



## SUPPRESSED HYDROGEN SOLUBILITY IN BODY CENTRED CUBIC Va-GROUP METAL (Nb AND Ta) BY ALLOYING WITH W OR Ru ANALYSED ON THE BASIS OF STATISTICAL THERMODYNAMICS

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### Abstract

Available equilibrium pressure-temperature-composition relationships for body centred cubic (*bcc*)  $\text{Nb}_{0.95}\text{M}_{0.05}\text{H}_x$  ( $\text{M} = \text{W}$  or  $\text{Ru}$ ) and *bcc*  $\text{Ta}_{0.95}\text{W}_{0.05}\text{H}_x$  are analysed on the basis of statistical thermodynamics. In the systems under consideration, H solubility  $x$  under given condition of temperature  $T$  and hydrogen partial pressure  $p(\text{H}_2)$  tends to diminish with increasing  $y$ . Extent of suppression of H absorption into the  $\text{Nb}_{1-y}\text{M}_y$  alloy lattice per  $y$  rise represented by a decrease of the parameter  $\theta$  for number of available sites for occupation by H atoms per metal atom was greater with Ru than with W and correspondingly extent  $Q$  of stabilisation of H in the  $\text{Nb}_{0.95}\text{M}_{0.05}$  alloy lattice was evaluated to be more negative (i.e. H being more stable) with W ( $-234.1 \text{ kJ}\cdot\text{mol}^{-1}$ ) than with Ru

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( $-221.8 \text{ kJ}\cdot\text{mol}^{-1}$ ) while  $Q$  in  $\text{NbH}_x$  was evaluated to be  $-223.6 \text{ kJ}\cdot\text{mol}^{-1}$ . In either Nb alloy under consideration, interaction  $E(\text{H-H})$  between the nearest neighbour H atoms was evaluated to be attractive (negative). On the other hand, in spite of suppressed solubility of H into  $\text{Ta}_{0.95}\text{W}_{0.05}\text{H}_x$ ,  $\theta$  value for this alloy remained unchanged from that (0.55) for  $\text{TaH}_x$  and the evaluated  $Q$  for this alloy ( $-228.6 \text{ kJ}\cdot\text{mol}^{-1}$ ) remained virtually comparable to that for  $\text{TaH}_x$  ( $-229.4 \text{ kJ}\cdot\text{mol}^{-1}$ ) while the entropy term  $R \ln f_{\text{H}}(T)$  for this alloy ( $32.1 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) changed appreciably from that for  $\text{TaH}_x$  ( $62.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ), where  $f_{\text{H}}(T)$  refers to the partition function of H in the metal lattice at  $T$ .

### 1. Introduction

Equilibrium  $P$ - $T$ - $C$  (pressure-temperature-composition) relationships for hydrogen solubility in  $bcc$  (body centred cubic)  $\text{Nb}_{1-y}\text{M}_y$  alloy lattice ( $\text{M} = \text{W}$  or  $\text{Ru}$ ;  $y \leq 0.15$ ) were reported recently by Yukawa et al. [1] in the work discussing designing of H-permeable membrane with enhanced resistance against hydrogen embrittlement. The reported equilibrium  $P$ - $T$ - $C$  relationships for  $\text{Nb}_{1-y}\text{M}_y\text{H}_x$  exhibited trend of suppressed hydrogen solubility in the  $\text{Nb}_{1-y}\text{M}_y$  lattice with increasing  $y$  under given condition of temperature  $T$  and hydrogen gas partial pressure  $p(\text{H}_2)$ . More recently, Yukawa et al. [2] reported H solubility suppression in  $bcc$  Ta lattice through alloying with W.

In a preliminary statistical thermodynamic analysis of  $P$ - $T$ - $C$  relationships reported for H absorption for Va-group transition metals (V, Nb and Ta) by Veleckis and Edwards [3], it was demonstrated [4] that number  $\theta$  of available interstitial sites for occupation by H atoms per metal atom was smaller than 1 whereas, in view of mere crystal geometry,  $\theta$  is as high as 6 provided that tetrahedral interstitial sites (T-sites) are occupied with H atoms or  $\theta = 3$  provided that octahedral interstitial sites (O-sites) are occupied with

H atoms. The  $\theta$  value determined was 0.75 for *bcc* NbH<sub>*x*</sub> or 0.55 for *bcc* VH<sub>*x*</sub> and for *bcc* TaH<sub>*x*</sub> [4]. The determination of  $\theta$  was made with an *a priori* assumption that the interaction energy  $E(\text{H-H})$  between the nearest neighbour H atoms would hold constant within the same phase at a given  $T$  and the subsequent statistical thermodynamic analyses for a variety of non-stoichiometric interstitial MX<sub>*x*</sub> systems ( $X = \text{H, C, N, P}$  or S but not O) were undertaken with this simplifying *a priori* assumption and the derived values for the interaction parameters  $E(i-j)$  between neighbouring constituents  $i$  and  $j$  in the MX<sub>*x*</sub> lattice appeared to be rational [4-12]. Thus, the employed *a priori* assumption for the series of statistical thermodynamic analyses was judged to be valid on the basis of the self-consistency of the evaluation results acquired by this simplifying postulate although there was no first-principle-based justification to validate this *a priori* assumption.

Before the author proposed to use this simplifying *a priori* assumption of constant  $E(\text{X-X})$  within the same phase at any given  $T$  for statistical thermodynamic analysis of non-stoichiometric interstitial compound MX<sub>*x*</sub>, statistical thermodynamic analyses used to be made by *a priori* accepted model of sub-lattice with specified geometrical configuration and, when variation of  $E(\text{X-X})$  with composition  $x$  was derived, it was interpreted as peculiar change of  $E(\text{X-X})$  with composition  $x$  (normally, transition of attractive (negative)  $E(\text{X-X})$  in low range of  $x$  to repulsive (positive)  $E(\text{X-X})$  in high range of  $x$  within the same phase). However, noting that energy involved even in the liquid/solid phase transition is mere  $10 \sim 20 \text{ kJ} \cdot \text{mol}^{-1}$  order [13], it is more natural and straightforward to accept that phase change is induced when considerable variation of  $E(\text{X-X})$  with  $x$  in MX<sub>*x*</sub> occurs at given  $T$ .

In Figure 1, isothermal plots of  $RT \ln \{[p(\text{H}_2)]^{1/2} \cdot (\theta - x)/x\}$  against  $x$  calculated from equilibrium  $P$ - $T$ - $C$  relationships reported for *bcc* NbH<sub>*x*</sub> by Veleckis and Edwards [3] with  $\theta = 1.5$  and those with  $\theta = 0.75$  are

reproduced from [4]. The slope of such isothermal plot is proportional to  $E(\text{H-H})$  (cf. equation (1) later in the text) and thus  $\theta = 0.75$  was chosen for the statistical thermodynamic analysis for  $bcc \text{ NbH}_x$  because this choice of  $\theta$  value led to constancy of  $E(\text{H-H})$  at any given  $T$  over entire homogeneity range of the  $bcc \text{ NbH}_x$  phase under consideration. Anyway,  $E(\text{H-H})$  varied with  $T$  [10].

For very dilute non-stoichiometric interstitial solutions  $\text{MX}_x$ ,  $\theta$  value for the statistical thermodynamic analysis was proposed to be determined to fulfil the condition  $E(\text{X-X}) = 0$  to represent realistic condition of absence of nearest neighbour X-X interaction [7].

In this paper, suppressed H absorption in  $bcc \text{ Nb}$  lattice by substitutional alloying with W or Ru represented in the  $P$ - $T$ - $C$  relationships reported by Yukawa et al. [1] as well as that in  $bcc \text{ Ta}$  lattice alloyed with W [2] is analysed on the basis of statistical thermodynamics in terms of the parameter  $\theta$ . Evaluated values referring to the enthalpy term  $Q$  ( $\text{kJ}\cdot\text{mol}^{-1}$ ) representing extent of stabilisation of H atom and the entropy term  $R \ln f_{\text{H}}(T)$  ( $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) of H atom in these alloy lattices are reviewed where  $f_{\text{H}}(T)$  refers to the partition function of H atom in the alloy lattice at  $T$ .

## 2. Standard Statistical Thermodynamic Analysis Procedure

In the statistical thermodynamics, partition function  $PF$  for condensed phase (either solid or liquid) under consideration is composed taking into account nearest neighbour atomic interactions. Then, from the partial derivation of  $PF$  with respect to number  $n_i$  of constituent element  $i$  in the condensed phase, chemical potential  $\mu(i)^c$  of constituent  $i$  in the condensed phase is derived. Then,  $\mu(i)^c$  in the condensed phase is put equal to  $\mu(i)^g$  of the same element  $i$  in the gas phase.

The expression for  $\mu(\text{X})^g$  of ideal diatomic gas  $\text{X}_2$  is readily available

in the classical text book authored by Fowler and Guggenheim [14]. The detailed derivation procedure of  $\mu(X)^c$  for the condensed phase  $MX_x$  might be referred to elsewhere [6-10]. Anyway, it is eventually reduced to the following equations for the purpose of analysing H solution under consideration:

$$A(x, T) \equiv RT \ln\{[p(H_2)]^{1/2} \cdot (\theta - x)/x\} = g + \beta x E(H-H), \quad (1)$$

$$K = g - [D(H_2)/2 - RT C(T)] = Q - RT \ln f_H(T), \quad (2)$$

$$C(T) = -(1/2) \ln\{(4\pi m_H)^{3/2} k^{5/2} / h^3\} \cdot [(T^{7/2} / \Theta_r) \cdot (1 + \Theta_r / 3T)] \cdot [\rho^2 v_0^* / 2] \\ + \Theta_v / 4T + (1/2) \ln[1 - \exp(-\Theta_v / T)], \quad (3)$$

$$\ln f_H(T) = - \int_0^\infty g(v) \ln[1 - \exp(-hv/kT)] dv + \ln \rho v_0, \quad (4)$$

$$Q + \beta x E(H-H) = \partial E / \partial n_H. \quad (5)$$

To start the statistical thermodynamic analysis using equation (1), the value for the parameter  $\theta$  must be chosen adequately to yield linear  $A(T)$  vs.  $x$  isotherms at any given  $T$ . This is to fulfill the *a priori* assumption of constant  $E(H-H)$  over a range of homogeneity composition  $x$  at a given  $T$  for non-stoichiometric interstitial alloy lattice  $A_{1-y}B_yH_x$  possessing composition  $y$  consisting of H absorbing constituent A and non-H absorbing constituent B.

### 3. Determining $\theta$ Parameter Value for *bcc* $Nb_{1-y}M_yH_x$ Lattice

To start statistical thermodynamic analysis for  $Nb_{1-y}M_yH_x$  systems ( $M = W$  or  $Ru$ ), the first step is to determine the value of  $\theta$  as a function of  $y$  for given  $M$ . For this purpose, Figure 2 in [1] summarising isothermal  $P$ - $C$  relationships at 673 K for  $Nb_{1-y}Ru_yH_x$  lattice were analysed. Table 1 summarises the  $P$ - $C$  relationships read from Figure 2 in [1].

Unit of  $p(H_2)$  in the  $P$ - $C$  plots presented in [1] is MPa. But numerical

table for values of  $[D(\text{H}_2)/2 - RT C(T)]$  in equation (2) was prepared earlier for  $p(\text{H}_2)$  in unit of atm as exhibited as Table 1 in [12]. Thus, to use straightforwardly the available tabulated values for  $[D(\text{H}_2)/2 - RT C(T)]$  for the present analysis, it was more convenient to use the value of  $p(\text{H}_2)$  in atm unit. The conversion between atm and MPa units is made through relationship

$$1 \text{ atm} = 1.01325 \cdot 10^{-1} \text{ MPa.} \quad (6)$$

In the present analysis, the read  $p(\text{H}_2)$  values in MPa unit from the graphs presented in [1] were simply multiplied by 10 to be accepted as the value in atm unit without being bothered to apply exact multiplication factor 9.869 ( $= 1/0.101325$ ). Noting the error margin of the graphical reading of the  $P$ - $C$  coordinate values and the fact that  $p(\text{H}_2)$  in equation (1) appears in natural logarithm in form of square root, eventual extent of imprecision of the calculation results by this approximation in  $p(\text{H}_2)$  unit conversion was judged to be trivial.

As reported earlier [4],  $\theta$  for  $bcc$   $\text{NbH}_x$  lattice was determined to be 0.75. Thus,  $\theta$  value for  $\text{Nb}_{1-y}\text{Ru}_y\text{H}_x$  with suppressed H solubility by alloying with Ru must be smaller than 0.75.

As plotted in Figure 2(a), slope of the isothermal  $A$  vs.  $x$  plot for  $\text{Nb}_{0.95}\text{Ru}_{0.05}\text{H}_x$  at 673 K with  $\theta = 0.75$  varied with  $x$  like that for  $\text{NbH}_x$  in Figure 1(a) with  $\theta = 1.5$ . Thus,  $\theta$  to yield linear  $A$  vs.  $x$  plot was sought by decreasing  $\theta$  with interval of 0.05 and  $\theta = 0.55$  was found to fulfill this condition. The similar search of  $\theta$  for  $\text{Nb}_{0.90}\text{Ru}_{0.10}\text{H}_x$  lattice was done starting from  $\theta = 0.55$  and then  $\theta$  for  $\text{Nb}_{0.90}\text{Ru}_{0.10}\text{H}_x$  was determined to be 0.35 (Figure 2(b)). Likewise,  $\theta$  for  $\text{Nb}_{0.85}\text{Ru}_{0.15}\text{H}_x$  was determined to be 0.15 (Figure 2(c)).

The evaluated  $\theta$  vs.  $y$  relationship for  $\text{Nb}_{1-y}\text{Ru}_y\text{H}_x$  is plotted in Figure 3 together with that evaluated for  $\text{Nb}_{1-y}\text{W}_y\text{H}_x$  at  $y = 0.05$  through analysis

of the  $P$ - $C$  relationship at  $T = 673$  K reported by Yukawa et al. [1] and that evaluated earlier for  $\text{Nb}_{1-y}\text{Mo}_y\text{H}_x$  [5] through analysis of  $P$ - $T$ - $C$  data reported by Inoue et al. [15]. It is noticed in Figure 3 that  $\theta$  variation pattern with  $y$  for  $bcc$   $\text{Nb}_{1-y}\text{Ru}_y\text{H}_x$  lattice is represented by

$$\theta(\text{Nb}_{1-y}\text{Ru}_y\text{H}_x) = 0.75 - 4y. \quad (7)$$

On the other hand, that for  $bcc$   $\text{Nb}_{1-y}\text{W}_y\text{H}_x$  is represented by

$$\theta(\text{Nb}_{1-y}\text{W}_y\text{H}_x) = 0.75 - 0.5y \quad (8)$$

provided that  $\theta$  vs.  $y$  relationship holds linear to  $y$  exceeding 0.05.

Extent of suppression of H absorption in  $bcc$  Nb lattice through alloying with Mo is slightly less than that with Ru while it is considerably greater than that with W according to the plots in Figure 3.

In the earlier work [6], the author analysed H absorption in  $bcc$   $\text{Nb}_{1-y}\text{M}_y\text{H}_x$  lattice for  $\text{M} = \text{Al}, \text{Cu}, \text{Sn}, \text{Ni}$  and  $\text{Pd}$  through analysis of  $P$ - $T$ - $C$  data reported by Burch and Francis [16] and derived that the  $\theta$  vs.  $y$  relationship up to  $y = 0.125$  was represented commonly with Mo,

$$\theta(\text{Nb}_{1-y}\text{M}_y\text{H}_x) = 0.75 - 3y \quad (y \leq 0.125 \text{ for Mo, Al, Cu, Sn, Ni and Pd}).$$

It is seen in Figure 3 that, in the range of  $y$  greater than 0.10, extent of suppression of hydrogen absorption in  $bcc$  Nb lattice per alloying with Mo tended to diminish from that in the range of  $y$  smaller than 0.10.

#### 4. Evaluating $Q$ and $R \ln f_H$ for $bcc$ $\text{Nb}_{0.95}\text{M}_{0.05}\text{H}_x$ with $\text{M} = \text{Ru}$ and $\text{W}$

As in the preceding section,  $\theta$  for  $bcc$   $\text{Nb}_{0.95}\text{M}_{0.05}\text{H}_x$  was determined to be 0.55 for  $\text{M} = \text{Ru}$  and 0.725 for  $\text{M} = \text{W}$ . Thus, using these  $\theta$  parameter values, statistical thermodynamic analysis was undertaken for the  $\text{Nb}_{0.95}\text{M}_{0.05}\text{H}_x$  lattices under consideration. The analysis results are summarised in Table 3.

Slope of the isothermal  $A$  vs.  $x$  plot calculated using equation (1) represents  $\beta E(\text{H-H})$ . Calculated values of  $\beta E(\text{H-H})$  for  $\text{Nb}_{0.95}\text{M}_{0.05}\text{H}_x$  with  $\text{M} = \text{Ru}$  and  $\text{W}$  are plotted as a function of  $T$  in Figure 4 together with those for  $\text{Nb}_{0.95}\text{M}_{0.05}\text{H}_x$  for  $\text{M} = \text{Al}, \text{Cu}, \text{Sn}, \text{Ni}$  and  $\text{Pd}$  evaluated earlier that were not given explicitly in the published works [5, 6] but are readily available in the author's filed record of calculation results.

As seen in Figure 4,  $\beta E(\text{H-H})$  in  $bcc$   $\text{NbH}_x$  over  $T$  range between 600 K and 1000 K fell between  $-20 \text{ kJ}\cdot\text{mol}^{-1}$  and  $-30 \text{ kJ}\cdot\text{mol}^{-1}$  showing slight variation with  $T$  and that in  $\text{Nb}_{0.95}\text{Ru}_{0.05}\text{H}_x$  was comparable to that in  $\text{NbH}_x$  while that in  $\text{Nb}_{0.95}\text{W}_{0.05}\text{H}_x$  was less attractive (less negative) than that in  $\text{NbH}_x$  when compared at the same  $T$ .

Then, from the intercept term  $g$  of the  $A$  vs.  $T$  isotherms,  $K$  vs.  $T$  relation was derived in which the intercept term refers to  $Q$  and the coefficient of  $T$  refers to  $-R \ln f_{\text{H}}$ . The calculated values for  $Q$  and  $R \ln f_{\text{H}}$  are listed in Table 4 together with those enumerated for other  $bcc$   $\text{Nb}_{1-y}\text{M}_y\text{H}_x$  lattices in the earlier works [4-6, 8].

It is noticed in Table 4 that  $Q(\text{Nb}_{0.95}\text{W}_{0.05}\text{H}_x)$  was more negative than  $Q(\text{NbH}_x)$  implying that H in the  $\text{Nb}_{0.95}\text{W}_{0.05}\text{H}_x$  lattice was more stable in terms of enthalpy than H in the  $\text{NbH}_x$  lattice in spite of certain extent of H solubility reduction for  $bcc$  Nb lattice through alloying with W as represented by reduction of  $\theta$  from 0.75 in  $\text{NbH}_x$  to 0.725 in  $\text{Nb}_{0.95}\text{W}_{0.05}\text{H}_x$ . On the other hand,  $Q(\text{Nb}_{0.95}\text{Ru}_{0.05}\text{H}_x)$  was less negative than  $Q(\text{NbH}_x)$  implying reduced extent of stability of H in the  $\text{Nb}_{0.95}\text{Ru}_{0.05}\text{H}_x$  lattice than in the  $\text{NbH}_x$  lattice.

As displayed by the bold letters in Table 4, only  $Q(\text{Nb}_{0.95}\text{Sn}_{0.05}\text{H}_x)$  and  $Q(\text{Nb}_{0.95}\text{Pd}_{0.05}\text{H}_x)$  were slightly more negative than  $Q(\text{NbH}_x)$  among  $Q(\text{Nb}_{1-y}\text{M}_y\text{H}_x)$  values for the alloying element M with which reduction of



H absorption was brought about for  $\text{NbH}_x$  [5, 6] while  $Q(\text{Nb}_{1-y}\text{Ti}_y\text{H}_x)$  was more negative than  $Q(\text{NbH}_x)$  in accordance with the enhanced H absorption into *bcc* Nb lattice through alloying with Ti [8]. Affinity of H was evaluated to be stronger for Ti than for Nb (e.g., Figure 1 in [9]).

In *bcc*  $\text{MH}_x$  lattice, it appears rational to assume that O-sites rather than T-sites are occupied with H atoms [5]. Provided that H atoms are distributed over O-sites in  $\text{Nb}_{1-y}\text{M}_y\text{H}_x$  lattice in which H solubility is less than that in  $\text{NbH}_x$ , expression for  $Q$  would become [5, 9]

$$Q = 2E(\text{H-Nb})^{(\text{I})} + 4E(\text{H-Nb})^{(\text{II})} - E(\text{Nb-Nb})^{(\text{II})}, \quad (9)$$

where superscripts, (I) and (II), respectively, refer to the first and the second nearest neighbours.

In the *bcc*  $\text{Nb}_{1-y}\text{M}_y\text{H}_x$  under consideration, substitutional alloying of Nb with M possessing affinity to H less stronger than Nb resulted in the reduction of H absorption and thence M-H pair was assumed not formed. The *bcc* lattice is more “open” than the closed packed *fcc* (face centred cubic) or *hcp* (hexagonal close packed) lattice and thence the second nearest neighbour interaction besides the first nearest neighbour interaction is taken into account in the expression for  $Q$ .

### 5. Estimating $x$ in $\text{Nb}_{1-y}\text{M}_y\text{H}_x$ for Given Values of $y$ , $T$ and $p(\text{H}_2)$

From equation (1) taking into account relationship represented by equation (2), we can derive expression for  $x$  as follows:

$$x = \theta \cdot [p(\text{H}_2)]^{1/2} / \{[p(\text{H}_2)]^{1/2} + \exp[Q + \beta x E(\text{H-H}) - RT \ln f_{\text{H}}(T) + \{D(\text{H}_2)/2 - RTC(T)\}]\}. \quad (10)$$

As we see in equation (10), parameter separation for  $x$  is not perfect in this expression and the term including  $x$ ,  $\beta x E(\text{H-H})$ , exists on the right hand side of equation (10). During the course of this series of statistical

thermodynamic characterisation of M-X systems [4-12], it became evident that  $E(X-X)$  interaction is at least by one order of magnitude less intense than  $E(X-M)$  interaction and that  $E(X-X)$  might be positive (repulsive) or negative (attractive) while  $E(X-M)$  in  $MX_x$  lattice is always negative.

This is understandable by referring to geometrical configuration of interstitial sites and relative size relationships of M atoms and O- and T-interstitial sites drawn assuming simplifying spherical atom model (for example, Figure 3 and Figure 4 in [10]). Thus, as a crude zeroth order approximation,  $\beta x E(H-H)$  term might be neglected and, accordingly, equation (10) is reduced to

$$x \approx \theta \cdot [p(H_2)]^{1/2} / \{[p(H_2)]^{1/2} + \exp[Q - RT \ln f_H(T) + \{D(H_2)/2 - RTC(T)\}]\}. \quad (11)$$

Further, from discrete data set for  $D(H_2)$  compiled in JANAF Thermochemical Tables [13] at 100 K interval, the least-mean-squares expression for the term  $\{D(H_2)/2 - RT \cdot C(T)\}$  over temperature range between 300 K and 1500 K is derived to be

$$D(H_2)/2 - RT \cdot C(T) = 192.669 + 0.092T \text{ (kJ}\cdot\text{mol}^{-1}\text{)}. \quad (12)$$

By substituting equation (12) into equation (11), we obtain

$$\begin{aligned} x &\approx \theta \cdot [p(H_2)]^{1/2} / \{[p(H_2)]^{1/2} \\ &\quad + \exp[Q - RT \ln f_H(T) + 192.669 + 0.092T]\} \\ &= \theta \cdot [p(H_2)]^{1/2} / \{[p(H_2)]^{1/2} + \exp[(Q + 192.66) \\ &\quad + [0.092 - R \ln f_H(T)]T]\} \text{ (kJ}\cdot\text{mol}^{-1}\text{)}. \end{aligned} \quad (13)$$

Thus, by substituting values of  $Q$  and  $R \ln f_H$  evaluated from statistical thermodynamic analysis into equation (13), rough estimate might be made for  $x$  at specified values of  $T$  and  $p(H_2)$  for  $Nb_{1-y}M_yH_x$  lattice at arbitrary  $y$  as long as  $\theta$  is known.

### 6. Analysis for *bcc* Ta<sub>0.95</sub>W<sub>0.05</sub>H<sub>x</sub>

Similar statistical thermodynamic analysis was made for *bcc* Ta<sub>0.95</sub>W<sub>0.05</sub>H<sub>x</sub> referring to the *P-T-C* relationships reported by Yukawa et al. [2]. To undertake statistical thermodynamic calculation using these *P-T-C* data, the composition values *x* were read from Figure 1 in [2] at four different *p*(H<sub>2</sub>) levels, 5, 1, 0.5 and 0.1 atm, as summarised in Table 5.

As shown in Figure 5(a), calculated *A* vs. *x* isotherms for *T* = 673 K, 723 K and 773 K all fell into linear relationships with the choice of  $\theta = 0.55$  implying that the statistical thermodynamic analysis for the *bcc* Ta<sub>0.95</sub>W<sub>0.05</sub>H<sub>x</sub> could be done using the same  $\theta$  as the one used for the analysis of *bcc* TaH<sub>x</sub> [4, 5]. That is, unlike for the *bcc* Nb<sub>0.95</sub>W<sub>0.05</sub>H<sub>x</sub>,  $\theta$  parameter value for the *bcc* Ta<sub>0.95</sub>W<sub>0.05</sub>H<sub>x</sub> remained unchanged from that for the *bcc* TaH<sub>x</sub> in spite of the reduced *H* absorption by the alloying with *W*.

These *A*(*T*;  $\theta = 0.55$ ) vs. *x* relationships are represented numerically by

$$A(773 \text{ K}; \theta = 0.55) = 9.473 - 25.4x \text{ (kJ}\cdot\text{mol}^{-1}\text{)}, \quad (14)$$

$$A(723 \text{ K}; \theta = 0.55) = 6.198 - 16.9x \text{ (kJ}\cdot\text{mol}^{-1}\text{)}, \quad (15)$$

$$A(673 \text{ K}; \theta = 0.55) = 3.667 - 16.7x \text{ (kJ}\cdot\text{mol}^{-1}\text{)}. \quad (16)$$

From the intercept values in these relationships, *K* vs. *T* relationship was derived as displayed in Figure 5(b) which is represented numerically by

$$K(T) = -228.598 - 0.0321T \text{ (kJ}\cdot\text{mol}^{-1}\text{)}. \quad (17)$$

As such, *Q* parameter value for the *bcc* Ta<sub>0.95</sub>W<sub>0.05</sub>H<sub>x</sub> was estimated to be  $-228.598 \text{ kJ}\cdot\text{mol}^{-1}$  and  $R \ln f_{\text{H}}$  to be  $+32.1 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  while the corresponding parameter values for *bcc* TaH<sub>x</sub> were reported to be,  $-229.413 \text{ kJ}\cdot\text{mol}^{-1}$  and  $+62.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , respectively [5].

That is,  $R \ln f_H$  value became slightly smaller for the *bcc*  $\text{Ta}_{0.95}\text{W}_{0.05}\text{H}_x$  than for the *bcc*  $\text{TaH}_x$  while the values for  $Q$  and  $\theta$  were comparable to each other between the *bcc*  $\text{Ta}_{0.95}\text{W}_{0.05}\text{H}_x$  and the *bcc*  $\text{TaH}_x$ . Accordingly, the observed H absorption reduction for *bcc* Ta lattice by alloying with W must be somehow interpreted in terms of the modified electronic structure in the metal sub-lattice through alloying with W as represented by the modified  $f_H$  for the *bcc*  $\text{Ta}_{0.95}\text{W}_{0.05}\text{H}_x$  from that for the *bcc*  $\text{TaH}_x$ .

## 7. Discussion

In the present work, suppressed H absorption in Va-group metals, Nb and Ta, with *bcc* lattice structure through alloying with W (VIa-group element) and Ru (VIIIa-group element) was analysed by means of statistical thermodynamics. The sample materials were all thin films with no mechanical constraining and thus H absorption performances in these sample materials were considered as being comparable to those in the bulk polycrystalline counterparts.

In a recent work [17], H absorption modification in epitaxial thin film samples of another Va-group element, vanadium (V), deposited over non-H absorbing substrate reported by Andersson et al. [18] was analysed on the basis of statistical thermodynamic in terms of deviation of the parameter value  $\theta$  from that in the bulk V like in the present work.

In [17], H absorption enhancement in epitaxial V (001) thin films of thickness, 50 and 100 nm, deposited over non-H absorbing MgO substrate was analysed assigning  $\theta$  value greater than that for the *bcc* V lattice with no mechanical constraining and the detected enhancement of the H absorption in the epitaxial V (001) thin films and the corresponding increase of  $\theta$  from that for the *bcc* V lattice with no mechanical constraining was ascribed to some mechanical lattice strain induced in the epitaxial V (001) thin films.

### 8. Concluding Remark

The present statistical thermodynamic analysis for  $bcc$   $Nb_{1-y}M_yH_x$  ( $M = W$  or  $Ru$ ;  $y \leq 0.15$ ) was made using the  $P$ - $T$ - $C$  relationships reported by Yukawa et al. [1] and that for  $Ta_{0.95}W_{0.05}H_x$  using the  $P$ - $T$ - $C$  relationships reported by Yukawa et al. [2].

Analysis results showed that the extent of the reduced H solubility in the  $bcc$  Nb lattice by substitutional alloying with  $M = W$  or  $Ru$  was represented by diminished value of the parameter  $\theta$  from that for the  $bcc$  Nb (0.75) whereas the value 0.55 for the  $\theta$  parameter for the  $bcc$   $Ta_{0.95}W_{0.05}$  lattice remained unchanged from that for the  $bcc$  Ta lattice.

Further, past analysis results for similar  $Nb_{1-y}M_yH_x$  phases [4-6, 8-10] were displayed altogether (Table 4) to review through general consistency among the statistical thermodynamic analysis results.

In addition, rough estimate procedure for  $x$  in  $Nb_{1-y}M_yH_x$  lattice with known values of statistical thermodynamic parameters,  $Q$ ,  $R \ln f_H$  and  $\theta$ , was proposed.

On the other hand, for the  $bcc$   $Ta_{0.95}W_{0.05}$ , decreased  $H$  absorption from that for the  $bcc$  Ta was concluded to be ascribable to the modified electronic structure as represented by the change in  $R \ln f_H$  value in the alloy lattice from that in the  $bcc$  Ta metal lattice and, with this extent of substitutional alloying with W ( $y = 0.05$ ), change in the number  $\theta$  of available sites for H occupation in the  $Ta_{1-y}W_y$  lattice remained indiscernible.

### Appendix: List of Symbols

$A(x, T): \equiv RT \ln\{[p(H_2)]^{1/2} \cdot (\theta - x)/x\}$  (kJ.mol<sup>-1</sup>); calculated from experimentally determined values of  $p(H_2)$ ,  $T$  and  $x$  for specified value of  $\theta$  using equation (1)

$C(T)$ : defined by equation (3) to represent contributions of translational, rotational and vibrational motions of  $H_2$  molecule

$D(H_2)$ : dissociation energy of  $H_2$  molecule per mole ( $\text{kJ}\cdot\text{mol}^{-1}$ )

$E$ : lattice energy ( $\text{kJ}\cdot\text{mol}^{-1}$ )

$E(i-j)$ : nearest neighbour pair-wise interaction energy between  $i$  and  $j$  atoms in  $\text{Nb}_{1-y}\text{M}_y\text{H}_x$  ( $y = 0.05$  or  $0.10$ ) or  $\text{Ta}_{0.95}\text{W}_{0.05}$  lattice

$f_H(T)$ : partition function of H in  $\text{Nb}_{1-y}\text{M}_y\text{H}_x$  or  $\text{Ta}_{0.95}\text{W}_{0.05}$  lattice at  $T$

$g$ : parameter determined as the intercept of the  $A(T)$  vs.  $x$  plot at  $x = 0$  using equation (1)

$g(v)$ : distribution function

$h$ : Planck constant

$k$ : Boltzmann constant

$K$ : parameter calculated from  $g$  using equation (2)

$m_H$ : mass of H atom

$n_H$ : number of H atoms in  $\text{Nb}_{1-y}\text{M}_y\text{H}_x$  or  $\text{Ta}_{0.95}\text{W}_{0.05}$  lattice

$p(H_2)$ : partial pressure of ideal  $H_2$  gas molecule (atm)

$P$ - $T$ - $C$ : pressure-temperature-composition

$Q$ : degree of stabilisation of H atom in  $\text{Nb}_{1-y}\text{M}_y\text{H}_x$  or  $\text{Ta}_{0.95}\text{W}_{0.05}$  lattice with reference to isolated H atom in vacuum

$R$ : universal gas constant ( $= 0.0083145 \text{ kJ}\cdot\text{mol}^{-1}$ )

$T$ : absolute temperature (K)

$x$ : atom fraction of  $H$  against total metal in  $Nb_{1-y}M_yH_x$  or  $Ta_{0.95}W_{0.05}$  lattice

$y$ : atom fraction of  $M$  (= W or Ru) in the metal sub-lattice in  $Nb_{1-y}M_yH_x$

$\beta$ : geometrical factor determined from crystal structure consideration

$\theta$ : number of available interstitial sites for occupation by H atom per metal atom in  $Nb_{1-y}M_yH_x$  or  $Ta_{0.95}W_{0.05}$  lattice

$\Theta_r$ : characteristic temperature for rotation of  $H_2$  molecule  
(= 85.4 K)

$\Theta_v$ : characteristic temperature for vibration of  $H_2$  molecule  
(= 6100 K)

$\mu(H)^c$ : chemical potential of H atom in the condensed phase  
 $Nb_{1-y}M_yH_x$  or  $Ta_{0.95}W_{0.05}$

$\mu(H)^g$ : chemical potential of H atom in the ideal diatomic  $H_2$  gas molecule

$\nu$ : vibrational frequency of H atom in  $Nb_{1-y}M_yH_x$  or  $Ta_{0.95}W_{0.05}$  lattice

$\rho$ : nuclear spin weight (= 2 for H while 3 for D)

$\nu_0$ : statistical weight of tightly bound electrons around H in  $Nb_{1-y}M_yH_x$  or  $Ta_{0.95}W_{0.05}$  lattice

$\nu_0^*$ : statistical weight of electrons in  $H_2$  molecule in normal state  
(= 1)

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**Table 1.** Isothermal *P-C* relationships at 673 K read from Figure 2 in [1]

$p(\text{H}_2)$ (atm)	$x = [\text{H}]/[\text{M}]$		
	$\text{Nb}_{0.95}\text{Ru}_{0.05}\text{H}_x$	$\text{Nb}_{0.90}\text{Ru}_{0.10}\text{H}_x$	$\text{Nb}_{0.85}\text{Ru}_{0.15}\text{H}_x$
5	0.491	0.229	0.089
2	0.422	0.164	0.059
1	0.351	0.122	0.040
0.5	0.273	0.086	0.029
0.1	0.104	0.036	0.010

**Table 2.** Equilibrium  $P$ - $T$ - $C$  relationships for  $\text{Nb}_{0.95}\text{M}_{0.05}\text{H}_x$  at  $T = 673$  K, 723 K and 773 K reported for  $\text{M} = \text{Ru}$  (Figure 3 in [1]) and for  $\text{M} = \text{W}$  (Figure 4 in [1])

$p(\text{H}_2)$ (atm)	$x$ in $\text{Nb}_{0.95}\text{Ru}_{0.05}\text{H}_x$			$x$ in $\text{Nb}_{0.95}\text{W}_{0.05}\text{H}_x$		
	$T = 673$ K	$T = 723$ K	$T = 773$ K	$T = 673$ K	$T = 723$ K	$T = 773$ K
5	0.491	0.451	0.371	0.654	0.600	0.655
2	0.422	0.359	0.263	0.604	0.525	0.416
1	0.351	0.266	0.176	0.551	0.429	0.289
0.5	0.273	0.186	0.115	0.477	0.309	0.176
0.2	0.163	0.100	0.064	0.324	0.168	0.094

**Table 3.** Statistical thermodynamic analysis results for  $bcc$   $\text{Nb}_{0.95}\text{M}_{0.05}\text{H}_x$  ( $\text{M} = \text{Ru}$  and  $\text{W}$ )

$T$ (K)	673	723	773
$D(\text{H}_2)/2 - RT \cdot C(T)^*$ (kJ·mol <sup>-1</sup> )	253.736	258.226	262.750
$A(\text{Nb}_{0.95}\text{Ru}_{0.05}\text{H}_x)$ (kJ·mol <sup>-1</sup> )	4.270 - 22.435 $x$	6.540 - 23.596 $x$	9.163 - 23.775 $x$
$K(\text{Nb}_{0.95}\text{Ru}_{0.05}\text{H}_x)$ (kJ·mol <sup>-1</sup> )	<b>-221.785 - 0.0412 <math>T</math></b>		
$A(\text{Nb}_{0.95}\text{W}_{0.05}\text{H}_x)$ (kJ·mol <sup>-1</sup> )	1.060 - 13.654 $x$	4.886 - 16.199 $x$	8.660 - 19.810 $x$
$K(\text{Nb}_{0.95}\text{W}_{0.05}\text{H}_x)$ (kJ·mol <sup>-1</sup> )	<b>-243.145 - 0.0141 <math>T</math></b>		

\*Values for  $[D(\text{H}_2)/2 - RT \cdot C(T)]$  at respective  $T$  were enumerated by interpolating the values listed in Table 1 in [12] as a function of  $T$  with 100 K interval.

**Table 4.** Available statistical thermodynamic parameter values for *bcc*  $\text{Nb}_{1-y}\text{M}_y\text{H}_x$

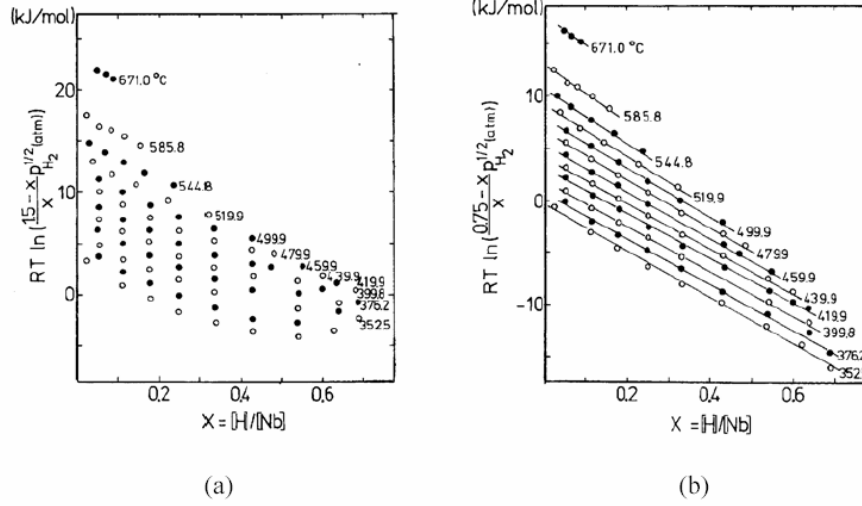
<i>bcc</i> $\text{Nb}_{1-y}\text{M}_y\text{H}_x$	$\theta$	$Q^{**}$ (kJ·mol <sup>-1</sup> )	$R \ln f_{\text{H}}$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	Reference (analysis)	P-T-C data source
$\text{NbH}_x$	0.75	-229.6 -229.5	61.8 61.7	4, 5 15	3 15
$\text{Nb}_{0.95}\text{Ru}_{0.05}\text{H}_x$	0.55	-221.8	41.2	present work	1
$\text{Nb}_{0.95}\text{W}_{0.05}\text{H}_x$	0.725	<b>-243.1</b>	14.1	present work	1
$\text{Nb}_{0.90}\text{Mo}_{0.10}\text{H}_x$	0.45	-225.5	65.4	5	15
$\text{Nb}_{0.80}\text{Mo}_{0.20}\text{H}_x$	0.30	-228.2	61.3	5	15
$\text{Nb}_{0.70}\text{Mo}_{0.30}\text{H}_x$	0.20	-220.8	67.7	5	15
$\text{Nb}_{0.95}\text{Al}_{0.05}\text{H}_x$	0.60	-225.8	36.9	6*	16
$\text{Nb}_{0.95}\text{Cu}_{0.05}\text{H}_x$	0.60	-223.5	41.2	6*	16
$\text{Nb}_{0.95}\text{Sn}_{0.05}\text{H}_x$	0.60	<b>-231.8</b>	30.6	6*	16
$\text{Nb}_{0.95}\text{Ni}_{0.05}\text{H}_x$	0.60	-219.2	45.0	6*	16
$\text{Nb}_{0.95}\text{Pd}_{0.05}\text{H}_x$	0.60	<b>-231.8</b>	26.1	6*	16
$\text{Nb}_{0.90}\text{Pd}_{0.10}\text{H}_x$	0.45	-213.9	45.5	6*	16
$\text{Nb}_{0.75}\text{Ti}_{0.25}\text{H}_x$	0.75	<b>-233.4</b>	35.4	8*	16
$\text{Nb}_{0.50}\text{Ti}_{0.50}\text{H}_x$	0.80	<b>-253.6</b>	26.5	8*	16
$\text{Nb}_{0.25}\text{Ti}_{0.75}\text{H}_x$	1.025	<b>-257.3</b>	29.7	8*	16
$\text{TiH}_x$	1.25	<b>-251.1</b>	35.2	8*	16

\*Values of  $Q$  and  $R \ln f_{\text{H}}$  for these  $\text{Nb}_{1-y}\text{M}_y\text{H}_x$  lattices were presented in graphical form and not given as numerals in [6, 8] but they are taken from the filed record of calculation results.

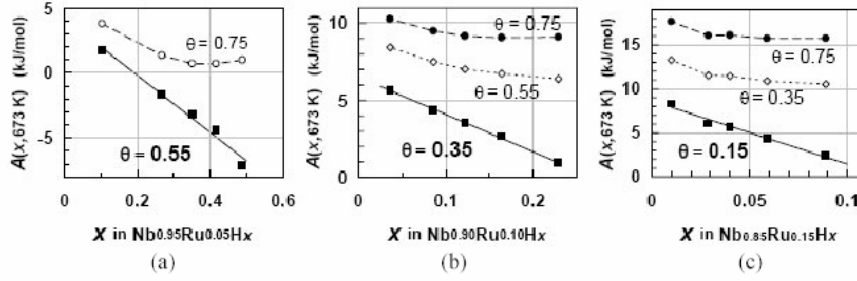
\*\* $Q$  values for  $\text{Nb}_{1-y}\text{M}_y\text{H}_x$  that were evaluated to be more negative than that for  $\text{NbH}_x$  are displayed with bold letter.

**Table 5.** Equilibrium  $P$ - $T$ - $C$  relationships for  $\text{Ta}_{0.95}\text{W}_{0.05}\text{H}_x$  at  $T = 673$  K, 723 K and 773 K read from Figure 1 in [2]

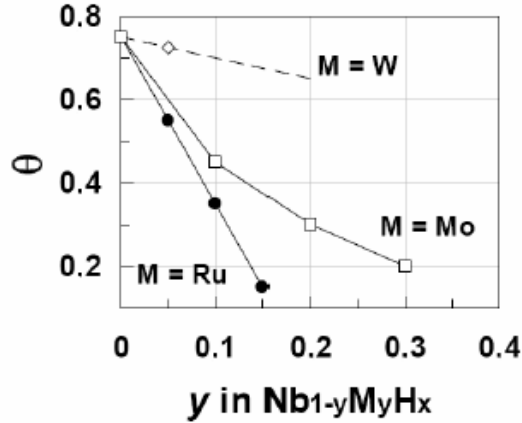
$p(\text{H}_2)$ (atm)	$x$ in $\text{Ta}_{0.95}\text{W}_{0.05}\text{H}_x$		
	$T = 673$ K	$T = 723$ K	$T = 773$ K
5	0.450	0.385	0.315
1	0.310	0.220	0.160
0.5	0.235	0.155	0.110
0.1	0.100	0.065	0.045



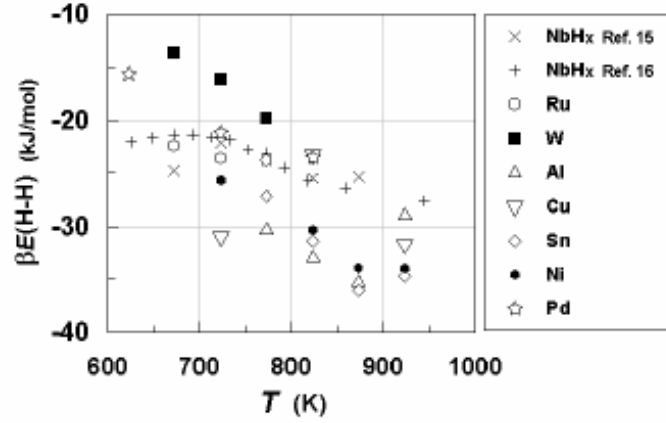
**Figure 1.** Comparative isothermal  $A(x, T) \equiv RT \ln \{ [p(\text{H}_2)]^{1/2} \cdot (\theta - x)/x \}$  vs.  $x$  plots for equilibrium  $P$ - $T$ - $C$  relationships for  $\text{bcc NbH}_x$  with  $\theta = 1.5$  and with  $\theta = 0.75$  (reproduced from [4]).



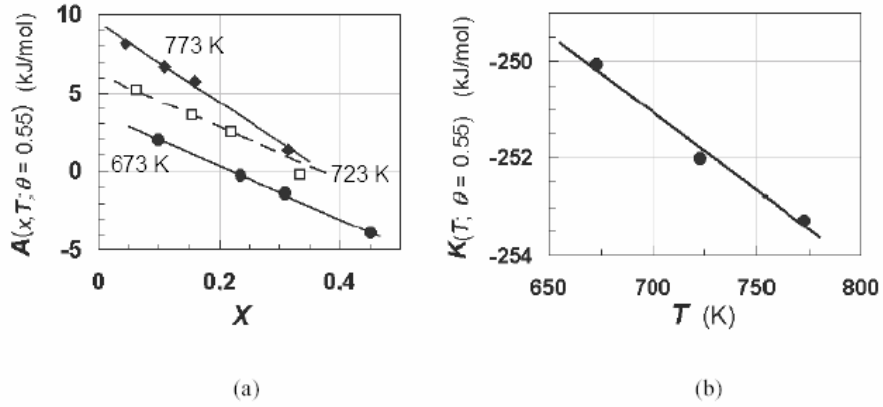
**Figure 2.** Comparative isothermal  $A(x, T) \equiv RT \ln\{[p(H_2)]^{1/2} \cdot (\theta - x)/x\}$  vs.  $x$  plots at  $T = 673$  K for equilibrium  $P$ - $T$ - $C$  relationships for  $bcc$   $Nb_{1-y}Ru_yH_x$  with varying choices of  $\theta$  parameter values. (a)  $\theta$  for  $Nb_{0.95}Ru_{0.05}H_x$  was determined to be 0.55; with  $\theta = 0.75$  specified for  $NbH_x$ , slope of the plot (proportional to  $E(H-H)$ ) varied with  $x$ . (b)  $\theta$  for  $Nb_{0.90}Ru_{0.10}H_x$  was determined to be 0.35; with  $\theta = 0.75$  specified for  $NbH_x$  and with  $\theta = 0.55$  specified for  $Nb_{0.95}Ru_{0.05}H_x$ , slope of the plot varied with  $x$ . (c)  $\theta$  for  $Nb_{0.85}Ru_{0.15}H_x$  was determined to be 0.15; with  $\theta = 0.75$  specified for  $NbH_x$  and with  $\theta = 0.35$  specified for  $Nb_{0.90}Ru_{0.10}H_x$ , slope of the plot varied with  $x$ .



**Figure 3.**  $\theta$  vs.  $y$  relationships determined for  $Nb_{1-y}MyH_x$  lattice with  $M = Ru$  and  $W$  and that reported for  $bcc$   $Nb_{1-y}Mo_yH_x$  [5].



**Figure 4.**  $\beta E(\text{H-H})$  values evaluated for  $\text{bcc Nb}_{0.95}\text{M}_{0.05}\text{H}_x$  plotted as a function of  $T$  ( $M = \text{Ru, W, Al, Cu, Sn, Ni}$  and  $\text{Pd}$ ). Partly reproduced from Figure 2 in [10].



**Figure 5.**  $A$  vs.  $x$  isotherms prepared for  $\text{Ta}_{0.95}\text{W}_{0.05}\text{H}_x$  using the  $P$ - $T$ - $C$  data reported by Yukawa et al. [2] with  $q = 0.55$  (a) and the derived  $K$  vs.  $T$  relationship for the  $\text{Ta}_{0.95}\text{W}_{0.05}\text{H}_x$  (b).