperature region, experimental results, by symbols \times , show the anomalous increase of the thermal expansion coefficients as increasing the temperature (which might be attributed to the extrinsic causes such as the oxidation of the specimen). Instead, the present SMM calculations of the thermal lattice expansion coefficients of bcc Ta crystal (solid curve) are in good agreement with the theoretical calculations of Ref.(19), symbols \circ , using the anharmonic PIC (particle in a cell) model. In the PIC model, an atom is displaced in its Wigner-Seitz cell in the potential field of all the other atoms fixed at their equilibrium positions. The partition function is factored by neglecting atomic correlations. The advantage of cell model over lattice dynamical approach based on the quasiharmonic approximation is that anharmonic contributions from the potential energy of the system have been included exactly without a perturbation expansion. However, in the PIC model, thermal expansivity do not valish at low temperatures (below the Debye temperature), since the quantum phonon effects are not included. The present SMM formalism takes into account the quantum-mechanical zero-point vibrations as well as the higher-order anharmonic terms in the atomic displacements and it enables us to calculate the thermodynamic quantities of bcc Ta crystal for a wide temperature range. Also shown in the inset are the thermal lattice expansion coefficients of W crystal calculated by using the SMM. One can see in the inset that the calculated thermal expansions are in good agreement with the experimental results.

In Figure 2 we show the bulk modulus, B_T , of bcc Ta crystal as a function of temperature, T (zero pressure) calculated by the present SMM, in comparison with those of the previous theoretical calculations and the experimental results. The experimental results of the bulk moduli, given by symbols Δ , of bcc Ta crystal are taken from Ref. (20), while the temperature dependence of the bulk moduli B_T by Wawra's scheme⁽²¹⁾ are shown by symbols \times . The theoretical calculation results of B_T by ab initio quasiharmonic approximation⁽²²⁾ using MGPT (model generalized pseudopotential theory) are presented by circles. The agreement in the bulk moduli B_T between the theoretical calculation and experimental results is better for the temperature region $T \leq 1500K$ with the use of the present SMM scheme, while the agreement seems to be better for higher temperatures than $T \%1500K$ with the use of the ab initio quasiharmonic approximation. However, it is difficult at present to draw definite conclusion on the applicability of the theoretical methods for the calculations of high temperature thermodynamic quantities of bcc Ta crystals because there are some experimental difficulties in the high temperature thermodynamic measurements.

3.2 Ta-W bcc Alloy

To calculate the thermodynamic quantities and the equilibrium phase diagram of bcc Ta-W alloys, we use the cluster variation method (CVM) and the first-principles TB-LMTO method coupled to the coherent potential approximation (CPA) and the generalized perturbation method (GPM). In Figure 3, we present the change in the free energy $\Delta\Psi$ (eV/atom) due to the inclusion of the thermal vibration effects of bcc Ta-W alloys as a function of the temperature T ; the concentrations of tantalum are chosen to be 0.0, 0.1, 0.2, 0.25, 0.3, 0.33, 0.4 0.5, 0.6, 0.67, 0.7, 0.8, 0.9 and 1.0. Also shown in the inset are the magnified view of the change in the free energy at $T=2500K$. Here, the change in the free energy $\Delta\Psi$ corresponds to the ordering energies $E_{AA} + E_{BB} - 2E_{AR}$ in the treatments without thermal lattice vibration effects. Figure 4 shows the change in the free energy $\Delta\Psi$ (eV/atom) due to the thermal lattice

vibrations of bcc TaW alloys at the temperature $T=1000\text{K}$. One can see in Figure 4 that the change in the free energy $\Delta\Psi$ (eV/atom) depends strongly on the concentration of tantalum C_{Ta} and takes positive value for higher Ta concentrations.

The resulting equilibrium phase diagrams of bcc Ta-W alloys are presented in Figure 5. The solid curve represents the phase boundaries between B2 and A2 phases of bcc Ta-W alloys, including the thermal lattice vibration effects while the dashed curves are the phase boundaries without including the thermal lattice vibration effects.⁽⁷⁾ It can be seen in Figure 5 that the B2 phases of Ta-W alloys are stabilized more strongly by including the anharmonicity of thermal lattice vibrations at higher Ta concentration. This theoretical finding is of great interest since the inclusion of the thermal lattice vibration effects is believed in most cases to destabilize the ordered phases as in the CuAu alloys.⁽²³⁾

3.3 Treatment of Liquid Phase

In the calculations of the thermodynamic quantities of high temperature alloys like Ta-W systems, it is highly desirable to give theoretical predictions on the melting temperatures and phase equilibria between the solidus and liquidus phases. In the present study, we present, as a first attempt, purely theoretical predictions on the melting phase transitions of TaW alloys. The present SMM scheme has the virtue of treating the liquid phase transitions of solids on the basis of the "Equation of State", in contrast to the molecular dynamics (MD) simulation method.

In this subsection, we discuss the melting transitions of metals and alloys on the basis of the statistical moment method.⁽¹⁻²⁾ From the Helmholtz free energy of the crystalline phase, one can derive the pressure P in the form

$$P = -\frac{r}{6V} \frac{\partial U_0}{\partial r} + \frac{3\gamma_G \theta}{v}, \quad (11)$$

where the Grüneisen constant γ_G is given by

$$\gamma_G = -\frac{r}{6k} \frac{\partial k}{\partial r} x \coth x. \quad (12)$$

We now use the limiting condition of absolute stability of the crystalline phase

$$\left(\frac{\partial P}{\partial V}\right)_r = 0, \text{ or } \left(\frac{\partial P}{\partial r}\right)_r = 0. \quad (13)$$

Then, we find the limiting (melting) temperature T_s as

$$T_s = \frac{r}{18k_B \gamma_G} \frac{\partial U_0}{\partial r} + \left(\frac{\partial T}{\partial P}\right)_r P. \quad (14)$$

In deriving the above eq. (14), the thermodynamic relation $\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1$ is used. The limiting temperature T_s can be determined in an iterative manner, and in the present calculation the second order approximation is used

$$T_s \approx T_s(0) + \frac{v(T_s(1))P}{3k_B \gamma_G(T_s(1))} - \frac{v(T_s(1))P}{3k_B \gamma_G^2(T_s(1))} \left(\frac{\partial \gamma_G}{\partial T}\right)_a T_s(1), \quad (15)$$

where the first approximation of the limiting temperature is

$$T_s(1) \approx T_s(0) + \frac{v(T_s(0))P}{3k_B \gamma_G}. \quad (16)$$

When the statistical moment method is used to evaluate the limiting temperature of crystalline materials, it is very important to satisfy the self-consistency conditions

between the equilibrium lattice spacings and the related thermodynamic quantities γ_G and U_0 . In such a calculation, the melting temperature T_m is approximated quite well by the limiting temperature T_s

$$T_m \approx T_s. \quad (17)$$

Then, the above eqs. (15) and (17) provide us a straightforward and quantitative evaluation of melting temperatures of metals and alloys.

We have applied the above eqs. (14)~(16) to calculate the melting temperature of Ta-W disordered alloys. The calculated melting temperatures of Ta-W alloys are presented in the equilibrium phase diagram of Figure 5, in comparison with the experimental solidus and liquidus curves.

4 CONCLUSIONS

We have presented the SMM formalism combined with the CVM and investigated the thermodynamic properties of metals and alloys. The linear thermal expansion coefficients, bulk modulus and root-mean-square atomic displacements are calculated as a function of the temperature as well as a function of the alloy compositions. The calculated results of the thermodynamic quantities are in good agreement with the corresponding experimental results. The equilibrium phase diagrams are calculated for bcc Ta-W alloys, including the anharmonicity of thermal lattice vibrations. It has been shown that the B2 phases of Ta-W alloys are stabilized more strongly by including the anharmonicity of thermal lattice vibrations for higher Ta concentration region.

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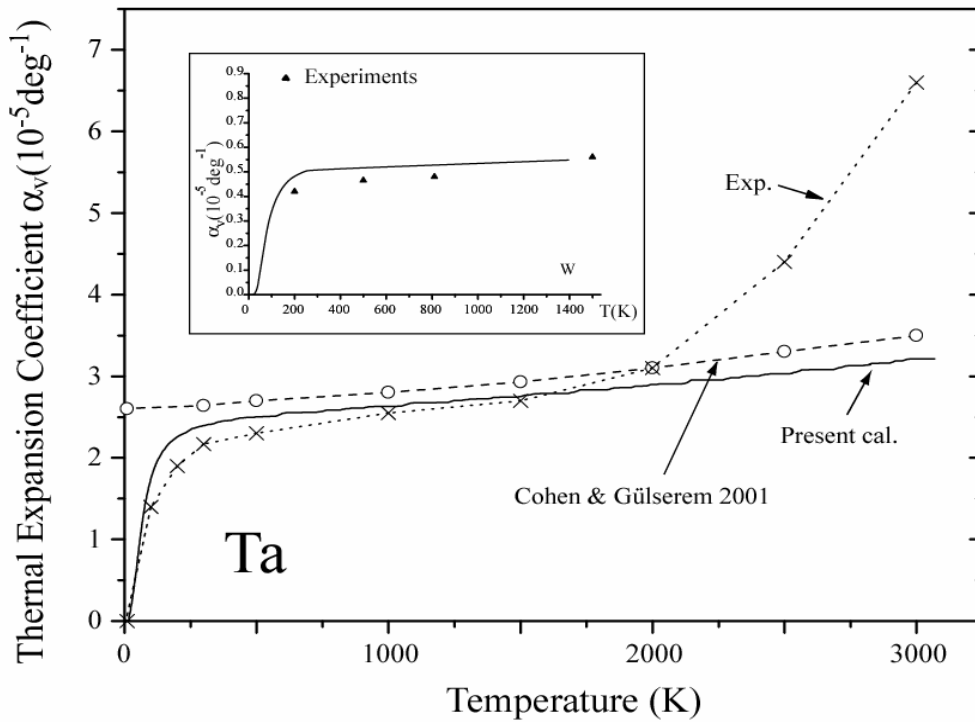


Figure 1. Thermal lattice expansion coefficients of Mo and W crystals, as a function of The temperature T.

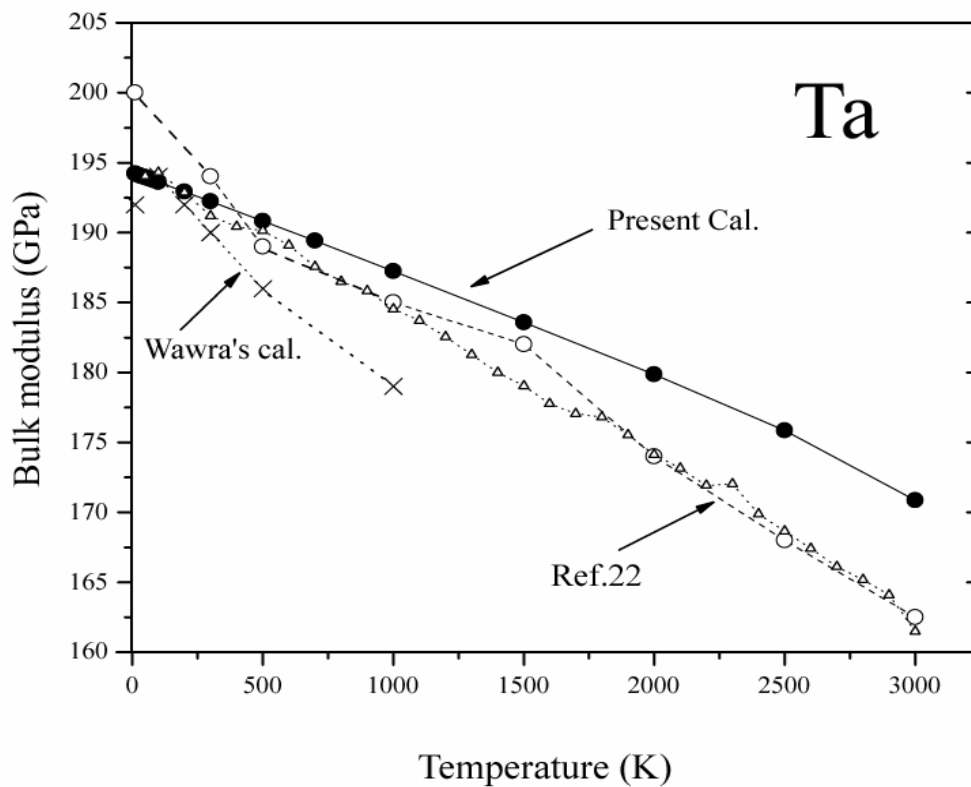


Figure 2. Temperature dependence of bulk modulus of bcc Ta crystal, compared with the experimental results and the theoretical calculations.

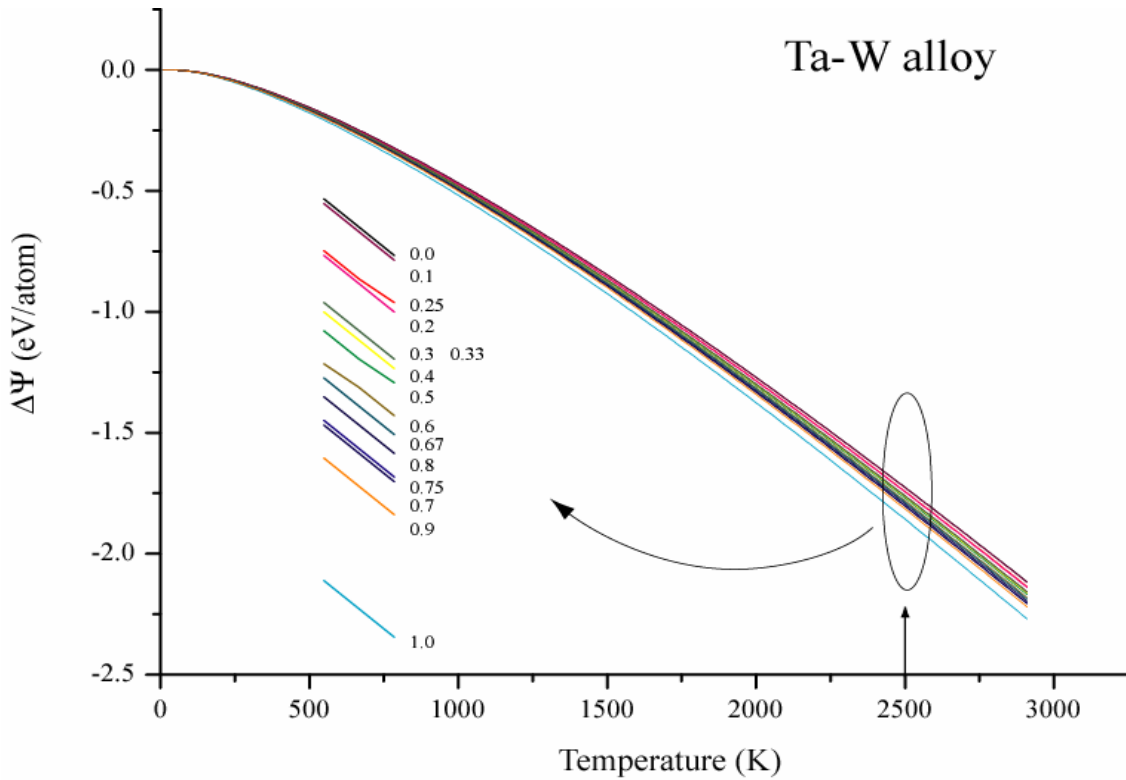


Figure 3. The change in the free energy due to the inclusion of the thermal lattice Vibrations of Ta-W alloys.

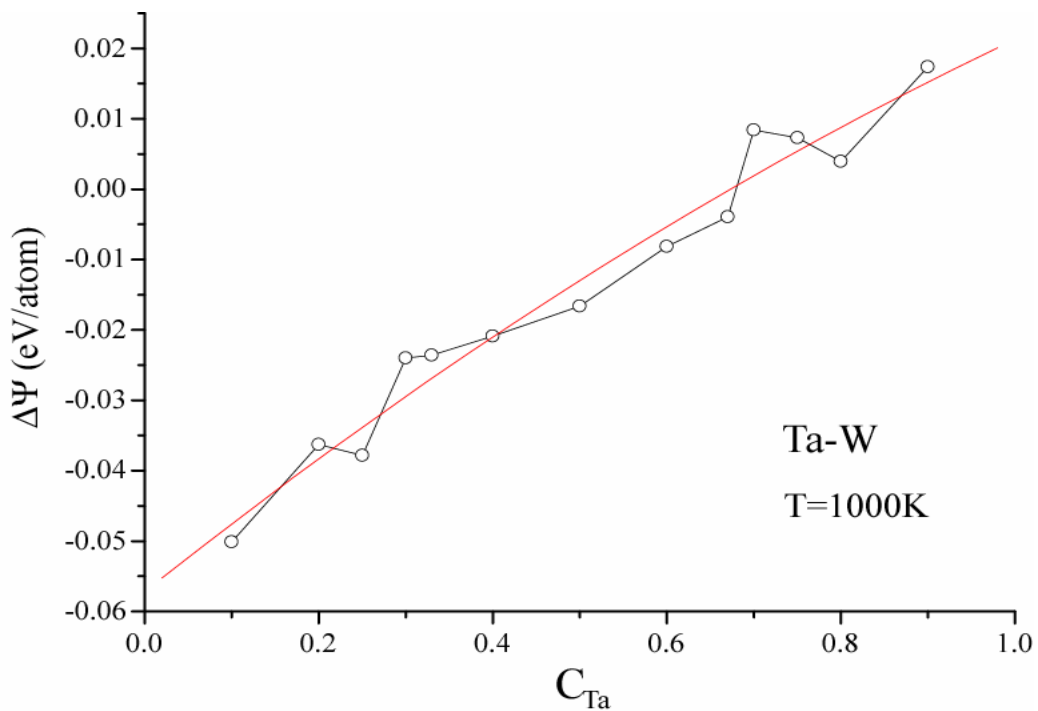


Figure 4. The change in the free energy due to the thermal lattice vibrations of TaW alloys at T=1000K.

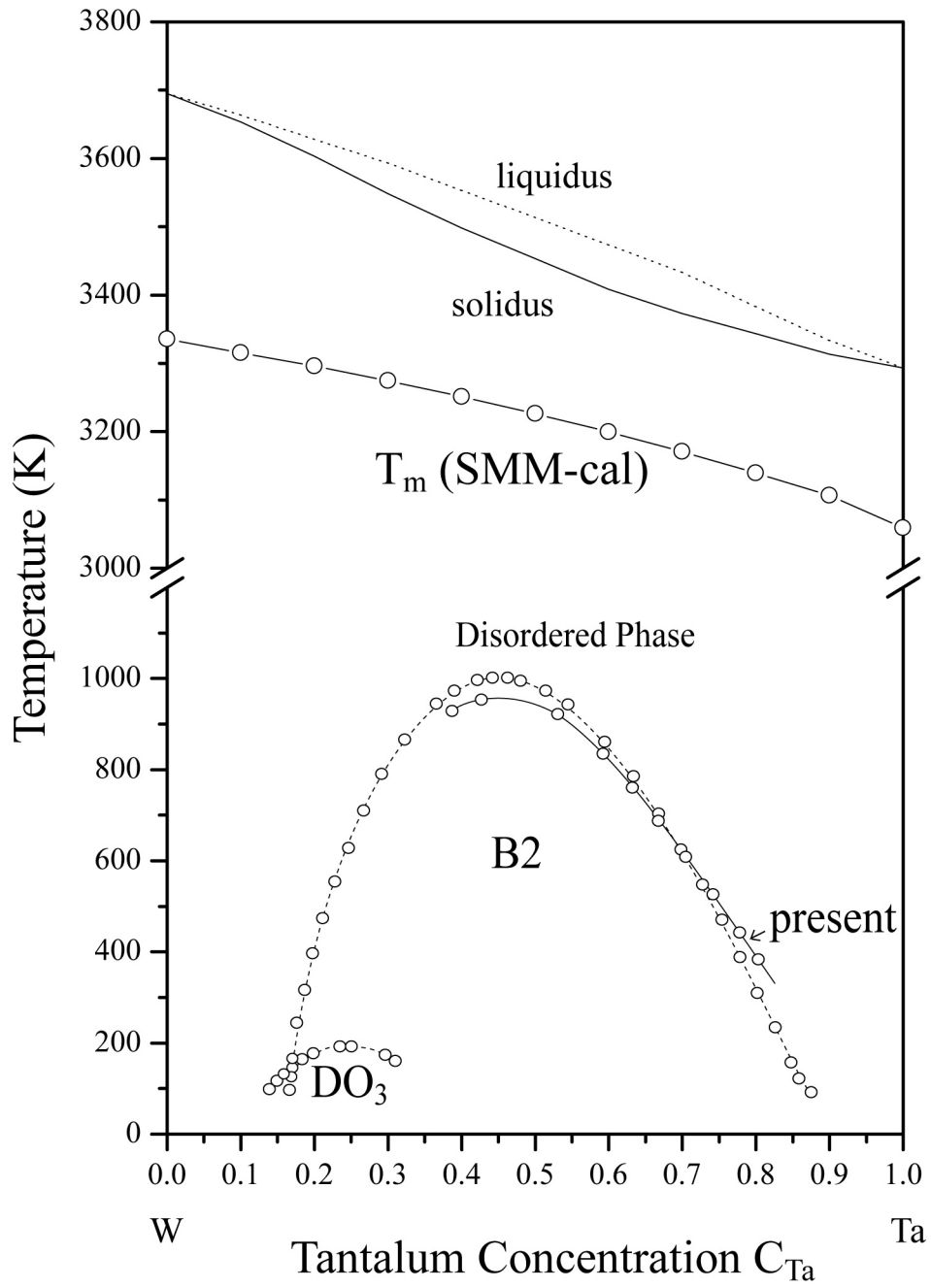


Figure 5. Equilibrium phase diagram of TaW alloys