

Sloping Plateaux in the Pressure–Composition Isotherms of the Titanium–Hydrogen and $\text{Ti}_{94}\text{Al}_6$ –Hydrogen Systems

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Pressure–composition isotherms of the titanium–hydrogen and $\text{Ti}_{94}\text{Al}_6$ –hydrogen systems have been measured in the temperature range 673–973 K and hydrogen-concentration range (atomic ratio) 0.01–1. The plateaux of the isotherms, which correspond to the $(\alpha + \beta)$ phase region, have been found to slope upward slightly in the titanium–hydrogen system and to slope upward appreciably in the $\text{Ti}_{94}\text{Al}_6$ –hydrogen system. The observed sloping plateaux are shown to be explicable on the basis of a lattice-gas model which incorporates in it a Gaussian distribution of energies of hydrogen in the metals with a standard deviation 0.0015 eV for the titanium–hydrogen system and 0.01 eV for the $\text{Ti}_{94}\text{Al}_6$ –hydrogen system. Possible origins of the energy distribution are also mentioned.

Titanium and some of its alloys can absorb a large amount of hydrogen and are suitable for hydrogen storage. Alloys of titanium and aluminium are also potential candidates for hydrogen-storage materials, particularly light hydrogen-storage materials.¹ In a practical application for hydrogen storage, full use is made of the properties of a plateau (such as the temperature and the hydrogen pressure at which the plateau occurs and the range of hydrogen concentration over which it extends) in the pressure–composition (p – θ) isotherms of metal–hydrogen systems.² Amongst these properties is the slope of the plateau, which plays a crucial role in determining the efficiency of hydrogen storage.

Sloping plateaux in the p – θ isotherms have been reported for alloy–hydrogen and amorphous-metal–hydrogen systems.^{2–7} Careful experimental investigations of the palladium–hydrogen,^{3,8–10} titanium–hydrogen¹¹ and hafnium–hydrogen¹² systems show that even in pure-metal–hydrogen systems, in which the plateaux are expected to be horizontal, the plateaux slope in that part of the isotherm which corresponds to the two-phase state of the systems, *i.e.* to the phase separation. Models to explain the sloping plateaux have been proposed for alloy–hydrogen,^{13,14} amorphous-metal–hydrogen¹⁵ and pure-metal–hydrogen¹⁶ systems. These models ascribe the slope of the plateaux to a distribution of the hydrogen-site energies in the metals, as well as to a hydrogen–hydrogen interaction that is non-linear with respect to θ .^{14,16} Although these models are capable of reproducing the slope of the plateaux, it is not clear whether or not the plateaux reproduced are associated with the phase separation. The sloping plateaux observed in the p – θ isotherms of the alloy–hydrogen^{2,3,5} and pure-metal–hydrogen^{8,11,12} systems do correspond in most cases to the phase separation and in the $\text{Ti}_{94}\text{Al}_6$ –hydrogen system, this is likely to be the case.^{1,17} Some modification of the proposed models is therefore needed to take into account the observed phase separation. To do this, we can apply either a rule of equal areas¹⁸ or Maxwell's rule¹⁹ to the isotherms *i.e.* a condition that a straight line intersecting the p – θ isotherm corresponds to the phase separation and is defined so that the areas enclosed between the single-phase isotherm and the

horizontal line are numerically equal. We then calculate the plateaux. In fact, Maxwell's rule has been applied to the isotherms with two kinds of site energies.^{20–22} To our knowledge, however, no reports dealing with a distribution of site energies are found in the literature.

In the present study we have measured the p – θ isotherms of the titanium–hydrogen and $\text{Ti}_{94}\text{Al}_6$ –hydrogen systems. The observed sloping plateaux are compared with a lattice-gas model, which has been modified to include a distribution of site energies. The component isotherms that correspond to the site energies are calculated and Maxwell's rule is applied to each of them. The isotherm is then calculated from the component isotherms and compared with the observed sloping plateaux. We also mention possible origins of the site-energy-distribution.

Experimental

Isotherms were obtained by measuring the amount of hydrogen gas absorbed by titanium and $\text{Ti}_{94}\text{Al}_6$ samples. The apparatus and procedure for measurements were the same as described previously.^{23–27} In the present study, we took the precaution of measuring correctly the isotherm in its plateau region, since the isotherm is likely to be influenced by the hysteresis¹⁰ accompanying absorption and desorption of hydrogen. Here, we examined the partial reversibility of the equilibrium hydrogen pressure,²⁷ *i.e.* whether the same equilibrium hydrogen pressure was reached or not after the temperature fluctuated by ± 50 K. The difference between the equilibrium pressures before and after applying the temperature fluctuation turned out to be less than 2%. This difference was small enough not to give serious effects on the observed slope of the plateaux.

We used the same titanium and $\text{Ti}_{94}\text{Al}_6$ samples as used in the previous study.²⁷ Measurements were made in the temperature range (T) 673–973 K and in the hydrogen-pressure range (p) 10^{-1} – 10^4 Pa, which corresponds approximately to the hydrogen-concentration range (θ , atomic ratio) 10^{-2} –1.

Results and Discussion

Experimental Results

Fig. 1 shows the p – θ isotherms measured for the titanium–hydrogen system at the temperatures indicated. For $\theta \leq 0.08$,

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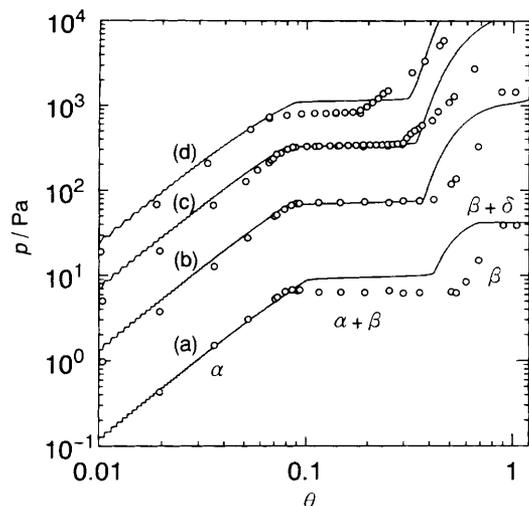


Fig. 1 p - θ isotherms of the titanium-hydrogen system; (a) 673, (b) 773, (c) 873 and (d) 773 K. (○), experiment. The solid lines have been computed from eqn. (10)–(12). α , β and δ indicate the phases. For the values used in the computation, see the text.

titanium is in the hexagonal close packed (hcp) α phase at all temperatures. The ($\alpha + \beta$) coexisting phase begins to appear near $\theta = 0.08$ and extends up to $\theta = 0.2$ – 0.5 , depending on the temperature. As θ increases, the body-centred cubic (bcc) β phase remains, and p increases as θ increases. Near $\theta = 1$, the coexisting $\beta + \delta$ phase begins to form, and a plateau appears again. (In Fig. 1, these plateaux can only be seen at 673 and 773 K). This observation agrees with previously reported results.^{11,28} If we look closely at the isotherms, we can see that at 773 K and above, the plateaux slope slightly upward with increasing θ . In addition, the measured isotherms for the α and β phases deviate from the linear relationship between $\log \theta$ and $\log p$, *i.e.* Sieverts' law, as they approach and leave the plateaux, respectively, so that the isotherms bend near the plateaux. This can clearly be seen in Fig. 2, in which the isotherm at 873 K is shown enlarged. This observation shows the possibility of sloping plateaux even in pure-metal-hydrogen systems and is consistent with the results reported for the titanium-hydrogen system at temperatures above *ca.* 830 K,¹¹ the palladium-hydrogen system^{3,8,9} and the hafnium-hydrogen system.¹² In the

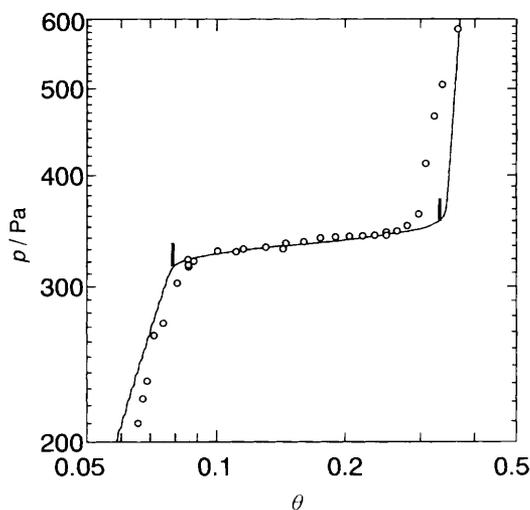


Fig. 2 Isotherm at 873 K shown enlarged: the region between the vertical bars corresponds to the ($\alpha + \beta$) phase, the symbols are the same as in Fig. 1

hafnium-hydrogen system, it has been confirmed by *in situ* X-ray diffraction that the sloping plateaux correspond to the phase separation.¹²

Fig. 3 shows the isotherms measured for the $\text{Ti}_{94}\text{Al}_6$ -hydrogen system. They are largely of similar form to those in the titanium-hydrogen system. In these cases, the ($\alpha + \beta$) phase appears near $\theta = 0.07$. In contrast to the case for the titanium-hydrogen system, the plateaux slope appreciably upward as θ increases and in the α and β phases near the plateaux we can see considerable deviations from the linear relationships. This is consistent with previously reported isotherms measured at $T > 1073$ K.¹⁷ Similar observations have been reported for the isotherms of several alloy-hydrogen systems,^{3,5} in which the sloping plateaux correspond to the phase separation. Steeper slopes have been found in the isotherms of amorphous-metal-hydrogen systems.^{2,4,7} In these cases the slopes, however, do not necessarily correspond to the phase separation and the model proposed to explain the slopes¹⁵ cannot be applied directly to the results in the present study.

Derivation of the Isotherm

We calculate the p - θ isotherm capable of describing the sloping plateaux by applying statistical mechanics to a lattice-gas model.^{3,9,18,20–22,29} To do so, a distribution of the site energies is introduced into the model and Maxwell's rule is applied to every component isotherm corresponding to each site energy. The following two points should be noted before the calculation is carried out. First, the lattice-gas model is used in the present study primarily because it is relatively easy, compared with other relevant models, to modify it so that the distribution of site energies is included, and to make numerical computations of the isotherm. However, we must keep in mind the fact that its applicability is not universal and is limited (as has already been discussed for the palladium-hydrogen system⁹). Secondly, when the isotherm has a sloping plateau, it is often accompanied by hysteresis.^{2,6} It is known that this hysteresis is closely related to the strain in the metal-hydrogen system as has been reported previously for the palladium-hydrogen system mentioned above.^{9,10} The importance of strain for the p - θ isotherm must be kept in mind. In the present study, since it is not clear at present whether or not the strain is a possible main origin of the sloping plateau, we introduce the site-energy distribution to account for the sloping plateau.

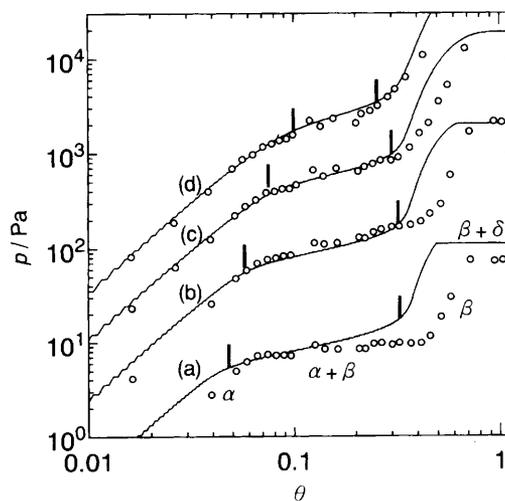


Fig. 3 p - θ isotherms of the $\text{Ti}_{94}\text{Al}_6$ -hydrogen system. The regions between the vertical bars correspond to the ($\alpha + \beta$) phase. The symbols *etc.* are the same as in Fig. 1.

Simplifying assumptions must be made in order to formulate the expression of the isotherm. We first assume that hydrogen atoms in the metal occupy sites whose energies follow a distribution, and positions of the sites and the site energies do not change on absorption of hydrogen. We next assume that the hydrogen atoms in the metal can interact with each other. This interaction, however, is assumed to be only between hydrogen atoms with the same site energies. The phase change, therefore, can occur only in those parts of the system associated with these hydrogen atoms.

We comment here on the assumptions made above. The assumption made concerning the site-energy distribution seems obvious in alloys,³⁰ especially in random alloys such as $\text{Ti}_{94}\text{Al}_6$.³¹ The distribution in pure metals, however, is not obvious and will be mentioned later. The assumption made concerning the unchanging positions and site energies is not fully justifiable because of the change of the crystal structure of the metal, which accompanies, for example, the $\alpha \rightarrow \beta$ phase change caused by hydrogen absorption. A model in which hydrogen atoms in the metal create new sites, different from those in the metal without the hydrogen atoms²⁰ can better simulate the crystal-structure change. By using this model, however, it is difficult to reproduce Sieverts' law at small θ . No reasonable model of the isotherm that successfully incorporates the crystal-structure change now seems available. We also cannot fully justify the assumption made concerning the interaction, although since the sites with smaller site energies are more densely populated by hydrogen atoms and the interaction prevails between these hydrogen atoms, this assumption does not seem to be totally unjustifiable. To simulate more precisely the isotherms, we need to have recourse to a microscopic description. Unfortunately such a description requires a large amount of numerical computation and is not feasible unless a simplified method is used, as has been done to simulate the isotherms of the palladium-hydrogen system,³² where embedded atom potentials, which are rather empirical, have been used. In the present study we are content to use the outcome of these assumptions, *i.e.* to see to what extent the sloping plateaux are reproduced on the basis of the assumptions, without making more efforts to justify them.

We now formulate the expression for the isotherms. Consider a system comprising N_{M} metal atoms with N_{S} sites available to N_{H} hydrogen atoms. The N_{S} sites are divided into sites of a given number of kinds, a representative of which we denote by i . We thus have

$$N_{\text{M}} = \sum N_{\text{M}}^i \quad (1)$$

$$N_{\text{H}} = \sum N_{\text{H}}^i \quad (2)$$

$$N_{\text{S}} = \sum N_{\text{S}}^i = \sum r^i N_{\text{M}}^i \quad (3)$$

where the superscript i indicates the i th kind and r^i is the number of sites per metal atom. The sum is taken over all kinds of sites. We define the density of sites of the i th kind as

$$d^i = N_{\text{S}}^i / N_{\text{S}} \quad (4)$$

This is the distribution of kinds of sites and, therefore, of site energies. The hydrogen concentration is written for the system as

$$x = N_{\text{H}} / N_{\text{S}} \quad (5)$$

and for the site of the i th kind as

$$x^i = N_{\text{H}}^i / N_{\text{S}}^i \quad (6)$$

We assume the heat of hydrogen absorption into the site of the i th kind, ε^i , increases as $(\frac{1}{2})k^i(x^i)^2$ where k^i is a constant. The expression $(\frac{1}{2})k^i(x^i)^2$ is of the same form as the hydrogen-

hydrogen interaction obtained by using the mean-field approximation, and is usually discussed in terms of the strain caused by the absorption of hydrogen.^{7,9,33} A more precise form, which we do not seek in the present study, may be obtained, *e.g.* from total energy calculations of the system at different hydrogen concentrations.⁷ The partition function for hydrogen atoms in the metal is thus written as²⁰

$$Z = \prod \frac{N_{\text{S}}^i!}{N_{\text{H}}^i!(N_{\text{S}}^i - N_{\text{H}}^i)!} \exp[N_{\text{H}}^i \varepsilon^i + (1/2)k^i(x^i)^2/k_{\text{B}} T] \quad (7)$$

where \prod denotes the product over all the different kinds of sites. From eqn. (7), we have for the chemical potential of the hydrogen atoms in the site of the i th kind

$$\mu^i = k_{\text{B}} T \ln \frac{x^i}{1 - x^i} - \varepsilon^i - k^i x^i \quad (8)$$

Hydrogen atoms in each kind of site must be in equilibrium with hydrogen gas outside the metal:

$$\mu^i = (1/2)\mu_{\text{H}_2} \quad (9)$$

where the subscript H_2 denotes the hydrogen molecule. Inserting eqn. (8) into eqn. (9), we have the component isotherm of the i th kind:

$$\frac{x^i}{1 - x^i} \exp(\varepsilon^i + k^i x^i / k_{\text{B}} T) = a(T) p^{1/2} \quad (10)$$

The right-hand side of this equation comes mainly from the partition functions for hydrogen atoms in the metal and hydrogen molecules in the gas phase and $a(T)$ is approximately proportional to $T^{7/4}$.^{7,16,18,20} Since eqn. (4)–(6) give the relationship between x and x^i , *i.e.*

$$x = \sum d^i x^i \quad (11)$$

we have, from eqn. (10) and (11), the p - x isotherms. For the convenience of comparison with the measured isotherms, the hydrogen concentration is converted from x to θ (atomic ratio). Using eqn. (1) and (5), we have $\theta = N_{\text{H}} / N_{\text{M}} = x N_{\text{S}} / \sum N_{\text{M}}^i$, which can then be rewritten as

$$\theta = x / \sum (d^i / r^i) \quad (12)$$

because $N_{\text{M}}^i = (d^i / r^i) N_{\text{S}}$ from eqn. (3) and (4). The p - θ isotherm is given by eqn. (10)–(12). The distribution, d^i , of ε^i , together with r^i and k^i , will be determined when the derived p - θ isotherm is compared with the experimental result.

Comparison between the Measured and Derived Isotherms

Fig. 1 shows, for the titanium-hydrogen system, a comparison of the measured isotherms with those derived as above. The solid lines are the result of fits of eqn. (10)–(12) to the measured isotherms. The method of computation of the isotherms is as follows. Values of x^i and p in eqn. (10) (the component isotherm) are computed for every site energy at a given temperature. Maxwell's rule is then applied to the component isotherms. For a given value of p , the hydrogen concentration of the system [x in eqn. (11)] is computed from the component isotherms and then converted to θ by using eqn. (12). Repeating this procedure for other values of p , we have the p - θ isotherm of the system. Values used for the parameters in eqn. (10)–(12) are as follows. Some of them have been determined by least-squares fits of eqn. (10)–(12) to the measured isotherms and are shown with errors; the others have been chosen so that eqn. (10)–(12) best simulate the measured isotherms, and are shown without errors. Two distributions of ε^i are considered in order to reproduce the two coexisting phases, *i.e.* the ($\alpha + \beta$) phase (the plateaux at lower hydrogen

concentrations in Fig. 1) and the ($\beta + \delta$) phase (the plateaux at higher hydrogen concentrations at 673 and 773 K). For the ($\alpha + \beta$) phase, we use $r^i = 1$, $k^i = 0.40 \pm 0.08$ eV, $\log a(T) = -3.9 \pm 1.3$ and a Gaussian distribution of the site energies and ε^i with the standard deviation 0.0015 eV and the mean 0.25 ± 0.20 eV while for the ($\beta + \delta$) phase, $r^i = 2$, $k^i = 0.25$ eV, $\log a(T) = -6.2$ and $\varepsilon^i = 0.6$ eV. The distribution, d^i , of ε^i [eqn. (4)] is normalized as $\sum d^i = 1$. We compute the component isotherms for 50 values of ε^i in the range 0.243–0.257 eV and for a value $\varepsilon^i = 0.6$ eV. The distribution for the ($\beta + \delta$) phase ($\varepsilon^i = 0.6$ eV) has been considered only to improve the fit in the ($\alpha + \beta$) phase region and not to simulate precisely the plateaux in the ($\beta + \delta$) phase region. Nevertheless, owing to the presence of the $\alpha \rightarrow \beta$ phase transformation of pure titanium at 1155 K,²⁸ the computed isotherms cannot very well reproduce the experimental result. The error involved in ε^i for the ($\alpha + \beta$) phase (0.25 ± 0.20 eV) seems to be rather large. The reason for this large error is that the position and range of the plateau is closely related to the value of ε^i , and the plateau can be relatively well simulated even by a nearly horizontal curve that corresponds to the isotherm without the phase separation, and therefore to the isotherm computed for a rather different value of ε^i . The mean $\varepsilon^i (= 0.25$ eV) for the ($\alpha + \beta$) phase differs considerably from the value of the heat of hydrogen absorption, $\varepsilon = 0.48$ eV reported previously for the α phase.²⁷ This difference arises because we have intended in this study to simulate the plateaux and so have introduced the hydrogen–hydrogen interaction, while we tried in the previous study to reproduce the isotherm of only the α phase. We can see that the introduction of the distribution of ε^i makes it possible to reproduce the slope of the plateaux and the bend of the isotherms in the α and β phases near the plateaux. To see this more clearly, we show enlarged, in Fig. 2, the isotherm at 873 K. Note that the bend in the computed isotherm is due to the distribution of ε^i and therefore includes the coexisting phase, and corresponds to the phase separation. Experimental evidence for this may be difficult to observe, because the amount of either of the two coexisting phases is too small to detect, *e.g.* with X-ray diffraction.

The origin of the distribution of ε^i in pure titanium is not obvious and needs to be commented on. As we can see in Fig. 1, the measured plateaux have slightly larger slopes at higher temperatures. This is in accordance with a previously reported result.¹¹ A simple, possible explanation of this fact is that the motion of hydrogen atoms and metal atoms is greater at higher temperatures, hence the broader distribution of ε^i . This explanation is consistent with that suggested for the larger width of inelastic neutron scattering (INS) peaks at higher temperatures, *i.e.* greater diffusion of hydrogen atoms and interaction of phonons of the metal at higher temperatures.³⁴ In the palladium–hydrogen system, we can clearly see the sloping plateaux in the isotherms measured at *ca.* 300 K.^{3,8} This may also be explained in terms of the motion of hydrogen atoms in palladium. According to the calculation of vibrational states of hydrogen atoms in palladium, the energy required for a hydrogen atom to move from one site to another is rather small,³⁵ suggesting that even a small hydrogen-atom energy can effectively cause a distribution of ε^i . In addition, the INS peaks measured for hydrogen atoms in palladium^{36,37} have some structure, which has been ascribed to the motion of hydrogen atoms and palladium atoms. An origin of the distribution of ε^i for pure metals is thus expected to be the motion of hydrogen atoms and of metal atoms.

In Fig. 3, the isotherms measured for the $\text{Ti}_{94}\text{Al}_6$ –hydrogen system are compared with those computed. The steeper slope of the plateaux and the greater bend

of the isotherms near the plateaux, compared with the titanium–hydrogen system, imply a broader distribution of ε^i . In fact, values of the parameters used in the computation are $r^i = 1$, $k^i = 0.36 \pm 0.07$ eV, $\log a(T) = -4.5 \pm 1.2$ and a Gaussian distribution of ε^i with a standard deviation of 0.01 eV and a mean of 0.36 ± 0.19 eV for the ($\alpha + \beta$) phase and $r^i = 2$, $k^i = 0.3$ eV, $\log a(T) = -5.9$ and $\varepsilon^i = 0.5$ eV for the ($\beta + \delta$) phase, the standard deviation being larger for this system. The values with errors have been determined by the least-square fit and those without errors have been chosen as done in the case of titanium. The distribution with a larger standard deviation for $\text{Ti}_{94}\text{Al}_6$ seems reasonable, considering the possible sites for hydrogen atoms in other alloys³⁰ and the chemical environment induced by substitutional aluminium atoms, whose electronic structure is highly different from that of titanium atoms. Note, however, that no clear evidence of the distribution of ε^i for $\text{Ti}_{94}\text{Al}_6$ have been found, although electronic-structure calculations of some titanium–aluminium and titanium–aluminium–hydrogen alloys have been made.^{38,39} Apart from the fact that the origin of the distribution of ε^i is not fully elucidated, we can say that the computed isotherms well reproduce the characteristics of the observed slope and bend in the measured isotherms.

Conclusions

The pressure–composition isotherms of the titanium– and $\text{Ti}_{94}\text{Al}_6$ –hydrogen systems have been measured. Sloping plateaux were observed in the coexisting-phase region and so was a bend in the single-phase regions near the plateaux. It has been shown that the sloping plateaux and the bend are explicable on the basis of the site-energy distribution for hydrogen atoms in the metals. In the titanium–hydrogen system, the origin of the distribution has been suggested to be the motion of hydrogen atoms and of metal atoms, while in the $\text{Ti}_{94}\text{Al}_6$ –hydrogen system, it has been suggested to be the presence of substitutional aluminium atoms, in addition to the motion of the hydrogen and metal atoms.

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References

- 1 P. S. Rudman, J. J. Reilly and R. H. Wiswall, *Ber. Bunsen-Ges. Phys. Chem.*, 1977, **81**, 76.
- 2 G. Sandrock, S. Suda and L. Schlapbach, *Hydrogen in Intermetallic Compounds*, ed. L. Schlapbach, Springer, Berlin, 1992, vol. 2, p. 197.
- 3 E. Wicke and H. Brodowsky, in *Hydrogen in Metals*, ed. G. Alefeld and J. Völkl, Springer, Berlin, 1978, vol. 2, p. 73.
- 4 E. Batalla, Z. Altounian, D. B. Boothroyd, R. Harris and J. O. Strom-Olsen, in *Hydrogen in Disordered and Amorphous Solids*, ed. G. Bambakidis and R. C. Brown Jr., Plenum, New York, 1986, p. 203.
- 5 A. Percheron-Guégan and J.-M. Welter, in *Hydrogen in Intermetallic Compounds*, ed. L. Schlapbach, Springer, Berlin, 1988, vol. 1, p. 11.
- 6 T. B. Flanagan and W. A. Oates, in *Hydrogen in Intermetallic Compounds*, ed. L. Schlapbach, Springer, Berlin, 1988, vol. 1, p. 49.
- 7 Y. Fukai, *The Metal–Hydrogen System*, Springer, Berlin, 1993, pp. 13, 43, 300.
- 8 H. Frieske and E. Wicke, *Ber. Bunsen-Ges. Phys. Chem.*, 1973, **77**, 50.
- 9 T. B. Flanagan and W. A. Oates, *Annu. Rev. Mater. Sci.*, 1991, **21**, 269.
- 10 B. Baranowski, *J. Alloys Comp.*, 1993, **200**, 87.
- 11 A. D. McQuillan, *Proc. R. Soc. London, A*, 1959, **204**, 309.

- 12 M. Kimura, S. Naito, M. Mabuchi and T. Hashino, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 2221.
- 13 R. Griessen, in *Hydrogen in Disordered and Amorphous Solids*, ed. G. Bambakidis and R. C. Brown Jr., Plenum, New York, 1986, p. 153.
- 14 E. Salomons, N. Koeman, J. Kector and R. Griessen, *J. Phys.: Condens. Matter*, 1990, **2**, 835.
- 15 R. Griessen, *Phys. Rev. B*, 1983, **27**, 7575.
- 16 K. Yura, S. Naito, M. Mabuchi and T. Hashino, *J. Chem. Soc., Faraday Trans. 2*, 1986, **82**, 101.
- 17 E. Schürmann, T. Kootz, H. Preisendanz, P. Schüler and G. Kauder, *Z. Metallkd.*, 1974, **65**, 167; 249.
- 18 R. H. Fowler, *Statistical Thermodynamics*, University Press, Cambridge, 1939, pp. 315, 421.
- 19 L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Pergamon, Oxford, 1981, p. 261.
- 20 A. L. G. Rees, *Trans. Faraday. Soc.*, 1954, **50**, 335.
- 21 T. Hashino and S. Naito, *J. Chem. Soc., Faraday Trans. 2*, 1979, **75**, 1351.
- 22 T. Tanaka, M. Keita and D. E. Azofeifa, *Phys. Rev. B*, 1981, **24**, 1771.
- 23 S. Naito, *J. Chem. Phys.*, 1983, **79**, 3113.
- 24 S. Naito, T. Hashino and T. Kawai, *J. Chem. Phys.*, 1984, **81**, 3489.
- 25 S. Naito, M. Yamamoto and T. Hashino, *J. Phys.: Condens. Matter*, 1990, **2**, 1963.
- 26 T. Meada, S. Naito, M. Yamamoto, M. Mabuchi and T. Hashino, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 4375.
- 27 S. Naito, M. Yamamoto, M. Doi and M. Kimura, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 1967.
- 28 A. San-Martin and F. D. Manchester, in *Phase Diagrams of Binary Titanium Alloys*, ed. J. L. Murray, ASM International, Materials Park, Ohio, 1987, p. 123.
- 29 J. R. Lacher, *Proc. R. Soc. London, A*, 1937, **161**, 525.
- 30 K. Yvon and P. Fisher, in *Hydrogen in Intermetallic Compounds*, ed. L. Schlapbach, Springer, Berlin, 1988, vol. 1, p. 87.
- 31 J. L. Murray, in *Phase Diagrams of Binary Titanium Alloys*, ed. J. L. Murray, ASM International, Materials Park, Ohio, 1987, p. 12.
- 32 R. J. Wolf, M. W. Lee, R. C. Davis, P. J. Fay and R. J. Ray, *Phys. Rev. B*, 1993, **48**, 12415.
- 33 H. Wagner, in *Hydrogen in Metals*, ed. G. Alefeld and J. Völkl, Springer, Berlin, 1978, vol. 1, p. 5.
- 34 R. Khoda-Bakhsh and D. K. Ross, *J. Phys. F: Met Phys.*, 1982, **12**, 15.
- 35 C. Elsässer, K. M. Ho, C. T. Chan and M. Fähnle, *J. Phys.: Condens. Matter*, 1992, **4**, 5207.
- 36 W. Drexel, A. Murani, D. Tocchetti, W. Kley, I. Sosnowska and D. K. Ross, *J. Phys. Chem. Solids*, 1976, **37**, 1135.
- 37 J. J. Rush, J. M. Rowe and D. Richter, *Z. Phys. B*, 1984, **55**, 283.
- 38 T. Hong, T. J. Watson-Yang, X. Q. Guo, A. J. Freeman and T. Oguchi, *Phys. Rev. B*, 1991, **43**, 1940.
- 39 P. Jund, W. Zhong and D. Tománek, *Phys. Rev. B*, 1995, **51**, 9569.

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