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The phase diagrams of β-RH_{2+x} systems (R=La, Ce, Tb). Results of mean-field calculations

I.G. Ratishvili[1], P. Vajda*

Laboratoire des Solides Irradiés, CNRS-CEA, Ecole Polytechnique, F-91128 Palaiseau France

Abstract

In recent publications, we had proposed phase diagrams in the β-phase regions of RH_{2+x} systems (R=La, Ce, Tb), using the mean-field approximation of the static concentration waves theory, applied to the subsystem of the octahedral x-hydrogen atoms (H_o-atoms). A comparison with experimental data shows that a much better agreement can be obtained when the concentration-dependent lattice contraction is taken into account through a linear variation of the energy constants characterizing the H_o–H_o interaction. The modified calculated phase diagrams are presented.

Keywords: Rare earth hydrides; Phase diagrams; Mean-field theory

1. Introduction

The ordering processes developing in the subsystem of xN hydrogen atoms (H_o) located on the set of N octahedral interstitial sites in the compounds β-RH_{2+x} are characterized by two long-range-order (LRO) parameters. In the mean-field approximation of the static concentration waves theory [1], the corresponding free-energy function is given by the expression

$$F(\eta_1,\eta_2;c) = (Nk_B/2)\{V_0c^2 + V_1(\gamma\eta_1)^2 + 2V_2(\gamma\eta_2)^2 + 2T\Sigma_i\nu_i[n_i ln n_i + (1-n_i)\ln(1-n_i)]\}, \qquad (1)$$

where η_1 and η_2 are the LRO parameters (representing the amplitudes of the two superimposed static concentration waves with the wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$), γ is a normalisation constant; c is the concentration of H_o-atoms in the O-sites (ideally, $c=x$); $n_i = n_1$, n_2, n_3 are the occupation probabilities of the O-sites by hydrogen atoms, and $\nu_i = \nu_1$, ν_2, ν_3 are the corresponding fractions of the N O-sites. In the earlier discussed cases with R=Tb [2], Ce [3], and La [4], treated with the wave vectors $\mathbf{k}_0 = 0$, $\mathbf{k}_1 = (2\pi/a)$-(100), and $\mathbf{k}_2 = (2\pi/a)(1/2\ 0\ 1)$, we had:

$$n_1 = c + \gamma(\eta_1 + 2\eta_2),\ n_2 = c + \gamma(\eta_1 - 2\eta_2),\ n_3 = c - \gamma\eta_1, \qquad (2)$$

where $\nu_1 = \nu_2 = 0.25$, $\nu_3 = 0.5$; $\gamma = 0.25$; and the $V(\mathbf{k}_i) = V_0$, V_1, V_2 are the Fourier components of the H_o–H_o interaction potential (in temperature units), called the ‘‘energy parameters’’. The thermodynamic behavior of the ordering system under consideration is mainly determined by the energy parameter ratio $p \equiv V_2/V_1$, which can be $p=1$ (TbH_{2+x} [2]), $p>1$ (CeH_{2+x} [3]), or $p<1$ (LaH_{2+x} [4]).

The lattice parameters a of the hydrides are known to vary with hydrogen concentration [5], and should, therefore, induce a variation of the $V(\mathbf{k}_i)$ with c. However, in Ref. [2–4], it was assumed that, as a first step of approximation, the energy parameters V_i were independent of c in the whole concentration range associated with the monophase states. As a result, the sequences of the calculated order–disorder and order–order transition temperatures were represented by curves symmetric with respect to $c=0.5$ (Fig. 4 in [3] and Fig. 8 in [4]), which did not agree satisfactorily with the measured experimental data.

At the same time, we had made a successful attempt to take into account $V_i(c)$ dependences to fit the observed order–disorder transition temperatures in a small concentration range, $0.1<c<0.2$, in the system $TbH(D)_{2+x}$ [2]. Based on this result, we have undertaken to analyse the influence of a V_i variation upon the phase boundaries in the systems with $p>1$, CeH_{2+x}, and with $p<1$, LaH_{2+x}, where, moreover, the existence range of the single-phase states extends to much higher concentrations [5].

Let us postulate a linear dependence of the energy parameters V_1 and V_2 on the concentration c:

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*Corresponding author.

[1] Permanent address: Institute of Physics, Georgian Academy of Sciences, Tbilissi 380077, Republic of Georgia.

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$$V_1 = A + B(c - c_0) \text{ and } V_2 = pV_1 \tag{3}$$

assuming, for simplicity, that $V_0(c) = \text{const} = 0$, since this does not influence the thermodynamic equilibrium states in our systems. It was shown previously [3] that, under conditions $V_i = \text{const}$, $V_0 = 0$, the free-energy function satisfied the relations

$$F(\eta_1, -\eta_2; c) = F(\eta_1, \eta_2; c) \text{ and } F(-\eta_1, -\eta_2; 1 - c) = F(\eta_1, \eta_2; c). \tag{4}$$

From Eqs. (1)–(3) it follows at once that the first relation in Eq. (4) is still valid while the second becomes:

$$F(-\eta_1, -\eta_2; 1 - c) = F(\eta_1, \eta_2; c) + Nk_B(0.5 - c)B\gamma^2(\eta_1^2 + 2p\eta_2^2). \tag{5}$$

This means that, for a transformation $c' = 1 - c$, $\eta_1' = -\eta_1$, $\eta_2' = \eta_2$, the first derivatives of the free-energy function satisfy the conditions

$$\partial F(\eta_1, \eta_2; c)/\partial \eta_1 = -\partial F(\eta_1', \eta_2'; c')/\partial \eta_1' - Nk_B(1 - 2c')\gamma^2 B\eta_1' \tag{6a}$$

and

$$\partial F(\eta_1, \eta_2; c)/\partial \eta_2 = \partial F(\eta_1', \eta_2'; c')/\partial \eta_2' + 2Nk_B(1 - 2c')\gamma^2 pB\eta_2'. \tag{6b}$$

Thus, the equilibrium states of compounds with concentration $c > 0.5$, determined by the extremal conditions $\partial F/\partial \eta_1 = 0$, $\partial F/\partial \eta_2 = 0$, and the sign of the discriminant $\Delta = (\partial^2 F/\partial \eta_1^2)(\partial^2 F/\partial \eta_2^2) - (\partial^2 F/\partial \eta_1 \partial \eta_2)^2$, can be related to those with the respective parameters: $c' = 1 - c$, $\eta_1' = -\eta_1$, $\eta_2' = \eta_2$. The temperatures corresponding to the related extrema in the (η_1, η_2) and the (η_1', η_2') planes, i.e., the transition temperatures for systems of concentrations c and $c' = 1 - c$, can be expressed as:

$$T(\eta_1, \eta_2) = T(\eta_1', \eta_2')[1 + (1 - 2c')B/V_1(c')]. \tag{7}$$

We shall call the pairs of points satisfying conditions in Eqs. (5), (6a), (6b), (7) "conjugated extrema". It is important to realize that, due to a generally different discriminant, $\Delta(\eta_1, \eta_2; c) \neq \Delta(\eta_1', \eta_2'; c')$, the conjugated extrema may well be of different types (saddle point and minimum, maximum and minimum etc.).

Thus, we note that the introduction of a linear variation of the energy parameters with concentration changes the symmetry properties of the free-energy function, leading to an asymmetry in the calculated mean-field phase diagrams with respect to the point $c = 0.5$.

2. Results and discussion

2.1. TbH_{2+x}

The β-phase exists within a restricted concentration range, $c \leq 0.25$ [5]. The ordering is a one-step process, which contains a discontinuous order–disorder transformation at $T = T_{tr}$, followed by continuous evolution. The low-temperature limiting ordered state is a "d-state" (cf. Ref. [3,4]), characterized by the set of equilibrium occupation numbers: $n_1 = 4c$, $n_2 = n_3 = 0$. In Fig. 1, taken from Ref. [2], the concentration dependence of the transition temperature $T_{tr}(c)$ is given for two different conditions: (i) $V_1 = -1523$ K = const, and (ii) V_1 as given by Eq. (3), where $A = -1523$ K, $B = 6050$ K, and $c_0 = 0.18$. The sequences $T_{tr}(c)$ are compared with experimental data [5].

2.2. CeH_{2+x}

A monophase state is supposed to exist within the concentration range $0 \leq c \leq 0.75$. Let us discuss the ordering process by introducing special concentrations c_1 to c_4 such that $c_1 < c_2 < c < c_3 < c_4$. For $c < c_1$ and $c > c_4$, the ordering is a single-step continuous process, which terminates in a state characterized by the occupation numbers $n_1 = 1$, $n_2 = 0$, $n_3 = 2c - 0.5$ (a so-called "b-state" [3,4]). Inside the region $c_1 < c < c_4$ the ordering is a multi-step process, beginning as a b-state but finishing as a d-state and described by the occupation numbers $n_1 = 1$, $n_2 = 4c - 1$, $n_3 = 0$. The b-state is in equilibrium at temperatures $T_{tr1} > T > T_{tr2}$, but, at $T < T_{tr2}$, the d-state becomes energetically more favorable and an order–order transformation occurs. For $c_1 < c < c_2$ and $c_3 < c < c_4$, the ordering process is two-step, containing a single order–order transformation of the "bd-type" at $T = T_{tr2}$. On the other hand, for $c_2 < c < c_3$, after a b-type ordered state, an "a-state" [3]

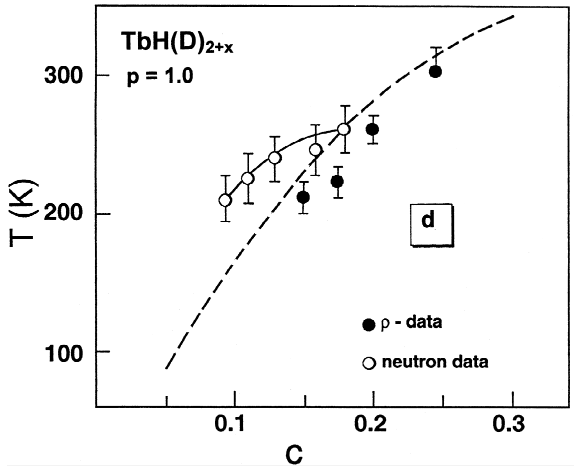

Fig. 1. Calculated [2] order–disorder transition temperatures in the system β-TbH(D)$_{2+x}$, compared with resistivity and neutron-scattering data [5]. Broken line: $V_i = \text{const}$, full line: $V_i = V_i(c)$ (see text).

is formed at $T<T_{tr2}$, which is characterized by the occupation numbers $n_1=n_2=2c$, $n_3=0$. It exists until $T=T_{tr3}$ where it is replaced by the d-state. The ordering is now a three-step process containing two order–order transformations, of the ‘‘ba-type’’ and of the ‘‘ad-type’’.

In Fig. 2 the phase diagram of β-CeH_{2+x} is given for the conditions: (i) $V_1=-1220$ K=const, and (ii) V_1 as defined by Eq. (3), where $A=-1220$ K, $B=1184$ K, and $c_0=0.41$. In both cases, we had taken $p=1.25=$const. The experimental data are given in Ref. [3].

Note that the special values c_1 and c_4 are not influenced by a variation of the energy constants, as they are determined only by the parameter p [6]. For $p=1.25$, we have $c_1=0.35$ and $c_4=0.65$. The V_i-dependence of c_2 and c_3 is less obvious; for both sets of V_i used here, it is the same: $c_2=0.45$ and $c_3=0.55$. As can be seen, $c_4=1-c_1$ and $c_3=1-c_2$.

2.3. LaH_{2+x}

The monophase equilibrium state exists within the interval $0 \leq c \leq 0.8$ [5]. The neutron scattering results [7,8] suggest that, in this system, $p<1$. This means [6] that the limiting low-T equilibrium state is the d-state, with $n_1=1$, $n_2=4c-1$, $n_3=0$. The special concentration values c_1 to c_4 are defined as above. For $c<c_1$ and $c>c_4$, the ordering is a one-step process with a d-state symmetry for $T<T_{tr1}$, which develops continuously. The order–disorder transformation itself is discontinuous. For concentrations $c_1<c<c_4$, the ordering is a two-step process with an a-state at $T<T_{tr1}$ and $n_1=n_2>n_3$, transforming to a d-state at $T=T_{tr2}$. For concentrations $c_1<c<c_2$, and $c_3<c<c_4$, the order–order transformation is discontinuous, while for $c_2<c<c_3$ it is continuous. At $c=0.5$, the a-state is stable for all temperatures $T<T_{tr1}$ and no order–order transformation takes place.

In Fig. 3 the phase diagram of β-LaH_{2+x} is given for the conditions: (i) $V_1=-1880$ K=const, and (ii) V_1 as given by Eq. (3), where $A=-1880$ K, $B=1360$ K, and $c_0=0.25$. In both cases, we have taken $p=0.7743=$const. The results are compared to the experimental data given in Ref. [4]. The special concentration values are: $c_1=0.15$, $c_2=0.27$, $c_3=0.73$ ($c_4=0.85$ lies outside the considered region).

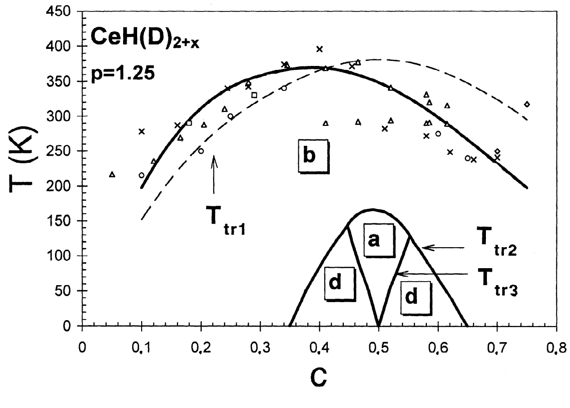

Fig. 2. Experimental transition temperatures [3] in the β-CeH_{2+x} system, compared with calculated order–disorder and order–order transformations (see text for details). Broken lines: $V_i=$const, full lines: $V_i=V_i(c)$.

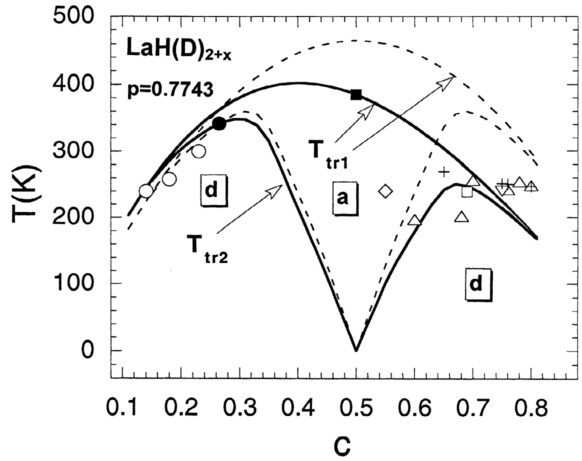

Fig. 3. Same as Fig. 2 but for the β-LaH_{2+x} system; data are from Ref. [4].

3. Conclusions

1. A comparison of the phase diagrams in Figs. 2 and 3 shows the principal differences between systems with $p>1$ and $p<1$: (i) the concentration dependence of the order–order transition temperature $T_{tr2}(c)$ possesses, at $c=0.5$, a minimum for $p<1$ and a maximum for $p>1$; (ii) there exists no other order–order transformation in the case of $p<1$. These distinctions are due to the fact that, in a system with $p<1$ (β-LaH_{2+x}), the b-state is never in equilibrium at any concentration and temperature; the ordered states can only have the symmetry of an a-state or a d-state, excluding the bd-transition. Therefore, the transitions at $T_{tr2}(c)$ of β-CeH_{2+x} (where $p>1$) do not exist in β-LaH_{2+x}; the $T_{tr3}(c)$ of the former system are analogous to the $T_{tr2}(c)$ of the latter.
2. Introduction of a concentration dependence for the energy parameters V_i changes the symmetry of the order–disorder transition temperatures $T_{tr1}(c)$ in the phase diagrams. A comparison with the experimental results shows that even a simple linear dependence of the energy parameters $V_i(c)$ as used here provides already a rather good description of the data, in particular the displacement of the maxima of $T_{tr1}(c)$ from $c=0.5$ to lower values. It is reasonable to attribute this effect to the concentration-dependent lattice contraction existing in these systems [5].
3. The multi-step ordering process has not yet been established experimentally, neither in β-CeH_{2+x} nor in β-LaH_{2+x}. This may be due to either very close-lying

values of T_{tr1} and T_{tr2}, or, in contrast, be caused by the fact that $T_{tr2} \ll T_{tr1}$. We suggest that, in the case of β-LaH_{2+x}, a compound with $c \sim 0.35$–0.40 will be optimal for the observation of both transitions. For β-CeH_{2+x}, a similarly suitable concentration lies in the vicinity of $c = 0.5$.

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