

Thermodynamic analysis on the Np–Zr–H system

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Abstract

The thermodynamic data base of the Np–Zr–H ternary system was developed based on the description of its binary constituents, coupling with the calculated enthalpies of formation obtained using the Miedema model and the Griessen–Driessen model. The provisional isothermal sections of the Np–Zr–H phase diagram were calculated using the data base. It was found that the Np–Zr–H ternary system at 972 K includes the liquid phase in the region of low hydrogen to metal ratio. It is pointed out that the composition of the Np–Zr–H hydride should be selected to avoid the hydride fuel melting in designing of a nuclear reactor fuel element.

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1. Introduction

The hydride fuel is an excellent integral fuel-moderator system, since the concentration of hydrogen in the hydride is comparable to that of hydrogen in liquid water of LWR cores. The hydride fuel of U–Zr hydride developed by general atomics (GA) is in use for more than 40 years in many TRIGA reactors around the world both in constant power and pulsed power operating conditions [1]. Recently, the use of actinide hydrides for transmutation of minor actinides has been proposed [2]. The actinide-hydride containing ²³⁷Np, ²⁴¹Am and ²⁴³Am was considered as a transmutation target fuel to

reduce the amount of long-lived actinides, which is included in high-level radioactive wastes generated after reprocessing spent nuclear fuels.

The thermodynamic properties of the Np–Zr–H system are not known from experiments and there is a need for information on the stability of the various phases and the Np–Zr–H phase diagram. This kind of information was the object of the present preliminary study on the Np–Zr–H system. The results were summarized in tables of thermodynamic parameters and calculated isothermal sections of phase diagram for 773 K, 873 K and 973 K.

The thermodynamic parameters obtained by Ogawa [3] on the Np–Zr systems were modified to obtain better reproducibility between the calculation and the reported experiments and literatures [4,5]. The thermodynamic parameters on the Zr–H system assessed by Dupin [4] were accepted with minor changes. The thermodynamic parameters for the Np–H system were obtained in the present work. The information from these three sub-systems and the excess Gibbs energy of the hydride phases

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then were used to construct the Np–Zr–H ternary phase diagram.

2. Experimental data

The experimental information on the phase relations, crystallography and thermodynamics of the Np–Zr [3,5], Zr–H [4] binary systems can be found in the references cited in these two publications. In the assessed Zr–H system in Ref. [4], the ZrH₂-Epsilon(FCT_L/2) phase was treated individually, while Wang and Olander [6] gave notes on the presence of this phase. However, in the present study we also treated the ZrH₂-Epsilon(FCT_L/2) phase individually, i.e. separately from the ZrH₂-Delta (FCC_A1) phase. The experimental data on the Np–H system assessed in the present work were mainly obtained from the works of Ward [7,19], which substantially agree with the values reported by Mulford and Wiewand [8]. There is no experimental information available on the Np–Zr–H ternary system up to the present time. Therefore, several reports on the related actinide hydrides, such as U–Zr–H [9–11] and Th–Zr–H [11–14] systems were studied for the comparison.

3. Thermodynamical model

3.1. Np–H

The NpH_{2+y} (CaF₂-C1) and NpH₃ (NpH₃-hexagonal) hydride phases were represented by the two-sublattice model (Np)_a(H, Va)_b [15,16], whereas the α -Np (Ortho_AC), β -Np (Tetra_AD), γ -Np (BCC_A2), and L-Np (Liquid) were treated as the neptunium end member, since the solubility of hydrogen in these phases is very low and can be neglected. In the two-sublattice model, Np was assumed to occupy the first sublattice, whereas H atoms and vacant interstitial sites (Va) were assumed to substitute for each other in the second one. The indexes *a* and *b* denote the number of sites of each sublattice. The Gibbs energy per mol formula unit for the CaF₂-C1 and NpH₃-hexagonal hydride phases then were expressed by,

$$G_m^\phi = y_{Va} {}^0G_{Np:Va}^\phi + y_H {}^0G_{Np:H}^\phi + cRT(y_H \ln y_H + y_{Va} \ln y_{Va}) + y_H y_{Va} ({}^0L_{Np:H,Va} + (y_H - y_{Va}) {}^1L_{Np:H,Va}). \quad (1)$$

The variable *y_i* denotes the site fraction of hydrogen and vacancies in its sublattice, respectively. The parameter ${}^0G_{Np:Va}^\phi$ is the Gibbs energy of pure component Np with the structure ϕ , and their values were referred to the enthalpy of standard state from SGTE [18]. The ${}^0G_{Np:H}^\phi$ is the Gibbs energy of a state where all the inter-

stitial sites are filled with H. For the CaF₂-C1 structure *b/a* = 2 and for the NpH₃-hexagonal structure *b/a* = 3.

3.2. Np–Zr–H

The Gibbs energy for the BCC_A2 (γ -Np, β -Zr), HCP_A3 (α -Zr, α -Np) solid solution phases was described by the two-sublattice model (Np, Zr)_a(H, Va)_b [15,16]. Np and Zr were assumed to occupy the first sublattice, whereas H atoms and vacant interstitial sites (Va) were assumed to substitute for each other in the second one. The Gibbs energy per mol formula units then was expressed by,

$$G_m^\phi = y_{Np} y_{Va} {}^0G_{Np:Va}^\phi + y_{Zr} y_{Va} {}^0G_{Zr:Va}^\phi + y_{Np} y_H {}^0G_{Np:H}^\phi + y_{Zr} y_H {}^0G_{Zr:H}^\phi + RT[a(y_{Np} \ln y_{Np} + y_{Zr} \ln y_{Zr}) + b(y_H \ln y_H + y_{Va} \ln y_{Va})] + {}^E G_m^\phi. \quad (2)$$

The *a* and *b* denote the number of sites of each sublattice. The variable *y_i* (*i* = Np, Zr, H, Va) is the site fraction of the component *i* in its sublattice. The parameter ${}^0G_{i:Va}^\phi$ is the Gibbs energy of pure component *i* with the structure ϕ , the ${}^0G_{i:H}^\phi$ is the Gibbs energy of a state where all the interstitial sites are filled with H. For the HCP_A3 structure *a* = 1 and *b* = 1 and the BCC_A2 structure was treated by adopting *a* = 1 and *b* = 3. Meanwhile, the Gibbs energies for the γ -Zr (FCC_A1) and ZrH₂-Epsilon(FCT_L/2) and those of NpH_{2+y} (CaF₂-C1) and NpH₃ (NpH₃-hexagonal) solid solution hydride phases originating, respectively, in the Zr–H and Np–H systems, were described by the two-sublattice model (Zr)_a(H, Va)_b and (Np)_a(H, Va)_b, respectively [15,16]. In the FCC_A1, ZrH₂-Epsilon(FCT_L/2) and CaF₂-C1 phase structures, *a* = 1 and *b* = 2, while in the NpH₃-hexagonal structure we adopted *a* = 1 and *b* = 3. The Gibbs energies for the α -Np (Ortho_AC), β -Np (Tetra_AD), and Liquid phases were described by using the substitutional solution model. We assumed that these phases do not significantly dissolve hydrogen and so treated it as a binary phase using the modified description.

All the ${}^0G_{i:Va}^\phi$ values in Eq. (2) were referred to the enthalpy of standard state from SGTE [18]. The ${}^0G_{Zr:H}^\phi$ quantities, which originate in the Zr–H system, were taken from Ref. [4], whereas the quantities, which originate in the Np–H system, were obtained from the present work. The excess Gibbs energy, ${}^E G_m^\phi$, was expressed as follows:

$${}^E G_m^\phi = y_{Np} y_{Zr} (y_H L_{Np,Zr:H}^\phi + y_{Va} L_{Np,Zr:Va}^\phi) + y_H y_{Va} (y_{Np} L_{Np:H,Va}^\phi + y_{Zr} L_{Zr:H,Va}^\phi), \quad (3)$$

where the *L* parameters are composition dependent according to the so-called Redlich–Kister [17] phenomenological power series, i.e.

$$L_{\text{Np,Zr},j}^{\varphi} = \sum_{k=0}^n {}^{(k)}L_{\text{Np,Zr},j}^{\varphi} (y_{\text{Np}} - y_{\text{Zr}})^k$$

with $j = \text{H or Va}$, (4)

$$L_{i,\text{H,Va}}^{\varphi} = \sum_{k=0}^n {}^{(k)}L_{i,\text{H,Va}}^{\varphi} (y_{\text{H}} - y_{\text{Va}})^k$$

with $i = \text{Np or Zr}$. (5)

The quantities ${}^{(k)}L^{\varphi}$ are, in general, functions of temperature. In Eqs. (3)–(5), the comma separates components that interact in the same sublattice, and the colon separates components of different sublattices. The parameters $L_{\text{Zr,H,Va}}^{\varphi}$ were taken from Ref. [4], and $L_{\text{Np,H,Va}}^{\varphi}$ were obtained in the present work. The parameters $L_{\text{Np,Zr,Va}}^{\varphi}$ which come from the Np–Zr system were taken from Ref. [3] and modified in the present study, whereas the quantities $L_{\text{Np,Zr,H}}^{\varphi}$ which originate in the Np–Zr–H system were assumed equal to zero due to lacking ternary phase information.

The delta (δ -NpZr₂)-phase is stable in the Np–Zr system [3,5]. The Gibbs energy has been calculated by applying the sub-regular solution model in Ref. [3]. Lacking experimental information on the properties of the δ -phase in the Np–Zr–H system, we assumed that this phase does not dissolve any hydrogen and treated it as a binary phase using the description assessed in Ref. [3], which is modified by applying three-sublattice model. Similar treatment was applied to the liquid phase.

3.3. Excess Gibbs energy

The Gibbs energy function of the BCC_A2 and HCP_A3 phases expressed by Eqs. (2) and (3) involves quantities originated in the lower order systems and the excess Gibbs energy parameters $L_{\text{Np,Zr,H}}^{\text{BCC_A2}}$ and $L_{\text{Np,Zr,H}}^{\text{HCP_A3}}$, respectively. They account phenomenologically for the interaction between the atoms of Np and Zr in the metallic sublattices of (Np,Zr)₁H₃ and (Np,Zr)₁H₁ hydrides, respectively, which in principle, to be determined from ternary experimental data.

3.4. Semi-empirical model

Given that no experimental data on the ternary hydride system are available in the literatures, we made estimations on the enthalpy of formation of selected Np_mZr_nH_x phases, using Miedema [20–25] and Griessen–Driessen [26–29] semi-empirical models and adopted the experimental entropy of formation of ThZr₂H_x [13] to construct their Gibbs energy of formation. The Gibbs energy information then was utilized to evaluate the thermodynamic stability of the system.

According to the Miedema atomic cell model, the enthalpy of formation of a ternary hydride, $\Delta\text{H}(\text{AB}_n\text{H}_{x+y})$,

can be expressed in terms of binary enthalpies of formation:

$$\Delta\text{H}(\text{AB}_n\text{H}_{x+y}) = \Delta\text{H}(\text{AH}_x) + \Delta\text{H}(\text{B}_n\text{H}_y) - (1 - F)\Delta\text{H}(\text{AB}_n). \quad (6)$$

The $(x + y)$ is the known hydrogen content and the factor $(1 - F)$ represents the extent to which A–B contacts between atomic cells are broken by hydrogen. Only the values $n = 1, 2, 3$ and 5 were considered, and for each n two sets of parameters (x, y, F) were given, one for smaller A atoms (Zr) and the other for larger A atoms (Np).

Meanwhile, Griessen and Driessen found that for the ternary hydride system the enthalpy of formation could be approximated by a linear equation:

$$\Delta\text{H}^0(\text{A}_{y_A}\text{B}_{y_B}\text{H}_x) = \alpha \left(\frac{y_A \Delta E_A^* + y_B \Delta E_B^*}{y_A + y_B} \right) + \beta \quad (7)$$

with

$$\Delta E_i^* = \Delta E_i^* + \phi_i' - \phi^*, \quad (8)$$

$\alpha = 29.62 \text{ kJ/eV mol H}$; $\beta = -135.0 \text{ kJ/mol H}$.

The $\Delta E_{i=A,B}^*$ corresponds to the band-structure energy parameter of the scaled density of state of metal i after allowing a transfer of electrons to bring the Fermi energy, E_{F_i} to a common level, while y_A and y_B are the concentration of A and B atoms. The ϕ' and ϕ^* are the work function of metal i after allowing a transfer of electrons to bring E_{F_i} to a common level and that of the alloy $\text{A}_{y_A}\text{B}_{y_B}$, respectively. The more detailed explanation on both the semi-empirical models can be found in the reference cited.

4. Results

4.1. Np–H system

The calculated phase diagram of the Np–H system shown in Fig. 1 indicates a narrow hexagonal phase and NpH_{2+y} (CaF₂_C1) and NpH_{3_hexagonal} two-phase region, both of which disappear above 400 °C as has been predicted by Ward [7]. The solubility of hydrogen was found to be very low at all temperatures.

4.2. Semi-empirical model

In general, the calculated enthalpies of formation obtained from the Miedema model and the Griessen–Driessen model, as shown in Table 1, are close to each other. However, the Griessen–Driessen model gives broader range of ternary hydride composition. In the present study we treated the Np_mZr_nH_x ternary hydrides as stoichiometric phases using the values obtained from the semi-empirical models.

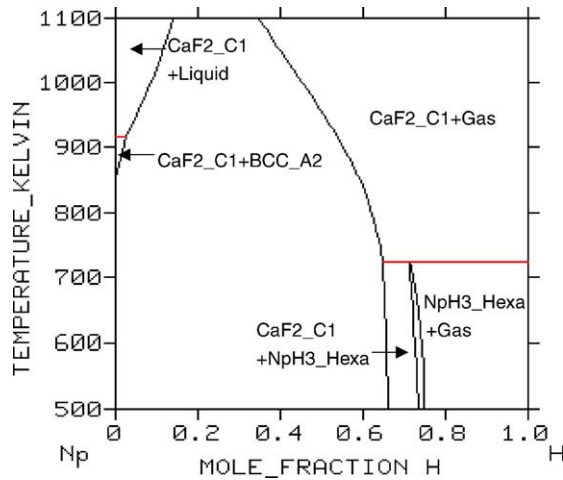


Fig. 1. Calculated Np–H phase diagram.

Table 1

Calculated enthalpies of formation of selected $\text{Np}_m\text{Zr}_n\text{H}_x$ systems

$\Delta\text{HNp}_m\text{Zr}_n\text{H}_x$ (kJ/mol) (Miedema model)	$\Delta\text{HNp}_m\text{Zr}_n\text{H}_x^a$ (kJ/mol H) (Griessen–Driessen model)
$\text{NpZrH}_{2.5}$ –115.23	Np_5ZrH_x –51.73
NpZr_2H_4 –203.10	Np_2ZrH_x –49.76
NpZr_3H_5 –289.06	NpZrH_x –49.69
NpZr_5H_6 –375.69	NpZr_2H_x –51.54
	NpZr_3H_x –53.17
	NpZr_5H_x –55.29

^a For $x = 1$; when $x = 1.8, 3, 4$ or 6 the values need to be multiply by the number of x and the unit in kJ/mol.

4.3. Np–Zr–H

Fig. 2 shows the provisional isotherm section of the Np–Zr–H ternary system at 773 K. At this temperature, the dissociation pressure of Zr–H is much lower than that of Np–H, which leads to the tendency of larger portion of hydrogen will occupy the zirconium sites rather than neptunium sites. It was found that the intermediate delta (δ -NpZr₂) phase is stable in the system and the solubility of Np in the Zr hydrides is small. At about 913 K, the liquid neptunium starts to solidify and to form γ -Np(BCC_A2), whereas, the addition of neptunium lowers the β -Zr(BCC_A2) \leftrightarrow α -Zr(HCP_A3) transformation from 1136 K in pure zirconium to eutectoid ($\alpha\text{Zr} + \gamma\text{Np}$) at around 912 K and 35 at.% neptunium. Meanwhile, in the Zr–H system, the addition of hydrogen lowers the β -Zr \leftrightarrow α -Zr transformation from 1136 K in pure zirconium to eutectoid ($\alpha\text{Zr} + \gamma\text{Zr}$ (FCC_A1)) at 820 K.

As seen in Fig. 3, in the ternary system at 873 K, the liquid neptunium phase is eliminated and replaced by γ -Np, and the addition of zirconium will lead to

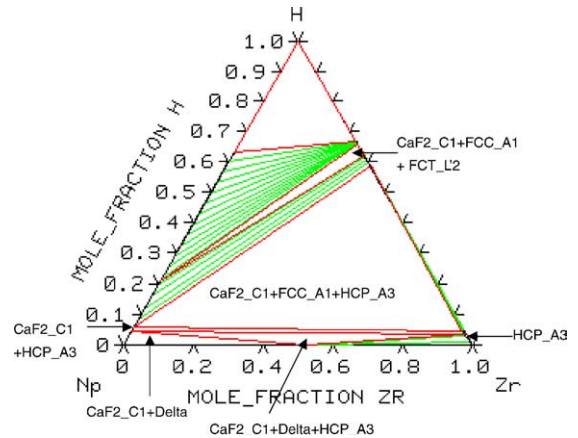


Fig. 2. Provisional Np–Zr–H isotherm section at 773 K.

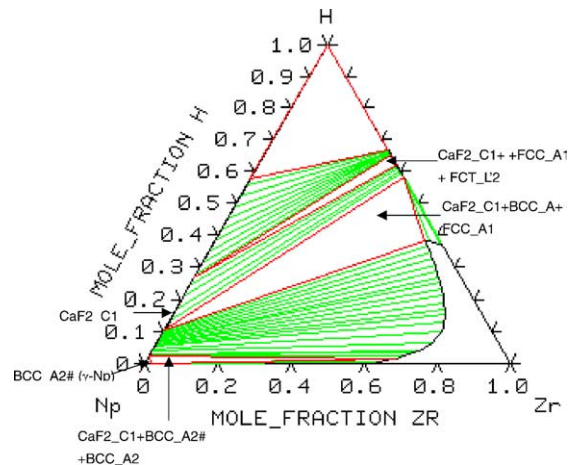


Fig. 3. Provisional Np–Zr–H isotherm section at 873 K.

mixture of the γ -Np phase with various zirconium phases, whereas the addition of hydrogen will bring to the mixture of γ -Np phase with the zirconium hydride after β -Zr (BCC_A2) has saturated with hydrogen at about 42 at.% H. According to Fig. 1, the CaF2_C1 (NpH_{2+y}) hydride is not stable at the Np–H side of the binary system at 973 K, whereas the FCC_A1 hydride is stable on the Zr–H side.

Fig. 4 shows the provisional isotherm section at 973 K. In alloys containing about 15 at.% neptunium, the two-phase (α -Zr + β -Zr) region is eliminated and there is rather a high solubility of hydrogen in the cubic hydride phase (BCC_A2). This phase diagram includes the liquid phase in the region of low hydrogen to metal ratio. The melting behaviour limits use of fuel materials in reactor core. It is necessary to choose carefully the fuel composition to avoid fuel melting. The thermodynamical

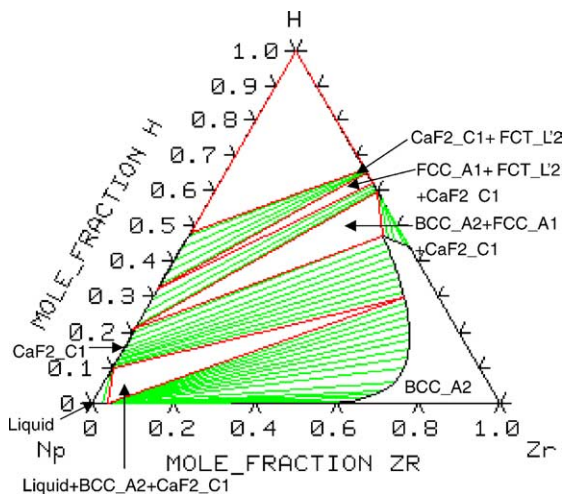


Fig. 4. Provisional Np–Zr–H isotherm section at 973 K.

analysis described above is useful to design the hydride nuclear fuel.

5. Summary

The Np–Zr–H ternary system was thermodynamically analyzed based on the description of its binary constituents available in the literatures. Provided that no experimental data are available in the literatures, the enthalpy of formation of selected $Np_mZr_nH_x$ was estimated using semi-empirical models and the experimental entropy of formation of $ThZr_2H_x$ was adopted, then together with the available binary data was employed to develop the thermodynamic database of the Np–Zr–H ternary system. The provisional isothermal sections of the Np–Zr–H phase diagram were calculated using the database. The thermodynamical analysis of the Np–Zr–H ternary system give the useful information for melting behavior of the hydride nuclear fuel, which is important for designing of a nuclear reactor fuel element.

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References

- [1] M.T. Simnad, Nucl. Eng. Des. 64 (1981) 403.
- [2] K. Konashi, B. Tsuchiya, M. Yamawaki, K. Fujimura, T. Sanda, in: International Conference on Back-End of the

Fuel Cycle from Research to Solutions, GLOBAL2001, Paris, France, 9–13 September 2001.

- [3] T. Ogawa, J.K. Gibson, R.G. Haire, M.M. Gensini, M. Akabori, J. Nucl. Mater. 223 (1995) 67.
- [4] N. Dupin, I. Ansara, C. Servant, C. Toffolon, C. Lemaignan, J.C. Brachet, J. Nucl. Mater. 275 (1999) 287.
- [5] M.M. Gensini, R.G. Haire, J.K. Gibson, in: Actinides'93 International Conference, Santa Fe, USA, 19–24 September 1993.
- [6] W. Wang, D.R. Olander, J. Am. Ceram. Soc. 78 (12) (1995) 3323.
- [7] J.W. Ward, W. Bartscher, J. Rebizant, J. Less-Common Met. 130 (1987) 431.
- [8] R.N.R. Mulford, T.A. Wiewandt, J. Phys. Chem. 69 (1965) 1641.
- [9] M.T. Simnad, The U–ZrHx Alloy: Its Properties and use in TRIGA Fuel, GA-A16029, August 1980.
- [10] G.G. Libowitz, in: W.M. Mueller, J.P. Blackledge, G.G. Libowitz (Eds.), Metal Hydrides, Academic Press, New York, 1968.
- [11] J.W. Ward, in: A.J. Freeman, C. Keller (Eds.), Handbook on the Physics and Chemistry of the Actinides, Elsevier Science Pub. B.V., 1985 (Chapter 1).
- [12] H.E. Flotow, J.M. Haschke, S. Yamauchi, The Chemical Thermodynamics of Actinide Element. Part 9: The Actinide Hydrides, IAEA, Vienna, 1984.
- [13] W. Bartscher, J. Rebizant, J.M. Haschke, J. Less-Common Met. 136 (1988) 385.
- [14] W. Bartscher, J. Rebizant, J.M. Haschke, J. Less-Common Met. 121 (1986) 455.
- [15] B. Sundman, J. Agren, J. Phys. Chem. Solids 42 (1981) 297.
- [16] M. Hillert, L.L. Staffanson, Acta Chem. Scand. 24 (1970) 3618.
- [17] O. Redlich, A.T. Kister, Ind. Eng. Chem. 40 (1948) 345.
- [18] A.T. Dinsdale, CALPHAD 15 (1991) 317.
- [19] J.W. Ward, J.M. Haschke, in: K.A. Gschneidner Jr., L. Eyring, G.R. Choppin, G.H. Lander (Eds.), Handbook on the Physics and Chemistry of the Rare Earths, Elsevier Science Pub. B.V., 1994 (Chapter 123).
- [20] A.R. Miedema, J. Less-Common Met. 32 (1973) 117.
- [21] H.H. van Mal, K.H.J. Buschow, A.R. Miedema, J. Less-Common Met. 35 (1974) 65.
- [22] A.R. Miedema, K.H.J. Buschow, H.H. van Mal, J. Less-Common. Met. 49 (1976) 463.
- [23] A.R. Miedema, F.R. de Boer, R. Boom, CALPHAD 1 (4) (1977) 341.
- [24] P.C.P. Bouten, A.R. Miedema, J. Less-Common Met. 71 (1980) 147.
- [25] K.H.J. Buschow, P.C.P. Bouten, A.R. Miedema, Rep. Prog. Phys. 45 (1982) 937.
- [26] R. Griessen, A. Driessen, D.G. de Groot, J. Less-Common Met. 103 (1984) 235.
- [27] R. Griessen, A. Driessen, Phys. Rev. B 30 (8) (1984) 4372.
- [28] R. Griessen, T. Riesterer, in: L. Schlapbach (Ed.), Heat of Formation Models, Chapter 6, Hydrogen in Intermetallic Compounds I, 1988.
- [29] R. Griessen, A. Driessen, Phys. Rev. B 38 (8) (1988) 3690.