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Hydrogen ordering in superstoichiometric rare-earth hydrides for a system with an energy-constants ratio $p=V_2/V_1<1$: LaH_{2+x}

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The processes of hydrogen ordering in the β phase of rare-earth hydrides RH_{2+x} depend on the hydrogen concentration in the set of octahedral interstices x and are determined by the value of the parameter $p=V_2/V_1$, the ratio of energy constants characterizing the interactions between the octahedral H atoms. Applying the mean-field approximation of the static-concentration-waves theory we had analyzed the cases of $p=1$ and $p>1$ in our previous publications which corresponded, respectively, to the systems TbH_{2+x} and CeH_{2+x}. In the present article, we have investigated the processes of H ordering in the La-H system, representative of the case $p<1$. An important result is the prediction of two transition temperatures corresponding to the separate vanishing of the two order parameters present. The theoretical treatment is applied to recent neutron-diffraction data by Udovic *et al.* on $LaD_{2.25}$ and compared to other earlier obtained experimental results obtained on LaH_{2+x} compounds.

I. INTRODUCTION

Experimental investigations of rare-earth (R)-hydrogen systems (see, e.g., the review, Ref. 1) have shown that in the fcc β-phase hydrides, i.e., in the RH_{2+x} compounds, the subsystem of hydrogen atoms undergoes an order-disorder transition. As was established, this structural transformation concerned only a part of the N_H hydrogen atoms [$N_H=N(2+x)$, where N is the number of R atoms], namely, the set of N_x H atoms located in the octahedral interstitial positions of the metal lattice and called hereafter H_o atoms. The remaining H atoms, located in the tetrahedral interstices of the R lattice (H_t atoms), as well as the R lattice itself, do not change their equilibrium states drastically in the vicinity of the corresponding transition temperature[2–4] and do not seem to affect significantly the structural transformation under consideration. The interaction within the H_o system is characterized by two energy constants, V_1 and V_2, related to the Fourier components of the H-H interaction potential.[5,6]

As it was noted previously,[5,6] the features of the ordering processes are determined by the numerical values of two parameters in the system: the concentration of H_o atoms in octahedral interstices x, and the ratio of the energy constants $p=V_2/V_1$. The systems we had treated already corresponded to the cases $p=1$ [TbH_{2+x}, $0\leqslant x\leqslant 0.3$ (Ref. 5)] and $p>1$ [CeH_{2+x}, $0\leqslant x\leqslant 0.75$ (Ref. 6)]. In the former case, we had succeeded in reproducing the experimental order-disorder transition temperatures as a function of the concentration x; in the latter we had obtained and interpreted order-order transformations in addition to the "classical" order-disorder transitions. In the present work, we are investigating the ordering processes in systems with $p<1$. This condition seems realized for the hydrides LaH_{2+x}, and we are performing our analysis based on the experimental data.[7–12]

The treatment of the thermodynamics of the ordering processes in the interstitial alloys RH_{2+x} presented below closely follows the detailed description given in Refs. 5 and 6. Thus, the subsystem of H_o atoms is considered an independent binary substitutional alloy with a constant concentration of xN H_o atoms and $(1-x)N$ H_o-atom vacancies, distributed in a rigid fcc lattice. The thermodynamic properties of this binary alloy are obtained by determining the coordinates of the absolute minimum of the free-energy function $F=E-TS$, accounting for the H-H interactions between the H_o atoms E, and the entropy S, of the redistribution of particles on the given set of sites.

We consider the development of ordering of N_o H particles on the set of the N sites of a fcc lattice, in accordance with the existing experimental results,[2–4] where the ordered state is described by the superstructure vectors (a is the lattice parameter)

$$\mathbf{k}_1=(2\pi/a)(100) \quad \text{and} \quad \mathbf{k}_2=(2\pi/a)(1/2\ 0\ 1).$$

Then, following the static-concentration-waves theory,[13] the distribution of particles can be represented by the superposition of the two concentration waves with the above wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$. The relevant distribution function is given by the expression[13,3]

$$n(x,y,z)=c+\eta_1\gamma_1\exp(i2\pi x)+2\eta_2\gamma_2\cos[\pi(x+2z)]. \tag{1}$$

Here $n(x,y,z)$ is the probability that the lattice site with the coordinates (x,y,z) will be occupied by an H_o atom; η_1 and η_2 are order parameters; γ_1 and γ_2 are normalization constants; and c is the precise value of the concentration of H_o particles in the octahedral sites, defined as $c=N_o/N$ (in the ideal case, when all tetrahedral sites are occupied by H_t atoms, one has $c=x$, but if $N_t=2N-\delta$, then it is assumed that $c=x+\delta$).

On the set of the fcc lattice sites, the function (1) takes three distinct values:

$$n_1 = c + \eta_1\gamma_1 + 2\,\eta_2\gamma_2,$$

$$n_2 = c + \eta_1\gamma_1 - 2\,\eta_2\gamma_2,$$

$$n_3 = c - \eta_1\gamma_1, \tag{2}$$

denoting the existence of three different probabilities of O-site occupation by the hydrogen atoms.

In the case of the mean-field approximation[13] and the distribution function (1), the internal energy and the entropy of the given ordering system will be represented by the expressions[5,6]

$$E(\eta_1,\eta_2) = (Nk_B/2)[V_0c^2 + V_1(\eta_1\gamma_1)^2 + 2V_2(\eta_2\gamma_2)^2] \tag{3}$$

and

$$S(\eta_1,\eta_2) = -(Nk_B)\Sigma_i\nu_i[n_i\ \ln n_i + (1-n_i)\ln(1-n_i)], \tag{4}$$

where ν_1,ν_2,ν_3 are the fractions of lattice sites, where the function $n(x,y,z)$ is equal, respectively, to n_1, n_2, and n_3. V_0, V_1, and V_2 are the energy constants, related to the Fourier components of the H-H interaction potential, $V(k_i)$, for different wave vectors:

$$V_0 = V(\mathbf{k}_0)/k_B,\ V_1 = V(\mathbf{k}_1)/k_B,\ V_2 = V(\mathbf{k}_2)/k_B \tag{5}$$

with $\mathbf{k}_0 = 0$.

Introducing Eqs. (3) and (4) into the expression for the free-energy function $F = E - TS$, we obtain

$$F = Nk_B\{0.5[V_0c^2 + V_1[(\eta_1\gamma_1)^2 + p(\eta_2\gamma_2)^2]$$
$$+ T\Sigma_i\nu_i[n_i\ \ln n_i + (1-n_i)\ln(1-n_i)]\}, \tag{6}$$

where, in our case,

$$\nu_1 = \nu_2 = 1/4, \quad \nu_3 = 1/2; \quad \gamma_1 = \gamma_2 \equiv \gamma = 1/4; \tag{6'}$$

and

$$p \equiv V_2/V_1. \tag{6''}$$

In the following, we examine the surface of the free-energy function F in the space of the variables defining the state of a thermodynamical system as a function of the order parameters η_1,η_2. The coordinates of the absolute minimum of F, denoted hereafter as m, will represent the values of these variables in equilibrium at a given temperature T.

The extremal values of η_1 and η_2 are determined as the solutions of equations

$$\partial F/\partial\eta_1 = 0, \quad \partial F/\partial\eta_2 = 0 \tag{7}$$

and the type of each extremum is determined by the sign of the determinant

$$\Delta(\eta_1,\eta_2) = (\partial^2F/\partial\eta_1^2)(\partial^2F/\partial\eta_2^2) - (\partial^2F/\partial\eta_1\partial\eta_2)^2. \tag{8}$$

The free-energy function (6), defined in the space of independent variables, η_1 and η_2, can possess more than one local minimum. In such a case, the absolute minimum of F, $F(m)$, can be determined by comparing the values of the F function in the different minima. In the study under consideration, i.e., for $p < 1$, one can distinguish three different local minima (see, e.g., Ref. 14) denoted as follows: m_0 is located at the origin $(\eta_1 = 0, \eta_2 = 0)$ and existing for temperatures $T > T_{\min}(m_0) = T_0$; m_1 is located on the η_1 axis [on the set of points $(\eta_1 \neq 0, \eta_2 = 0)$] and existing within the interval $T_{\max}(m_1) = T_0 > T > T_{\min}(m_1) = T_1$; and m_2 is located outside the n_1 axis and existing inside the temperature region $T_{\max}(m_2) = T_2 > T > T_{\min}(m_2) = 0$ K.

As $T_{\min}(m_0) = T_{\max}(m_1)$, we conclude that the minima m_0 and m_1 cannot coexist at any temperature. On the other hand, the limiting temperature T_2 of m_2 is not strictly related to the limiting temperatures T_1 or T_0, characterizing the m_0 and m_1 minima, and depends on the values of the system parameters c and p. As we shall see below, for different values of c and p, we can have $T_2 = T_1$, as well as $T_2 > T_1$, and even $T_2 > T_0$. The first condition implies that the minimum m_2 appears at temperatures below the existence range of m_1, while in the last two cases, the local minimum m_2 coexists, in a certain temperature interval, with either the minimum m_1 or m_0. Hence, to find the location of the absolute minimum $F(m)$, we have to compare the free-energy values $F(m_2)$ with $F(m_1)$ or $F(m_0)$.

Thus, in the different temperature intervals, the equilibrium values of the order parameters $\eta_1(T)$ and $\eta_2(T)$ can be represented by the coordinates of the minima m_0, m_1, or m_2. It must be noted that any shift of the absolute minimum from one local minimum to another reveals itself by phenomena characteristic for a phase transition of the first or second order. In the next section, we present the numerical solutions of Eqs. (7) and (8), as well as the calculated thermodynamical parameters of the system.

II. NUMERICAL RESULTS

An example of the developing ordering process in a system, close to one studied experimentally,[10] is shown in Fig. 1, where we have chosen $c = 0.25$, $V_1 = -1860$ K and $p = 0.6$ to reproduce qualitatively the development of the ordering process and its transition temperature as reported by Udovic *et al.*[10] (It has to be noted here that the value of V_1 determines only the temperature of the ordering process, not its evolution.)

Figure 1(a) gives the sequence of points in the (η_1,η_2) plane, with the equilibrium values of the order parameters η_1 and η_2 at a given temperature [i.e., defining the trajectory of the ordering process on the (η_1,η_2) plane] as coordinates. Figure 1(b) yields the temperature dependences of the equilibrium values for the order parameters $\eta_1(m)$ and $\eta_2(m)$, and Fig. 1(c) those for the site occupation probabilities (site occupation numbers) n_1, n_2, and n_3, related to the order parameters by the expressions (2).

First of all, we note [Figs. 1(b) and 1(c)] that the ordering turns out to be a two-step process: after a disorder-order transition at the temperature $T_{\rm tr1} = 349$ K, when an ordered state characterized by $\eta_1 = 0$, $\eta_2 = 0$ is created, there appears a second transition at $T_{\rm tr2} = 276$ K, where an order-order transformation occurs. This point coincides with the low-temperature limit of the m_1 minimum T_1, and that is why, in the vicinity of $T_{\rm tr2}$, the ordering system undergoes a second-order-type phase transformation. The first transition is also a continuous one, as its temperature coincides with the low-temperature limit T_0 of the minimum m_0. Hence, the discussed example of ordering represents a two-step continuous

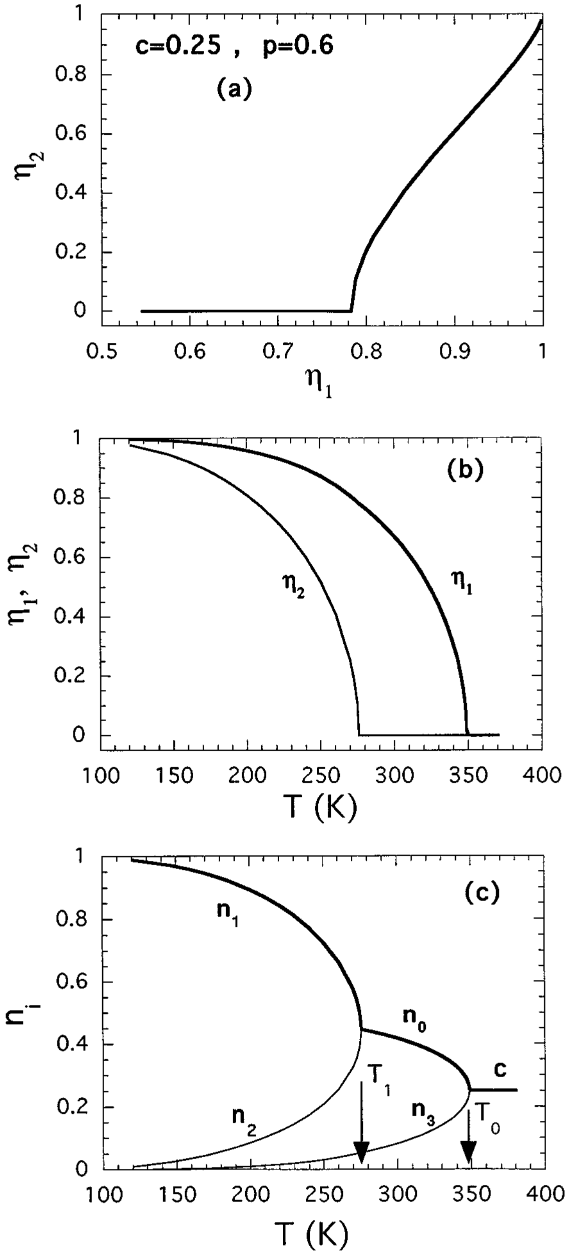

FIG. 1. Ordering process in a system with the parameters $c=0.25$, $V_1=-1860$ K, $p=0.6$ (see the text for definitions). (a) Sequence of pairs of equilibrium values of order parameters, forming a trajectory in the (η_1,η_2) space. (b) Temperature dependence of the equilibrium values of order parameters; both transitions (for $\eta_2=0$ and $\eta_1=0$) are continuous transformations. (c) Temperature dependence of the equilibrium values of occupation numbers n_1, n_2, n_3; the transition temperatures coincide with the corresponding special points T_0 and T_1, the branching points of the solutions of Eqs. (7).

process, where first, below T_0, is created a state with two different site occupation probabilities, $n_0=(c+\eta_1\gamma)$, $n_3=(c-\eta_1\gamma)$, and then, for $T<T_1$, is formed an ordered state with three different occupation probabilities given by (2).

The variations of the limiting points of the minima, T_0 and T_1, and of the location of the limit on the η_1 axis, $\eta_1(T_1)$, with varying c and p are depicted in Fig. 2. As seen in Fig. 2(a), T_0 is independent of p and changes only with c (and V_1, of course). In order to reveal the variations of T_1 and $\eta_1(T_1)$ with concentration c, we have to compare the reduced values $\tau_1=(T_1/T_0)$ and $\sigma_1=[\eta_1(T_1)/\eta_1(T=0)]$. They are shown in Figs. 2(b) and 2(c).

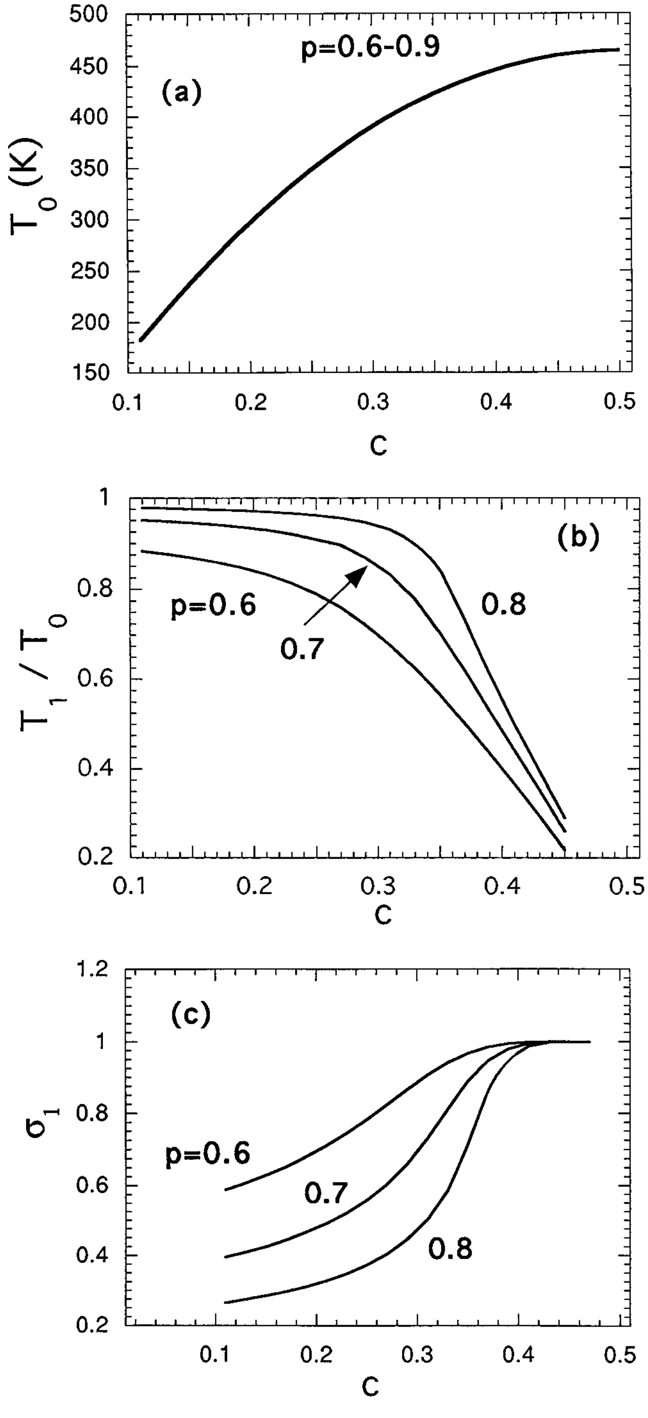

FIG. 2. Concentration dependence of the special points T_0 and T_1 and of the reduced order parameter $\sigma_1\equiv\eta_1(T_1)/\eta_1(T=0)$, for various values of $p=V_2/V_1$. (a) Stability limit T_0 of the disordered high-temperature state (T_0 is independent of p). (b) Reduced value $\tau_1\equiv T_1/T_0$ of the low-temperature limit for the existence of the ordered state $(\eta_1\neq 0, \eta_2=0)$. (c) Reduced order parameter σ_1 for the transition at T_1.

The temperature points T_0 and T_1 approximately charac-

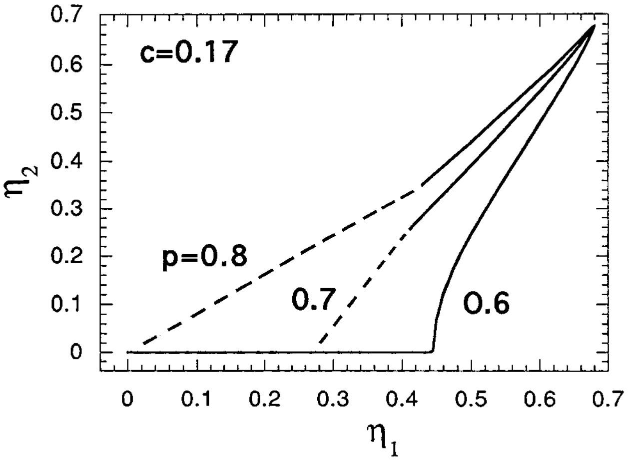

FIG. 3. Sequences of pairs of equilibrium values of order parameters with decreasing T, in the case $c = 0.17$ and for different values of p.

terize the ordering process, but, as we shall see below, they coincide with the transition temperatures T_{tr1} and T_{tr2} only in the case of high concentrations c and low values of p. To visualize the situation, we show in Figs. 3–5 the development of the ordering processes in the system with a fixed concentration $c = 0.17$ and a given value of the energy constant $V_1 = -1860$ K but with different values for the parameter p: 0.6, 0.7166, and 0.8. In these figures are presented the trajectories of the equilibrium state of the (η_1, η_2) plane (Fig. 3), the temperature dependences of equilibrium values of the order parameters (Fig. 4), and of the site occupation numbers (Fig. 5).

We see, that for $p = 0.6$ [Figs. 3, 4(a), and 5(a)], the process is quite similar to that shown in the Figs. 1(a)–1(c). There are two transition points T_{tr1} and T_{tr2} coinciding, respectively, with the temperature points $T_0 = 262$ K and $T_1 = 226$ K; both transitions are continuous.

For the value $p = 0.7166$ [Figs. 4(b) and 5(b)], we have $T_{tr1} = T_0$, and the order-disorder transition is continuous, but as $T_2 = 249$ K$> T_1 = 247$ K, the minima m_1 and m_2 coexist within an interval of 2 K, and this is sufficient for the second, order-order transformation, which occurs at the temperature $T_{tr2} = 248.5$ K, to become a discontinuous, first-order-like transition. For $p = 0.8$ we obtain $T_2 = 265$ K$> T_0 = 262$ K $> T_1 = 256$ K. Here the ordering is described by a single-step process and contains, therefore, only one transition point, associated with the absolute minimum when going from m_0 to m_2, missing m_1. It occurs at $T_{tr} = 263$ K. Since the minima m_0 and m_2 coexist within an interval of 3 K, the order-disorder transformation is a first-order like process.

III. COMPARISON WITH EXPERIMENTAL DATA

Neutron diffraction studies of the ordering process in the subsystem of octahedral hydrogen atoms in the hydride LaH_{2+x} ($x = 0.25$) have been performed recently by Udovic *et al.*[10] Very careful measurement were carried out in a wide temperature range, between 400 and 15 K. From their results, we shall utilize the temperature dependences of the o-site occupation probabilities by hydrogen atoms, i.e., in our notations, the values of the occupation numbers $n_1(T)$, $n_2(T)$, and $n_3(T)$ (in the authors' notation, the values of $n(01)$, $n(02)$, and $n(03)$, respectively). On Fig. 6(a) are given the calculated and the measured dependences of occupation numbers $n_i(T)$. The calculated curves $n_i(T)$ were obtained by taking $c = 0.25$ and normalizing it to the corresponding experimental values at 340 K, which in Ref. 10 is the reported order-disorder transition temperature. These normalization conditions result in the selection of the following values for the energy parameters: $V_1 = -2010$ K, $p = 0.7166$.

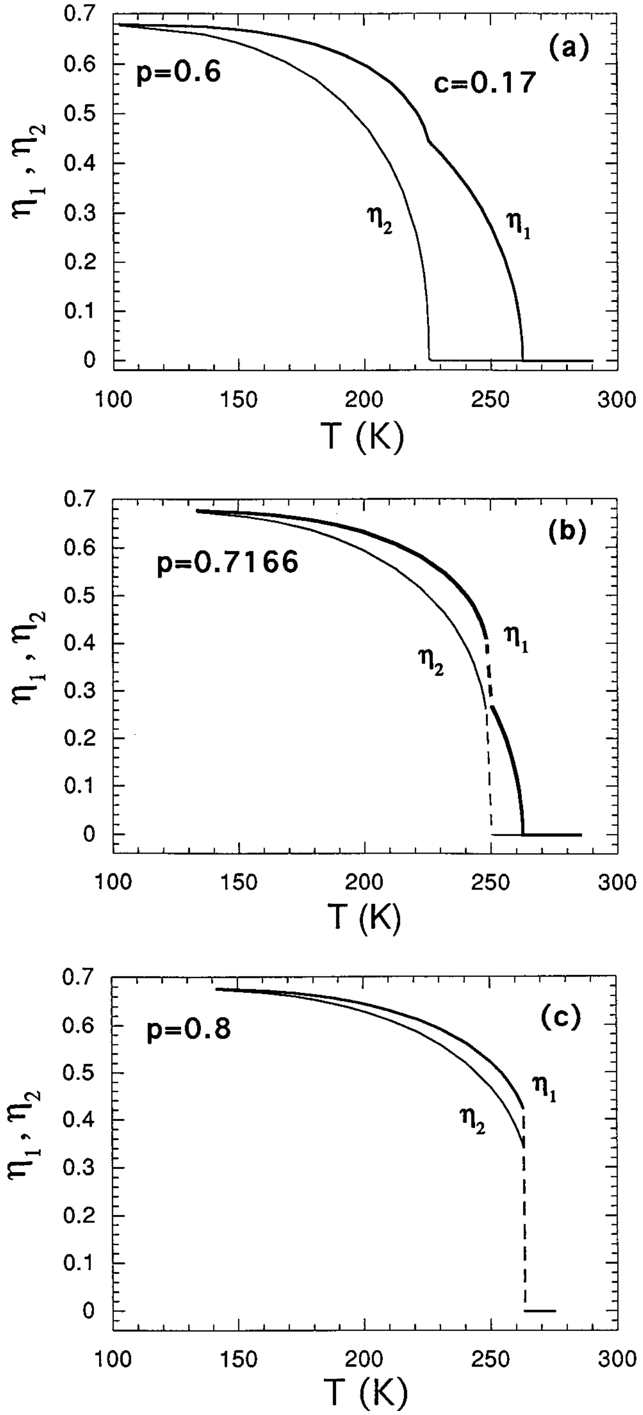

FIG. 4. Temperature dependence of the equilibrium values of order parameters, in the case $c = 0.17$ and for different values of p.

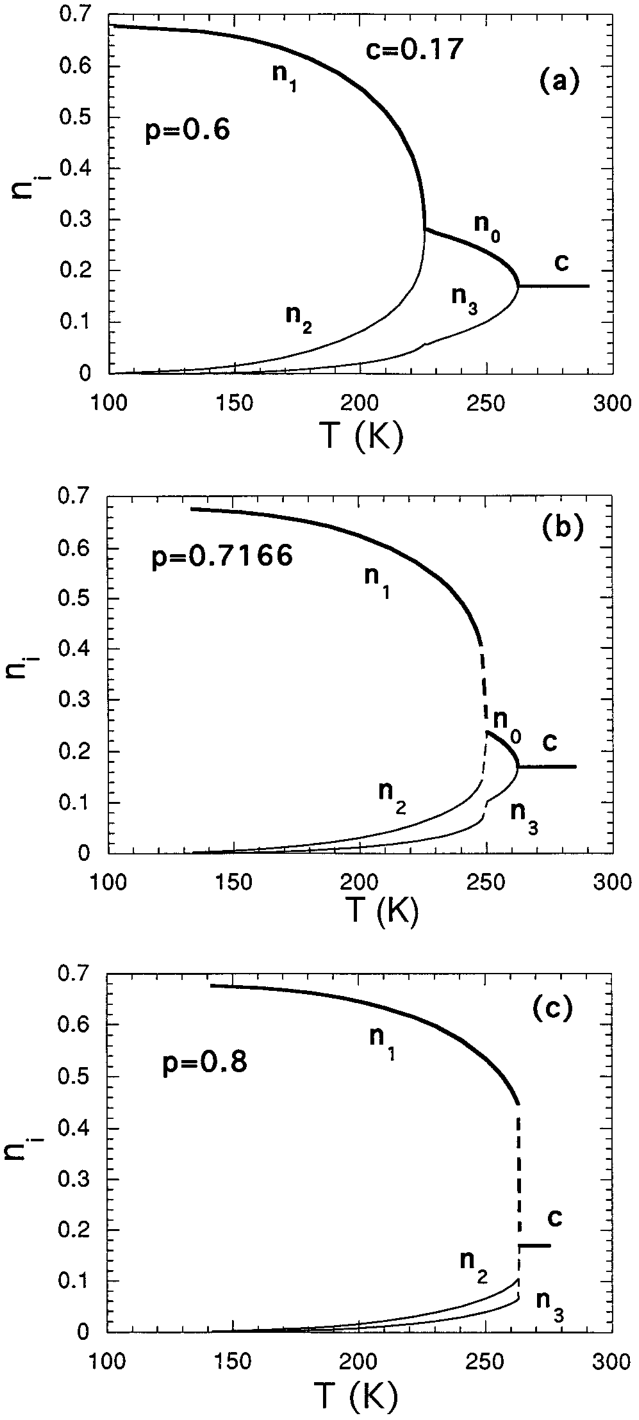

FIG. 5. Temperature dependence of the equilibrium values of the site occupation numbers, in the case $c=0.17$ and for different values of p.

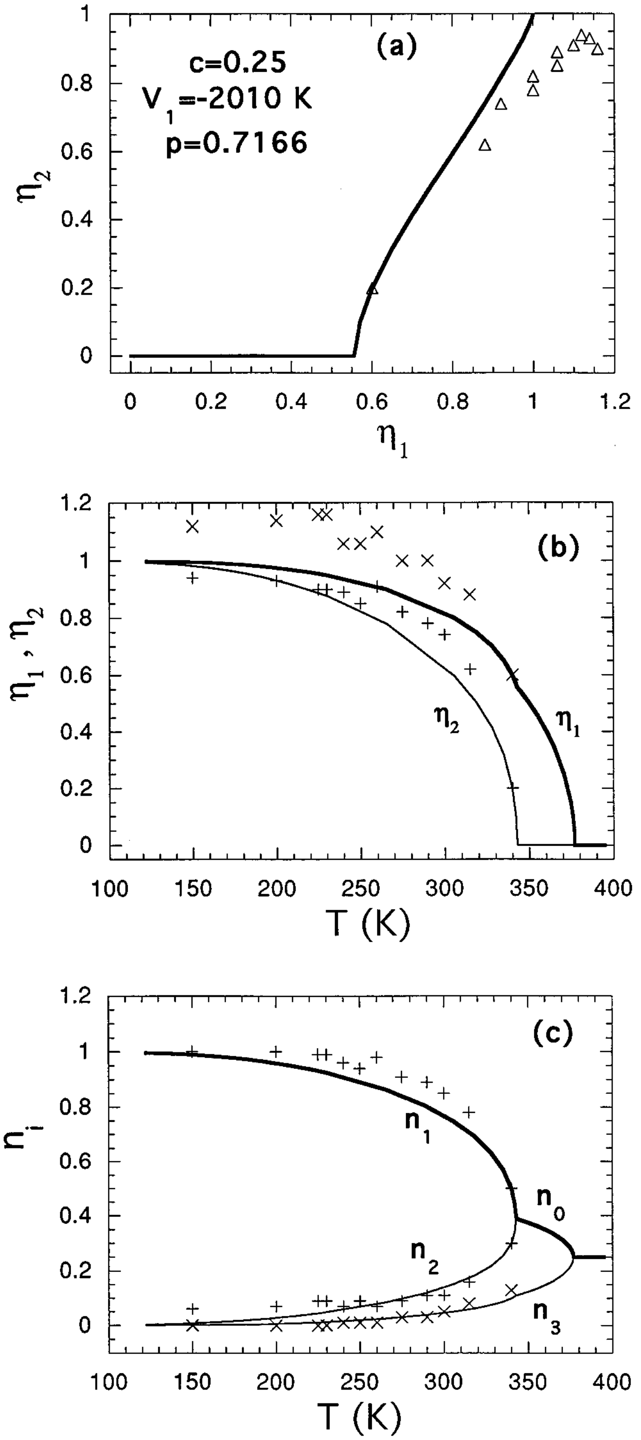

FIG. 6. Same as Fig. 1, for $c=0.25$ but with $p=0.7166$ and $V_1=-2010$ K. The solid lines are the computed results, the signs correspond to the experimental data from Ref. 10.

In Figs. 6(b) and 6(c) are given the values of the order parameters η_1 and η_2 in equilibrium, at different temperatures, which are obtained from the measured and calculated values of $n_i(T)$, utilizing the expressions (2). There can be seen the differences between the theory and experiment at low and moderate temperatures, but from Fig. 6(a) it is obvious that the principal distinction between the two sets of data is observed within the interval just above the transformation temperature. Following our calculations, only the order parameter η_2 disappears above $T=340$ K, while η_1 remains nonzero, diminishes gradually, and disappears only at temperatures above $T=377$ K [just as in the cases shown in Figs. 1(c), 5(a), and 5(b)].

This means that, at 340 K, only the set of superstructure reflections associated with the wave vector $\mathbf{k}_2=(2\pi/a)(1/2\ 0\ 1)$ disappears, while the superstructure lines related to the wave vector $\mathbf{k}_1=(2\pi/a)(100)$ must exist until $T=377$ K. On the other hand, according to the experimental results given by Udovic *et al.*[10] [Fig. 4(d) and the Table III of Ref. 10], there is no difference between the occupation numbers n_1, n_2, and n_3 at temperatures $T>340$ K, which means that both sets of superstructure reflections are absent. This is a real contradiction between the theoretical and experimental results. One might wonder about the possible lack of measuring sensitivity in the experiment of Udovic *et al.*;[10] on the other hand, the presence of some unidentified lines in their spectra (e.g., at $2\Theta=34°$ in their Fig. 2) observed at 340 K and remaining visible at 350 K could be an indication of the superstructure with wave vector $\mathbf{k}_1$.

We wish also to note, in this context, that there exists a relation[5,6] between the values of the occupation numbers (2):

$$\Sigma_i \nu_i n_i = c. \tag{9}$$

If we take the experimental values of n_i from Ref. 10 and the values of ν_i from Eq. $(6')$, then, for the great majority of temperatures, we obtain a value $c>0.25$: in particular, for $T=340$ and 15 K we have $c=0.265$.

If we suppose that this is the real concentration of octahedral hydrogen atoms in the sample used in Ref. 10 and normalize the calculated $n_i(T)$ dependences to the experimental values of n_i at the same temperature 340 K (setting $c=0.265$), then, instead of Figs. 6(a)–6(c), we obtain the dependences shown in Figs. 7(a)–7(c). The new normalization requires the following set of energy parameters:

$$V_1=-1860 \text{ K} \quad \text{and} \quad p=0.7743. \tag{10}$$

Comparing the Figs. 6 and 7, we conclude that the agreement between the measured and calculated data is somewhat better in the case of the suggested concentration $c=0.265$, with the corresponding energy parameters (10). It is, thus, reasonable to suppose that the $\mathrm{LaD}_{2.25}$ sample in question was in fact composed at $\mathrm{LaD}_{1.985+0.265}$ (cf. also the discussion in the Introduction), which could explain at least some of the difficulties.

If we assume that the values for the energy parameters are characteristic for the LaH_{2+x} system through the whole β-phase range and do not change significantly with temperature, then one can calculate a set of transition temperatures for various concentrations. The results of these calculations are presented in the form of a phase diagram in Fig. 8. In the same plot are also shown the experimental values obtained for various hydrides in different measurements.[7–12]

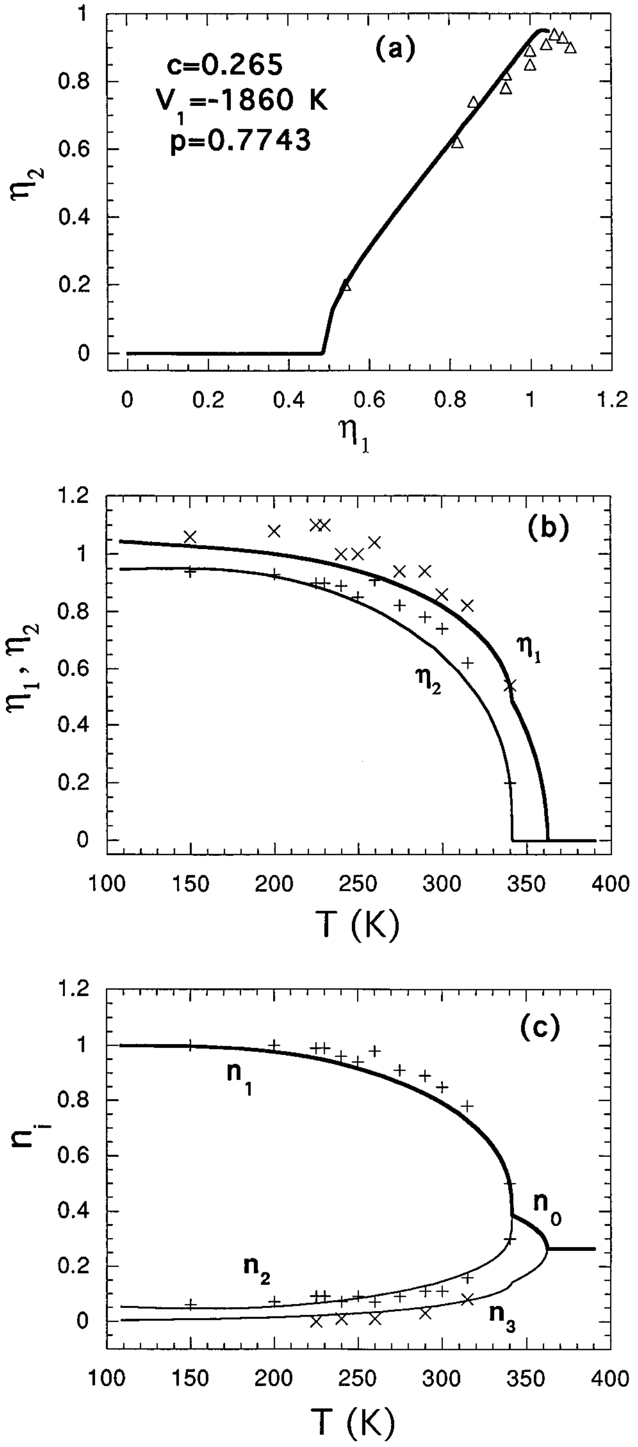

FIG. 7. Same as Figs. 1 and 6, but for $c=0.265$ (our suggested choice for x in Ref. 10) and with $p=0.7743$ and $V_1=-1860$ K.

IV. CONCLUDING REMARKS

We have analyzed the ordering processes that take place in a system described by the distribution function (1) and the free-energy function (6) for the case $p=V_2/V_1<1$, corresponding to the fcc β-phase compound LaH_{2+x}. We have found three different possible minima, m_0, m_1, m_2, on the F surface in the space of the order-parameter variables (η_1,η_2), located, respectively, at the origin, on the η_1 axis, and outside the η_1 axis. The equilibrium ordered state for a fixed concentration c is determined by the location of the absolute minimum at a given temperature T. The type of ordering transition depends in an intricate way on the relative extensions [upper and lower limits, $T_{\max}(m_i)$ and $T_{\min}(m_i)$] of the existence regions for each minimum. For

$$T_{\min}(m_0)=T_{\max}(m_1)>T_{\min}(m_1)=T_{\max}(m_2), \tag{11}$$

the absolute minimum is located subsequently in m_0, m_1, m_2, yielding a two-step character for the ordering process: a disorder-order transition when going from m_0 to

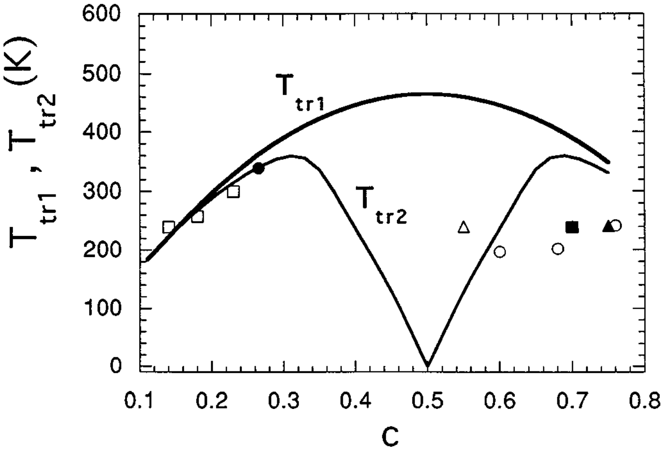

FIG. 8. Calculated, for the two wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ (solid lines), and experimental [□ (Ref. 7), ▲ (Ref. 8), ♦ (Ref. 9), ● (Ref. 10), ■ (Ref. 11), and △ (Ref. 12)] transformation temperatures as a function of c, in the system LaH_{2+x}.

m_1, and an order-order transformation for m_1 to m_2. Both transitions are continuous. When

$$T_{\min}(m_0)=T_{\max}(m_1)>T_{\max}(m_2)>T_{\min}(m_1), \tag{12}$$

the order-order transformation m_1 to m_2 changes its type and becomes discontinuous. For the case

$$T_{\max}(m_2)>T_{\min}(m_0)=T_{\max}(m_1)>T_{\min}(m_1), \tag{13}$$

the system performs the same sequence of steps as in case (12) if there exists a temperature interval where $F(m_1)<F(m_2)$; however, the ordering becomes a single-step discontinuous process if, for all T, $F(m_1)>F(m_2)$. [In the particular case $T_{\max}(m_2)=T_{\min}(m_0)$, the transition remains continuous.]

In the case $p>1$,[6] the trajectory of the equilibrium ordered states lay always outside the η_1 axis and the type of the order-disorder transition depended on whether the transition point on the trajectory was located inside or outside the origin. As to the second, order-order transformation, it exhibited a discontinuous, first-order-type character, which, for some concentrations, gave rise to a two-step transition. Thus, the features of the ordering process (such as the existence of two transformations and their type change) are qualitatively similar in both cases, $p>1$ and $p<1$, but the intrinsic reasons for this are quite different.

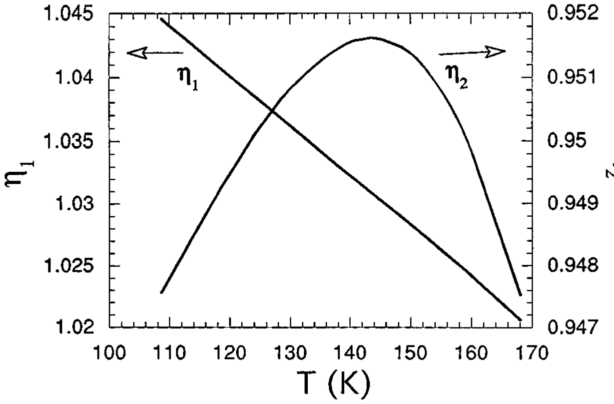

FIG. 9. Temperature dependence of the order parameters for LaH_{2+x}, with $x=0.265$, showing anomalous behavior of η_2 below 140 K. The experimental values from Ref. 10, taken at $T=80$, 150, and 200 K, would correspond to $\eta_1=1.04(3)$ and to $\eta_2=0.93(1)$.

The comparison with the neutron-diffraction data of Udovic *et al.*[10] is qualitatively satisfying, but the agreement is better if we assume that their $LaD_{2.25}$ specimen corresponded in reality to the composition $LaD_{1.985+0.265}$ rather than to $LaD_{2.00+0.25}$. This small difference is qualitatively important as, for $c>0.25$, an anomalous behavior can develop at low temperatures, where one of the order parameters may decrease with decreasing T (for details, cf. Ref. 6). As can be seen in Fig. 9, this type of anomaly is observed in the present case for the order parameter η_2, while η_1 varies normally.

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[1] P. Vajda, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner and L. R. Eyring (North-Holland, Amsterdam, 1995), Vol. 20, p. 209.

[2] A. K. Cheetham and B. E. F. Fender, J. Phys. C **5**, L35 (1972); C. G. Titcomb, A. K. Cheetham, and B. E. F. Fender, *ibid.* **7**, 2409 (1974).

[3] V. K. Fedotov, V. G. Fedotov, M. E. Kost, and E. G. Ponyatovskii, Sov. Phys. Solid State **24**, 1252 (1982) [Fiz. Tverd. Tela **24**, 2201 (1982)].

[4] G. André, O. Blaschko, W. Schwarz, J. N. Daou, and P. Vajda, Phys. Rev. B **46**, 8644 (1992).

[5] I. G. Ratishvili and P. Vajda, Phys. Rev. B **47**, 14 062 (1993).

[6] I. G. Ratishvili, P. Vajda, A. Boukraa, and N. Z. Namoradze, Phys. Rev. B **49**, 15 461 (1994).

[7] E. Boroch, K. Conder, C. Ru-Xiu, and E. Kaldis, J. Less-Common Met. **156**, 259 (1989).

[8] K. Conder, L. Wang, E. Boroch, E. Kaldis, and J. Schefer, Eur. J. Solid State Inorg. Chem. **28**, 487 (1991).

[9] P. Klavins, R. N. Shelton, R. G. Barnes, and B. J. Beaudry, Phys. Rev. B **29**, 5349 (1984).

[10] T. J. Udovic, Q. Huang, J. J. Rush, J. Schefer, and I. S. Anderson, Phys. Rev. B **51**, 12 116 (1995).

[11] Z. Bieganski and M. Drulis, Phys. Status Solidi A **44**, 91 (1977).

[12] M. R. Chowdhury, G. A. Styles, E. F. W. Seymore, S. F. J. Cox, C. A. Scott, and G. H. Eaton, J. Phys. Condens. Matter **1**, 4659 (1989).

[13] A. G. Khachaturyan, *Theory of Structural Transformations in Solids* (Wiley, New York, 1983).

[14] I. G. Ratishvili, Phys. Status Solidi B **87**, 461 (1978).