

## MODELLING OF PHASE EQUILIBRIA IN THE Hf-V SYSTEM BELOW ROOM TEMPERATURE

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(Received 04 July 2017; accepted 15 September 2017)

### Abstract

Phase transformation from orthorhombic  $HfV_2$  structure to cubic C15 Laves phase structure, which occurs during heating at about 114 K, is well known. In this contribution, a thermodynamic description of this phenomenon is provided supported by *ab initio* calculations. We utilize the third generation of thermodynamic database extending the Scientific Group Thermodata Europe (SGTE) unary data to zero Kelvin and demonstrate that it may be also applied to intermetallic phases. The data from a recent thermodynamic assessment of the Hf-V system (valid for temperatures above 298.15 K) were used and extended to zero Kelvin by the same method as it was used for unary data. Under the assumption of validity of harmonic approximation and electronic contribution to the heat capacity, the thermodynamics of C15 and orthorhombic phase were described. With the help of *ab initio* approach, we demonstrate that the  $HfV_2$  orthorhombic phase and C15 Laves phase are mechanically stable at 0 K and thanks to entropy stabilization they are in equilibrium with pure element phases in the temperature region of structural change.

**Keywords:** Laves phases; Hf-V system; *Ab initio* calculations; Phase diagram; Zero Kelvin; CALPHAD method

### 1. Introduction

$HfV_2$  C15 Laves phase has been studied as an attractive superconducting material for technical applications [1,2] which can be influenced by its structural transformation [3-5]. Electronic structure, elastic properties and total energies of C15 Laves phases of  $MV_2$  type ( $M = Zr, Hf, \text{ or } Ta$ ) were studied with the help of *ab initio* calculations in [6-8] and the relations between electronic structure, elastic moduli and stability were analysed. It was found that the  $HfV_2$  C15 Laves phase compound, which is cubic at room temperature, undergoes a structural transformation to a non-Laves orthorhombic phase at low temperatures [9-11]. The transformation temperature was determined as 120 K by Lawson and Zachariassen [12], 118 K by Drymiotis et al. [2] and  $107.8 \pm 2$  K by Rapp and Benediktsson [10], who also determined the corresponding latent heat of transformation as 15 J/mol of atoms. Weighted average of transformation temperature (i.e. 114 K) was used for further thermodynamic modelling. In

general, it is very difficult to explore low temperature phase diagrams describing such transformations both experimentally and theoretically and it is great challenge to perform thermodynamic modelling in this region.

The basis for the low temperature predictions of thermodynamic functions represents the works of Chen and Sundman [13, 14], where the equations for Gibbs energy valid at low temperatures are provided. In our works [15, 16], the expressions of Gibbs energies of 52 elements were extended to zero Kelvin on this basis and they were used for modelling of thermodynamic functions below room temperature in the V-Zr system in our recent work [17]. This approach forms the base for modelling of phase equilibria by the CALPHAD method at low temperatures and its applicability to Hf-V system is demonstrated here.

A fundamental prerequisite for the success of this method is the existence of a reliable expression for the Gibbs energy of studied phases at high temperatures i.e. above 298.15 K. In the Hf-V system, the data of

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phase equilibria above room temperature were determined in [18, 19] and a thermodynamic assessment for equilibria above room temperature was published by Servant [20], which was used for extension below room temperature in this work.

However, Drymiotis et al. [2], Rapp and Benediktsson [10], and Lawson and Zachariassen [12] have found orthorhombic phase as stable phase below 114 K, which does not appear in high-temperature phase diagram. Therefore, the extension of calculation of phase diagram down to zero Kelvin was performed, using the description of unary data below room temperature [15, 16] and the new extension of expression of Gibbs energy of C15 Laves phase and orthorhombic phase to zero Kelvin compatible with Gibbs energy expressions above 298.15 K.

In addition to that, our *ab initio* calculations of energy of formation and phonon spectra bring new findings concerning the stability and behaviour of C14, C15 and C36 Laves phase and non-Laves orthorhombic and tetragonal HfV<sub>2</sub> phase.

## 2. *Ab initio* calculations of stability

The energy of formation of studied phases at 0 K was obtained with the help of *ab initio* electronic structure calculations, performed within the Density Functional Theory (DFT). The pseudopotential method [21] incorporated into the Vienna *Ab initio* Simulation Package (VASP) code [22, 23] combined with the Projector Augmented Wave - Perdew-Burke-Ernzerhof (PAW-PBE) pseudopotential [24-26] (i.e. the Generalized Gradient Approximation (GGA) for the exchange-correlation energy was employed) was used and the total energies of the Laves phases in various configurations, orthorhombic and tetragonal structure as well as the total energy of the Standard Element Reference (SER) states i.e. HCP\_A3 Hf and BCC\_A2 V, which are phases stable at pressure of 10<sup>5</sup> Pascal (1 bar) and temperature 298.15 K, were evaluated.

The number of k-points and of plane waves in a basis set was optimised using the convergence criterion of ±0.05 kJ per mol of atoms. The cut-off energy restricting the number of plane waves in a basis set was 287 eV for HCP\_A3 Hf, Laves phases, orthorhombic and tetragonal structures except for pure V structures (BCC\_A2 and V<sub>2</sub>V orthorhombic, tetragonal and Laves phase modifications) where the value of 251 eV was used.

The convergence tests of total energies with respect to the number of k-points were also performed. In the case of SER states with 2 atoms in the unit cell, we used a grid of 19x19x19 k-points for nonmagnetic (NM) BCC\_A2 V and of 21x21x13 k-points for NM HCP\_A3 Hf. The optimum values obtained for the C14 Laves phases are 15x15x13 (V<sub>2</sub>V), 21x21x13 (HfV<sub>2</sub>), 19x19x15 (Hf<sub>2</sub>V) and 21x21x17 (Hf<sub>2</sub>Hf) grid of

k-points, for the C15 Laves phases 19x19x19 (V<sub>2</sub>V, Hf<sub>2</sub>V) and 21x21x21 (HfV<sub>2</sub>, Hf<sub>2</sub>Hf) grid of k-points and for the C36 Laves phases 13x13x13 (V<sub>2</sub>V), 17x17x13 (Hf<sub>2</sub>Hf, HfV<sub>2</sub>) and 19x19x13 (Hf<sub>2</sub>V) grid of k-points. The optimum 15x15x13 (HfV<sub>2</sub>, Hf<sub>2</sub>V), 19x19x13 (V<sub>2</sub>V) and 19x19x15 (Hf<sub>2</sub>Hf) grid of k-points were found in case of orthorhombic phase and 15x15x15 (HfV<sub>2</sub>) and 19x19x13 (Hf<sub>2</sub>Hf, Hf<sub>2</sub>V, V<sub>2</sub>V) in case of tetragonal phase. A spin polarization was not included in our calculations. Each structure was fully relaxed yielding the minimum total energy and the equilibrium structural parameters. For the structure relaxation, the convergence criterion for energy (EDIFF) was set to 8\*10<sup>-5</sup> kJ per mol of atoms. The criterion for convergence of forces (EDIFFG) was one order lower. In addition to this, the relaxation calculations were repeated until the change of lattice parameters, volume and energy was lower than 0.0005 %, 0.0006 % and 0.002 kJ per mol of atoms, respectively. The calculated optimum lattice parameters for SER states, C14, C15 and C36 Laves phases and the non-Laves orthorhombic and tetragonal structure are listed in Tables 1 and 2.

**Table 1.** Calculated and experimental lattice parameters of the SER states. Symbols *a* and *c* stand for lattice parameters,  $V_{at}$  is the atomic volume and  $\Delta$  shows the relative difference between the calculated and experimental atomic volume.

| SER state       |                        | <i>a</i> / pm | <i>c</i> / <i>a</i> | $V_{at} / 10^3 \text{pm}^3$ | $\Delta$ % |
|-----------------|------------------------|---------------|---------------------|-----------------------------|------------|
| NM<br>BCC_A2 V  | Exp. [27]              | 303.09        | 1                   | 1.392                       | -5.11      |
|                 | This work <sup>a</sup> | 297.83        | 1                   | 1.321                       |            |
| NM<br>HCP_A3 Zr | Exp. [27]              | 512.00        | 15.851              | 2.313                       | -3.63      |
|                 | This work              | 504.34        | 15.787              | 2.229                       |            |

<sup>a</sup> Calculated value published in Ref. [17].

Experimental (where available) and calculated structural parameters of SER states and HfV<sub>2</sub> agree quite well. Concerning the orthorhombic phase, the situation is more complicated for pure vanadium and hafnium. The analyses of nearest neighbours distances and primitive cells were performed and the results obtained were compared with C15 Laves phase equilibrium data. It was found that the V<sub>2</sub>V configuration of both orthorhombic and tetragonal phase transforms to the C15 Laves phase during the relaxation which is confirmed by the identity of their primitive cells. The similar situation occurred for orthorhombic Hf<sub>2</sub>Hf phase which transformed to tetragonal one. Furthermore, the corresponding total energy differences  $\Delta^0 E^{L-SER}$  between the V<sub>2</sub>V orthorhombic, tetragonal and C15 Laves phase taken with respect to SER states given in Table 3 are almost identical. The same statement is valid for Hf<sub>2</sub>Hf orthorhombic and tetragonal phase.



**Table 2.** Equilibrium structural parameters of Laves phases and a non-Laves orthorhombic and tetragonal phase found in this work. Symbols  $a$ ,  $b$  and  $c$  stand for lattice parameters and  $V_{at}$  is the atomic volume and  $\Delta$  denotes the relative difference between the calculated and experimental atomic volume.

| Structure          |                        |                        | $a$ / pm | $b/a$  | $c/a$  | $V_{at} / 10^7 \text{ pm}^3$ | $\Delta$ % |
|--------------------|------------------------|------------------------|----------|--------|--------|------------------------------|------------|
| C14                | $V_2V$                 | This work <sup>a</sup> | 493.22   | 1      | 1.5652 | 1.355                        | ---        |
|                    | $HfV_2$                | This work              | 518.20   | 1      | 1.5965 | 1.603                        | ---        |
|                    | $Hf_2V$                | This work              | 551.20   | 1      | 1.6368 | 1.978                        | ---        |
|                    | $Hf_2Hf$               | This work              | 569.53   | 1      | 1.6689 | 2.225                        | ---        |
| C15                | $V_2V$                 | This work <sup>a</sup> | 688.17   | 1      | 1      | 1.358                        | ---        |
|                    | $HfV_2$                | Exp. [27]              | 737.73   | 1      | 1      | 1.673                        | ---        |
|                    |                        | This work              | 727.85   | 1      | 1      | 1.607                        | -3.96      |
|                    |                        | This work VASP-LDA     | 710.91   | 1      | 1      | 1.497                        | -10.52     |
|                    |                        | This work Wien2k-GGA   | 733.03   | 1      | 1      | 1.641                        | -1.90      |
|                    | $Hf_2V$                | This work              | 786.14   | 1      | 1      | 2.024                        | ---        |
| $Hf_2Hf$           | This work              | 815.72                 | 1        | 1      | 2.262  | ---                          |            |
| C36                | $V_2V$                 | This work <sup>a</sup> | 493.30   | 1      | 3.1324 | 1.357                        | ---        |
|                    | $HfV_2$                | Exp. [27]              | 506.40   | 1      | 3.2524 | 1.524                        | ---        |
|                    |                        | This work              | 524.64   | 1      | 3.0816 | 1.606                        | 5.36       |
|                    | $Hf_2V$                | This work              | 559.03   | 1      | 3.1600 | 1.992                        | ---        |
| $Hf_2Hf$           | This work              | 569.26                 | 1        | 3.3654 | 2.240  | ---                          |            |
| Orthorhombic phase | $V_2V$                 | This work <sup>b</sup> | 486.56   | 1      | 1.4145 | 1.358                        | ---        |
|                    | $HfV_2$                | Exp. [28]              | 517.35   | 1.01   | 1.4366 | 1.673                        | ---        |
|                    |                        | This work              | 496.91   | 1.05   | 1.5067 | 1.610                        | -3.76      |
|                    | $Hf_2V$                | This work              | 503.14   | 1.16   | 1.7308 | 2.123                        | ---        |
| $Hf_2Hf$           | This work <sup>c</sup> | 558.42                 | 1        | 1.5576 | 2.260  | ---                          |            |
| Tetragonal phase   | $V_2V$                 | This work <sup>b</sup> | 486.58   | 1      | 1.4144 | 1.358                        | ---        |
|                    | $HfV_2$                | Exp. [28]              | 520.71   | 1      | 1.4214 | 1.672                        | ---        |
|                    |                        | This work              | 508.36   | 1      | 1.4696 | 1.609                        | -3.79      |
|                    | $Hf_2V$                | This work              | 556.09   | 1      | 1.4127 | 2.024                        | ---        |
| $Hf_2Hf$           | This work              | 558.41                 | 1        | 1.5577 | 2.260  | ---                          |            |

<sup>a</sup> Calculated value published in Ref. [17]. <sup>b</sup> These values correspond to the C15 Laves phase arrangement and were obtained by the full structure relaxation. <sup>c</sup> These values correspond to the tetragonal phase arrangement and were obtained by the full structure relaxation.

On the other hand, the  $Hf_2V$  and  $HfV_2$  configurations of orthorhombic and tetragonal phase do not converge to the C15 Laves phase arrangement during its structural relaxation. Even more, these structures become more stable than the C15 Laves phase. Nevertheless these differences are very small and their importance should be suppressed by entropy effect at higher temperatures.

The values of energies of formation of  $Hf_2V$  configuration of C14, C15 and C36 Laves phase and the orthorhombic and tetragonal structure are much

higher, than those of  $HfV_2$  configuration. This is a quantitative confirmation of the fact that the  $Hf_2V$  arrangement of the above mentioned structures is energetically very disadvantageous.

The stability of the C15 Laves phase structure and orthorhombic phase at higher temperatures is facilitated by the vibrational energy effect in spite of their positive value of energy of formation at 0 K. For modelling of Gibbs energy at temperatures above 298.15 K, the experimental value of enthalpy of formation ( $-16.7 \text{ kJ.mol}^{-1}$  of atoms<sup>-1</sup>) from [30] was



**Table 3.** The total energy differences  $\Delta^0 E^{L-SER}$  between the Laves phases of various types, orthorhombic and tetragonal structure with respect to the weighted average of the SER states (NM BCC\_A2 V and NM HCP\_A3 Hf) calculated in this work and compared with values available in literature [29-31]. The *ab initio* results published in [29] were obtained using the VASP code and GGA and in [31] by full-potential linear muffin-tin orbital method (FP-LMTO). The experimental result in [30] were measured by high temperature direct synthesis calorimetry at 1373±2K. All values are given in kJ per mol of atoms ( $1 \text{ eV atom}^{-1} = 96\,485 \text{ kJ mol of atoms}^{-1}$ ).

| Composition        |                      | V <sub>2</sub> V   | HfV <sub>2</sub>         | Hf <sub>2</sub> V | Hf <sub>2</sub> Hf        |
|--------------------|----------------------|--------------------|--------------------------|-------------------|---------------------------|
| C14                | This work            | 9.81 <sup>a</sup>  | 1.06                     | 75.49             | 32.10                     |
|                    | Ref.                 | 9.6 [29]           | ---                      | ---               | 31.45 [29] <sup>d</sup>   |
| C15                | This work            | 11.23 <sup>a</sup> | 3.36                     | 83.03             | 38.00                     |
|                    | This work VASP-LDA   | ---                | 2.59                     | ---               | ---                       |
|                    | This work Wien2k-GGA | ---                | 2.61                     | ---               | ---                       |
|                    | Ref.                 | 11.0 [29]          | -16.7 [30]<br>-1.51 [31] | ---               | 36.35 [29] <sup>d,e</sup> |
| C36                | This work            | 10.42 <sup>a</sup> | 1.91                     | 78.42             | 34.14                     |
| Orthorhombic phase | This work            | 11.23 <sup>b</sup> | 3.29                     | 80.17             | 37.00 <sup>c</sup>        |
| Tetragonal phase   | This work            | 11.23 <sup>b</sup> | 3.32                     | 83.03             | 37.00                     |

<sup>a</sup> Calculated value published in Ref. [17]. <sup>b</sup> These values correspond to the C15 Laves phase arrangement and were obtained by the full structure relaxation. <sup>c</sup> These values correspond to the tetragonal phase arrangement and were obtained by the full structure relaxation. <sup>d</sup> These values were evaluated using the energy difference between hcp and bcc Hf (hcp-bcc) -17.45 kJ/mol of at. calculated in this work. <sup>e</sup> A magnetic structure with average magnetic polarization in excess of 0.1μB/atom.

taken into account. For confirmation of the VASP GGA values of energy of formation, the calculations by Wien2k code [32] and VASP code using and LDA [33] were performed. Results are summarized in Table 2 and 3 and confirm the thermodynamic instability of both, C15 and orthorhombic phases, at 0 K with respect to standard reference structures in contradiction to value -1.51 kJ/mol of at. [31] for C15 calculated by full-potential linear muffin-tin orbital method.

### 3. Phonon spectra of HfV<sub>2</sub> phases

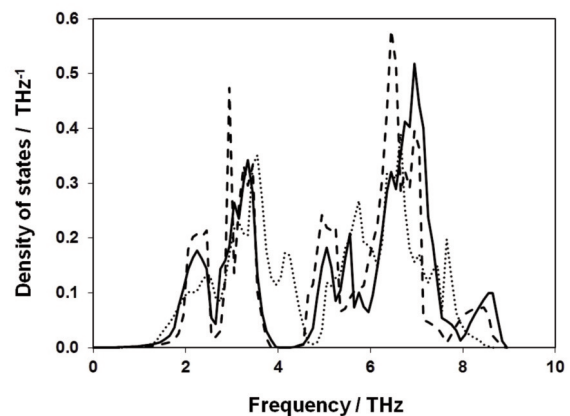
The phonon spectra of HfV<sub>2</sub> C15 and C14 Laves phase and orthorhombic phase were calculated using the Phonon software [34]. The behaviour of phonon density of states (DOS) is displayed in Figure 1.

It may be seen that the HfV<sub>2</sub> in C15 and C14 Laves phase and orthogonal structure are dynamically stable at zero Kelvin.

### 4. Thermodynamic modelling and phase diagram above 298.15 K

In this temperature region, a recent assessment of thermodynamic parameters of Hf-V system [20] was adopted, which is in reasonable agreement with the new calorimetric data for enthalpy of formation of HfV<sub>2</sub> phase (-16.7 kJ/mol of atoms) [30]. The used data [20] are presented in Table 4.

The C15 Laves phase in this work is modelled as (Hf)<sub>1</sub>(V)<sub>2</sub>, in the work [20] is modelled as (Hf)<sub>0.33333</sub>(V)<sub>0.66667</sub>. From this reason, the parameters used in our database are 3 times higher than those in Ref. [20], i.e. -10800 + 0.3\*T + 2\*GHSERV + GHSERHF. The orthorhombic phase has not been modelled at this stage as it is not stable in this temperature region. The calculated phase diagram is shown in Figure 2 and the temperatures of invariant reactions are listed in Table 5.



**Figure 1.** Density of states of phonons of HfV<sub>2</sub> C15 Laves phase (dashed line), C14 Laves phase (dotted line) and orthogonal phase (full line) calculated by Phonon software [34].



Table 4. Parameters of phases in Hf-V system

| Phase     | T / K    | Parameter / J.mol <sup>-1</sup> of f.u.     | Ref. [20]                                       |
|-----------|----------|---|---|
| LIQUID    | 298-4000 | <sup>0</sup> L <sub>V,HfV<sub>2</sub></sub> | -20910.43+13.3729*T                             |
| LIQUID    | 298-4000 | <sup>1</sup> L <sub>V,HfV<sub>2</sub></sub> | -18615.7038+4.1206*T                            |
| LIQUID    | 298-4000 | <sup>2</sup> L <sub>V,HfV<sub>2</sub></sub> | -5168.9233                                      |
| BCC_A2    | 298-4000 | <sup>0</sup> L <sub>V,HfV<sub>2</sub></sub> | 16753.4911+7.6642*T                             |
| BCC_A2    | 298-4000 | <sup>1</sup> L <sub>V,HfV<sub>2</sub></sub> | -5012.00-6.1986*T                               |
| BCC_A2    | 298-4000 | <sup>2</sup> L <sub>V,HfV<sub>2</sub></sub> | 3370.6775                                       |
| HCP_A3    | 298-4000 | <sup>0</sup> L <sub>V,Hf</sub>              | 33570.00+0.1000*T                               |
| LAVES_C15 | 298-4000 | <sup>0</sup> G <sub>V,Hf</sub>              | -3600.0+0.1*T+ 0.33333*GHSERHF + 0.66667*GHSERV |

The expression “f.u.” stands for formula unit

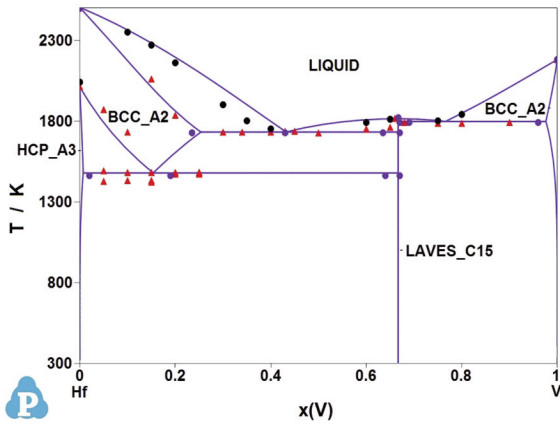


Figure 2. Phase diagram of Hf-V system above 298.15 K calculated in this work (data for BCC\_A2, HCP\_A3, LIQUID and C15 Laves phase were taken from [20] - Table 4), compared with experimental data: triangles from [18], circles from [19].

Table 5. Calculated temperatures of invariant reactions in the Hf-V system

| Reaction                          | T / °C |
|-----------------------------------|--------|
| Liquid → LAVES_C15 + V-BCC_A2     | 1546   |
| Liquid → LAVES_C15 + Hf-BCC_A2    | 1470   |
| Hf-BCC_A2 → LAVES_C15 + Hf-HCP_A3 | 1216   |

### 5. Thermodynamic modelling of HfV<sub>2</sub> phases below 298.15 K

The Compound Energy Formalism (CEF) [35, 36] was also employed for thermodynamic modelling of the Hf-V system down to zero Kelvin. In this temperature region, the Gibbs energy of elemental constituents may be expressed by equation [13,14]:

$$G^0(T) = E_0 + \frac{3}{2}RT_E + 3RT \ln(1 - e^{-T_E/T}) - \frac{a}{2}T^2 - \frac{b}{20}T^5 - \frac{c}{6}T^3 \quad (1)$$

where T<sub>E</sub> is Einstein temperature.

It is assumed that the Gibbs energy of stoichiometric phase can be also expressed in the form of equation 1 and it is evaluated to reach a smooth connection to high temperature polynomial at limiting temperature T<sub>lim</sub>. Namely, the extended Gibbs energy of C15 Laves phase should have the same function value and the same values of the first and the second derivatives as the Gibbs energy of polynomial for HfV<sub>2</sub> found in [20] (Tab. 4) at the limiting temperature, which was chosen as 298.15 K. The resulting system of equations is based on general expressions for Gibbs energy valid for low temperatures published in [13, 14] and is presented in the following equations 2.1-2.3 where GHSERHF and 2\*GHSERV on both sides of equations are omitted.

$$G^{C15}(T) = E_0^{C15} + \frac{3}{2}RT_E^{C15} + 3RT_{lim} \ln(1 - e^{-T_E^{C15}/T_{lim}}) - \frac{a}{2}T_{lim}^2 - \frac{b}{20}T_{lim}^5 - \frac{c}{6}T_{lim}^3 = -10800 + 0.3 * T_{lim}, \quad (2.1)$$

where E<sub>0</sub><sup>C15</sup> = +7830 J.mol<sup>-1</sup> of f.u., which corresponds to Wien2k GGA value from Tab 3.

$$\frac{dG^{C15}(T)}{dT} = 3R \ln(1 - e^{-T_E^{C15}/T_{lim}}) - 3R \frac{T_E^{C15} e^{-T_E^{C15}/T_{lim}}}{T_{lim}(1 - e^{-T_E^{C15}/T_{lim}})} - aT_{lim} - \frac{b}{4}T_{lim}^4 - \frac{c}{2}T_{lim}^2 = 0.3 \quad (2.2)$$

$$\frac{d^2G^{C15}(T)}{dT^2} = -3R \frac{T_E^{C15} e^{-T_E^{C15}/T_{lim}} (T_E^{C15} / T_{lim}^2)}{T_{lim}(1 - e^{-T_E^{C15}/T_{lim}})^2} - a - bT_{lim}^3 - cT_{lim} = 0 \quad (2.3)$$

The solution of this system of equations by elimination method is:

$$a = 2.2151; b = 1.9474 * 10^{-7}; c = -0.024466;$$

The Einstein temperature (T<sub>E</sub>) for C15 Laves phase used in this work was calculated from the Debye temperature (T<sub>D</sub>) from our phonon spectra calculations



according to the relation [38]:  $T_E = 0.77 \cdot T_D$ , particularly:  $T_D^{C15} = 197.8$  K,  $T_E^{C15} = 0.77 T_D^{C15} = 152.3$  K. The shape of Gibbs energy of C15 Laves phase below room temperature is shown in Figure 3.

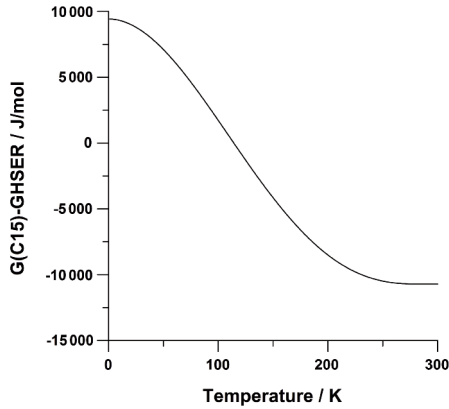


Figure 3. Gibbs energy of C15 Laves phase below room temperature.

For the Gibbs energy of  $\text{HfV}_2$  orthorhombic phase the same approach is used and its Gibbs energy is defined as:

$$G^{ORTHO}(T_{\text{lim}}) = E_0^{ORTHO} + \frac{3}{2}RT_E^{ORTHO} + 3RT_{\text{lim}} \ln\left(1 - e^{-T_E^{ORTHO}/T_{\text{lim}}}\right) - \frac{a_1}{2}T_{\text{lim}}^2, \quad (3)$$

where the parameters  $b$ ,  $c$  used in original equation 2.1 are neglected. Furthermore, the value  $E_0^{ORTHO} = E_0^{C15}$  was used here because the *ab initio* calculated total energy difference between the relaxed orthorhombic structure and C15 Laves phase is negligible (see Table 3). In the case of  $\text{HfV}_2$  orthorhombic phase, we have used  $T_E^{ORTHO} = 130.3$  K based on  $T_D^{ORTHO} = 169.3$  K calculated in this work.

The solution of the thermodynamic equation (3) is:

$$a_1 = 1.2376,$$

which is calculated under the condition that  $G^{ORTHO}(T) = G^{C15}(T) = 22.9$  J/mol at the transformation temperature 114 K.

The latent heat of reaction

$\text{HfV}_2$  C15 Laves phase  $\rightarrow$   $\text{HfV}_2$  orthorhombic phase equal to -45 J/mole of f.u. [10] was added to  $G^{ORTHO}(T)$  at low temperatures. The Gibbs energy for  $\text{HfV}_2$  orthorhombic phase above 114 K is expressed simply as constant (see Figure 4)

$$G^{ORTHO}(T) = 22.9 - 45 = -22.1 \text{ J/mol of f.u.}$$

The shape of molar Gibbs energy functions  $G(T)$  for  $\text{HfV}_2$  C15 Laves phase and for  $\text{HfV}_2$  orthorhombic phase in the temperature region 0 – 120 K is illustrated in Figure 4.

The values of  $a$ ,  $a_1$ ,  $b$  and  $c$  parameters obtained in this section were successfully employed in the phase diagram calculations.

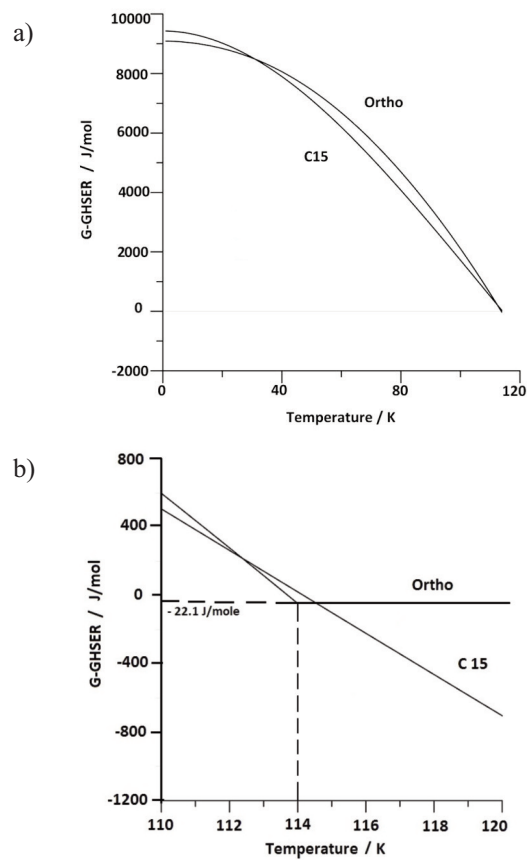


Figure 4. Temperature dependence of the molar Gibbs energy of  $\text{HfV}_2$  C15 Laves phase and of  $\text{HfV}_2$  orthorhombic phase: a) in the temperature region 0 – 120 K; b) in details in temperature region 110 – 120 K

For elemental constituents, we employed SGTE data [39] above 298.15 K and data from [15, 16] below 298.15 K.

## 6. Calculation of phase diagram

The thermodynamic basis of the CALPHAD method relies explicitly on the assumption that the equilibrium phase composition arises as a result of a minimization of Gibbs energy in a closed system at constant external conditions (temperature and pressure) [36].

For the modelling of C15 Laves phase in the Hf-V system below  $T_{\text{lim}}$ , we employed the model of stoichiometric phase, where a continual extension of Gibbs energy from temperature region above  $T_{\text{lim}} = 298.15$  K (eq. 2.1 to 2.3) was included.

The  $\text{HfV}_2$  orthorhombic phase was described above  $T_{\text{lim}}$  as constant (see Fig. 4b). The optimized thermodynamic parameters describing both  $\text{HfV}_2$  C15 Laves phase and  $\text{HfV}_2$  orthorhombic phase in the Hf-V system are summarized in Table 6 where  $\text{GHSERV} = G(\text{V BCC\_A2})$  and  $\text{GHSERHF} = G(\text{Hf HCP\_A3})$  is used.



**Table 6.** The Gibbs energy data for HfV<sub>2</sub> C15 Laves phase and HfV<sub>2</sub> orthorhombic phase

|   |  |
|---|--|
| HfV <sub>2</sub> C15 Laves phase<br>(0 <T< 298.15)    | 9429+24.9435*T*ln(1-exp(-152.3*T <sup>-1</sup> ))-1.1075*T <sup>2</sup> -0.9737*10 <sup>-8</sup> *T <sup>5</sup> +<br>0.00407735*T <sup>3</sup> +2*GHSERV + GHSERHF; |
| HfV <sub>2</sub> C15 Laves phase<br>(298.15 <T< 4000) | -10800+0.3*T+2*GHSERV + GHSERHF;   |
| HfV <sub>2</sub> orthorhombic phase<br>(0 <T< 114)    | 9156+24.9435*T*ln(1-exp(-130.3*T <sup>-1</sup> ))-0.6188*T <sup>2</sup> +2*GHSERV + GHSERHF - 45;  |
| HfV <sub>2</sub> orthorhombic phase<br>(114<T< 4000)  | + 2*GHSERV + GHSERHF-45+22.9;  |

The thermodynamic *L*-parameters of both BCC\_A2 and HCP\_A3 phase for the temperatures below 298.15 K are kept equal to those published for temperatures above 298.15 K listed in Table 4. Their unary data were taken from [15, 16]. For the sake of completeness, they are presented in Table 7 (hafnium) and in Table 8 (vanadium). Thermodynamic model for liquid phase, as metastable phase below 298.15 K, was extrapolated from temperature above 298.15 K.

**Table 7.** The hafnium Gibbs energy unary data extended to zero Kelvin (J.mol<sup>-1</sup>) connected with corresponding SGTE data [15, 16, 39].

|                                    |  |
|------------------------------------|--|
| Hf LIQUID<br>(0<T< 1000) [39]      | +27402.256-10.953093*T+GHSERHF;  |
| Hf LIQUID<br>(1000<T< 2506) [39]   | +49731.499-149.91739*T+12.116812*T*LN(T)-0.21262021*T**2<br>+1.376466E-06*T**3-4449699*T**(-1);  |
| Hf LIQUID<br>(2506<T< 3000) [39]   | -4247.217+265.470523*T-44*T*LN(T);   |
| Hf HCP_A3<br>(0 <T< 298.15) [16]   | -7609.05+1733.58+24.9435*T*ln(1-exp(-139*T <sup>-1</sup> )) +0.013107/2*T <sup>2</sup><br>-8.95372*10 <sup>-5</sup> /6*T <sup>3</sup> +3.61883*10 <sup>-10</sup> /20*T <sup>5</sup> ;          |
| Hf HCP_A3<br>(298.15<T< 2506) [39] | -6987.297 +110.744026*T-22.7075*T*ln(T) - 0.004146145*T <sup>2</sup> -4.77*10 <sup>-10</sup> *T <sup>3</sup><br>-22590*T <sup>-1</sup> ;   |
| Hf HCP_A3<br>(2506<T< 3000) [39]   | -1446776.33+6193.60999*T-787.536383*T* ln(T)+0.1735215*T <sup>2</sup><br>-7.575759*10 <sup>-6</sup> *T <sup>3</sup> +5.01742495*10 <sup>8</sup> *T <sup>-1</sup>                               |
| Hf BCC_A2<br>(0 <T< 298.15) [15]   | 4357.63+1574.934+ 24.9435*T*ln(1-exp(-126.28*T <sup>-1</sup> ))-0.0193112*T <sup>2</sup><br>+0.288928*10 <sup>-4</sup> *T <sup>3</sup> -3.04866*10 <sup>-11</sup> *T <sup>5</sup> ;            |
| Hf BCC_A2<br>(298.5 <T< 2506) [39] | 5370.703+103.836026*T-22.8995*T*ln(T)-4.206605*10 <sup>-3</sup> *T <sup>2</sup> -8.71923*10 <sup>-7</sup> *T <sup>3</sup><br>-22590*T <sup>-1</sup> -1.446*10 <sup>-10</sup> *T <sup>4</sup> ; |
| Hf BCC_A2<br>(2506<T< 3000) [39]   | 1912456.77-8624.20573*T+1087.61412*T*ln(T)-0.286857065*T <sup>2</sup><br>+1.3427829*10 <sup>-5</sup> *T <sup>3</sup> -6.1008509*10 <sup>8</sup> *T <sup>-1</sup> ;                             |

**Table 8.** Vanadium Gibbs energy unary data extended to zero Kelvin (J.mol<sup>-1</sup>) connected with corresponding SGTE data [15, 16, 39].

|                                    |   |
|------------------------------------|---|
| V LIQUID<br>(0<T< 2183) [39]       | +20764.117-9.455552*T+GHSERV-5.19136E-22*T**7;  |
| V LIQUID<br>(2183<T< 4000) [39]    | -19617.51+311.055983*T-47.43*T*LN(T);   |
| V BCC_A2<br>(0 <T< 298.15) [16]    | - 8120.64+3267.60+24.9435*T*ln(1-exp(-262*T <sup>-1</sup> ))-0.012991/2)*T <sup>2</sup><br>+(5.43850*10 <sup>-5</sup> /6)*T <sup>3</sup> -1.21275*10 <sup>-11</sup> *T <sup>5</sup> ; |
| V BCC_A2<br>(298.15 <T< 790) [39]  | - 7930.430+133.346053*T-24.134*T*ln(T)-3.098*10 <sup>-3</sup> *T <sup>2</sup> +1.2175*10 <sup>-7</sup> *T <sup>3</sup> +69460*T <sup>-1</sup> ;                                       |
| V BCC_A2<br>(790 <T< 2183) [39]    | -7967.84+143.291*T-25.9*T*ln(T)+6.25*10 <sup>-5</sup> *T <sup>2</sup> -6.8*10 <sup>-7</sup> *T <sup>3</sup> ;   |
| V BCC_A2<br>(2183 <T< 4000) [39]   | -41689.86+321.1407*T-47.430*T*ln(T)+6.4439*10 <sup>31</sup> *T <sup>9</sup> ;   |
| V HCP_A3<br>(0 <T< 298.15) [15]    | -4580.80+3975.749+24.9435*T*ln(1-exp(-318.78*T <sup>-1</sup> )) -0.012936*T <sup>2</sup><br>+1.6044*10 <sup>-5</sup> *T <sup>3</sup> -1.5817*10 <sup>-11</sup> *T <sup>5</sup> ;      |
| V HCP_A3<br>(298.15 <T< 4000) [39] | GHSERV+4000+2.4*T; (GHSERV = G(V BCC_A2));  |



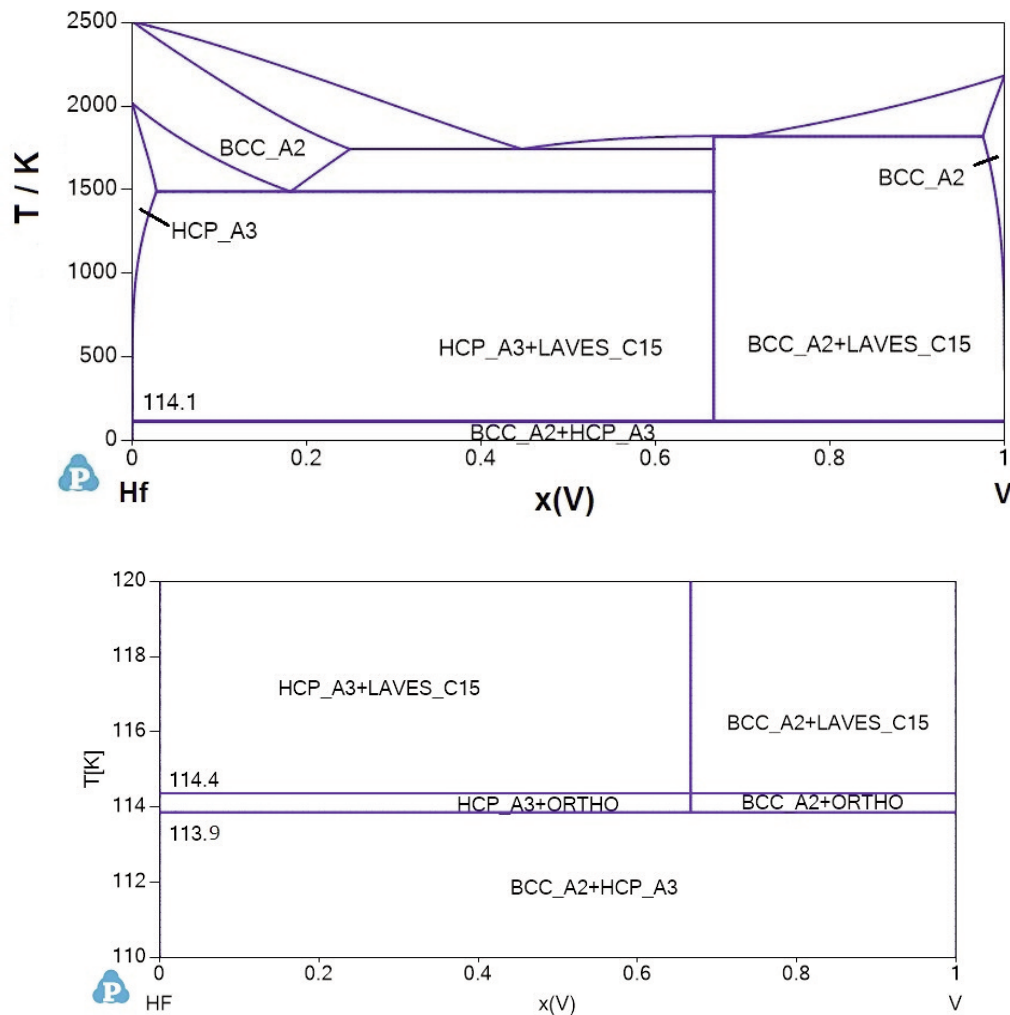


Figure 5. The Hf-V stable phase diagram (without orthorhombic phase) and detail of this phase diagram (including orthorhombic phase) around 114 K, both calculated in this work.

The phase diagram calculated by using of these parameters is shown in Figure 5.

In the temperature region 0 – 113.9 K, the  $\text{HfV}_2$  orthorhombic phase is metastable and only stable BCC/HCP equilibrium is calculated in this region.

## 7. Conclusions

A thorough *ab initio* analysis of phases found in Hf-V system was performed at 0 K. *Ab initio* calculated values of lattice parameters and energies of formation of Laves phases and orthogonal and tetragonal structures with respect to the SER states, i.e. BCC\_A2 for V and HCP\_A3 for Hf, correspond in general reasonably well to both experimental data wherever available and previous theoretical results. The exceptions are structural parameters of  $\text{HfV}_2$  C15 Laves phase evaluated by VASP code employing the LDA. Furthermore, there are two values of energies of

formation of  $\text{HfV}_2$  C15 Laves phase which differ from the other positive values: from experiment we have  $-16.7 \text{ kJ mol of atoms}^{-1}$  [30] and FP-LMTO calculations give  $-1.51 \text{ kJ mol of atoms}^{-1}$  [31]. It is shown from *ab initio* calculations that the  $\text{HfV}_2$  orthorhombic phase is not stable at 0 K with respect to SER states similarly as C15 Laves phase. Their stability at higher temperatures is caused by entropy contribution. The orthorhombic phase becomes stable at 113.9 K and C15 Laves phase above 114.1 K, where orthorhombic phase transforms to this structure. The stability of C15 Laves phase and C14 Laves phase and orthogonal phase was also tested by analysis of phonon spectra calculations, which proved them to be mechanically stable.

It was shown that the methodology of calculation of unary data [13, 14] at temperatures below 298.15 K is transferable to more complicated structures leaving Gibbs energy data above 298.15 K unchanged. The



proposed procedure, using the Gibbs energy expression based on Debye (Einstein) temperature of modelled phases and on compatibility with SGTE unary data, extends CALPHAD type modelling to the third generation of databases and enables us to calculate phase diagrams down to zero Kelvin. This may be important for modelling of phase equilibria in multicomponent systems in materials in extreme conditions.

### Acknowledgement

*This research was supported by the Grant Agency of the Czech Republic (Project No. 14-15576S) and by the project CEITEC 2020 (LQ1601) with financial support from the Ministry of Education, Youth and Sports of the Czech Republic under the National Sustainability Programme II. Financial support of the Academy of Sciences of the Czech Republic (Project No. RVO:68081723) is also gratefully acknowledged. Computational resources were provided by the Ministry of Education, Youth and Sports of the Czech Republic under the Projects CESNET (Project No. LM2015042) and CERIT-Scientific Cloud (Project No. LM2015085).*

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