Hydrogen ordering induced resistivity anomalies in the superstoichiometric light rare-earth dihydrides

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Abstract

The ordering superstoichiometric light rare-earth dihydrides MH_{2+c} (M–La, Ce; H–hydrogen atoms) characterized by two long-range order parameters, η_1 and η_2, are considered. The electroresistivity R_H associated with the redistribution of hydrogen atoms during the ordering processes is investigated. An analytical expression describing dependence of R_H on the equilibrium values of order parameters is obtained. It is shown that in the disorder–order and order–order transition points, the resistivity temperature dependences $R_H(T)$ reveal the discontinuity- or kink-like anomalies. Residual resistivity and the possible quenching effect concentration dependences are given.
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1. Introduction

The light rare-earth superstoichiometric MH_{2+c} dihydrides are considered. It is assumed that N metal atoms form an unperturbed fcc lattice, 2N hydrogen atoms completely fill the set of 2N interstitial tetra-positions (they are called H_T-atoms, or tetra-H-atoms) and the remained cN part of hydrogen atoms (called H_O-atoms, or octa-H-atoms) are distributed among N octa-positions which form themselves a fcc lattice [1]. It is assumed as well that the ordering process in the subsystem of H_O-atoms does not influence on the subsystems of H_T-atoms and metal atoms and the ordering process of H_O-atoms can be considered as developed within the lattice of given MH_2 complexes.

It was established that the ordered configurations formed in the subsystem of H_O-atoms in some MH_{2+c} compounds can be described by the distribution function [2,3]

$$n(\boldsymbol{R}_i) = c + \eta_1 \ \gamma_1 \exp\ (i\mathbf{K}_1 \boldsymbol{R}_i) + \eta_2 \ \gamma_2 \left[\exp\ (i\mathbf{K}_2 \boldsymbol{R}_i) + \text{c.c.}\right] \tag{1.1}$$

where η_1 and η_2 are the long-range order parameters, $\gamma_1 = \gamma_2 = 0.25$ are normalizing factors, and $\mathbf{K}_1$ and $\mathbf{K}_2$ are the superstructure wave vectors:

$$\mathbf{K}_1 = \left(\frac{2\pi}{a}\right)(1\,0\,0), \quad \mathbf{K}_2 = \left(\frac{\pi}{a}\right)(1\,0\,2) \tag{1.2}$$

Function (1.1)–(1.2) on the set of fcc lattice sites takes three different values $-n_1$, n_2, and n_3:

$$n_1 = c + \eta_1\gamma_1 + 2\eta_2\gamma_2, \quad n_2 = c + \eta_1\gamma_1 - 2\eta_2\gamma_2,$$
$$n_3 = c - \eta_1\gamma_1. \tag{1.3}$$

The ordering doubles the fcc unit cell in one direction ($2a$, a, a). Corresponding unit cell is shown in Fig. 1. The fcc lattice of N octa-positions can be considered as formed by 8 bcc interpenetrating sublattices characterized by radius-vectors $\mathbf{R}_1,\ldots,\mathbf{R}_8$.

Conduction electron states in MH_{2+c} compounds have a specific peculiarity. In the N-site lattice of trivalent light rare-earth metal M the conduction band contains 3N electrons, but in the case of MH_{2+c} compounds the set of $N(2+c)$ H-atoms introduced in the lattice absorbs $N(2+c)$ conduction electrons into the low-lying impurity band and leaves in the conduction band only $N(1-c)$ electrons which take part in the electroconductivity.

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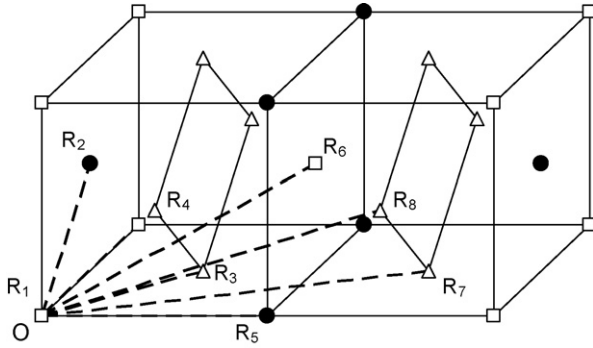*E-mail address:* ratisoso@hotmail.com (I.G. Ratishvili).

Fig. 1. The unit cell (*2a, a, a*) of an ordered state of octa-hydrogen atoms. $\mathbf{R_1}$–$\mathbf{R_8}$ are radius-vectors of the origins of different *bcc* sublattices. $\mathbf{R_1}$—(0 0 0), $\mathbf{R_2}$—(0 1/2 1/2), $\mathbf{R_3}$—(1/4 1/2 0), $\mathbf{R_4}$—(1/4 0 1/2), $\mathbf{R_5}$—(1/2 0 0), $\mathbf{R_6}$—(1/2 1/2 1/2), $\mathbf{R_7}$—(3/4 1/2 0), $\mathbf{R_8}$—(3/4 0 1/2).

The aim of the present investigation can be formulated as an attempt to describe the influence of the ordering process developed in the subsystem of H_O-atoms on the scattering of electrons, which remain in the conduction band of MH_{2+c} compounds.

2. Mathematical scheme

Let us begin by a reminder of some general relations for resistivity of metals.

Equilibrium distribution of conduction electrons on the set of **k**-states is given by the Fermi-function

$$f_k^0 = \left\{ \exp\left[\frac{(\varepsilon_\mathbf{k} - \zeta)}{\kappa_B T} \right] + 1 \right\}^{-1} \tag{2.1}$$

where ζ is the Fermi-level and $\varepsilon_\mathbf{k}$ is the conduction electron energy in the given **k**-state.

The external electric field accelerates the conduction electrons and modifies the Fermi-distribution function, $f_\mathbf{k}^0 \to f_\mathbf{k}$. A stationary state is reached when the time-dependent field-effect is compensated by the scattering of accelerated electrons on the imperfections of an ideal lattice (impurities and/or lattice oscillations):

$$\left(\frac{\partial f_\mathbf{k}}{\partial t} \right)_\text{field} + \left(\frac{\partial f_\mathbf{k}}{\partial t} \right)_\text{scatter} = 0 \tag{2.2}$$

Taking into account that the induced modifications of the distribution function are assumed to be small, it is written usually [4]

$$f_\mathbf{k} = f_\mathbf{k}^0 + g_\mathbf{k} \tag{2.3}$$

On assuming that conduction electrons are characterized by the electric charge e and velocity $\mathbf{v_k}$, the current density can be represented by the expression [4]

$$\boldsymbol{J} = e \int \boldsymbol{v_k} f_\mathbf{k}\, d\mathbf{k} = e \int \boldsymbol{v_k} g_\mathbf{k}\, d\mathbf{k} \tag{2.4}$$

In conditions of a constant electric field $\boldsymbol{E}$ it can be written [4],

$$\left(\frac{\partial f_\mathbf{k}}{\partial t} \right)_\text{field} = \left(-\frac{\partial f_\mathbf{k}^0}{\partial \varepsilon_\mathbf{k}} \right) (\mathbf{v_k} \cdot e\boldsymbol{E}) \tag{2.5a}$$

The second term of the Boltzmann Eq. (2.2) is presented usually as [4]

$$\left(\frac{\partial f_\mathbf{k}}{\partial t} \right)_\text{scatter} = \int (g_{\mathbf{k}'} - g_\mathbf{k}) P(\mathbf{k}, \mathbf{k}')\, d\mathbf{k} \tag{2.5b}$$

where $P(\mathbf{k}, \mathbf{k}')$ denotes the transition probability between the **k**- and **k**'-states described by the Bloch-functions $\psi_\mathbf{k}(\mathbf{r})$ and $\psi_{\mathbf{k}'}(\mathbf{r})$.

Transitions between **k**- and **k**'-states are caused by different type of perturbations. In all cases, within the limits of the first-order perturbation theory

$$P(\mathbf{k}, \mathbf{k}') \sim |U_{\mathbf{kk}'}|^2 \tag{2.6}$$

where $U_{\mathbf{kk}'}$ is the matrix element of the corresponding perturbation potential $V'(\mathbf{r})$,

$$V'(\mathbf{r}) \equiv V(\mathbf{r})|_\text{perturbed lattice} - V_0(\mathbf{r})|_\text{ideal lattice} \tag{2.7}$$

Time-dependent corrections $g_\mathbf{k}(t)$ of the distribution function (2.3) are usually assumed to satisfy the Eqs. (4) and (5)

$$\left(\frac{\partial g_\mathbf{k}}{\partial t} \right) = \left(-\frac{g_\mathbf{k}}{\tau} \right) \tag{2.8}$$

and consequently can be written as:

$$g_\mathbf{k}(t) = g_\mathbf{k}(0) \exp\left(-\frac{t}{\tau} \right) \tag{2.9}$$

Here τ is the relaxation time of the conduction electron system. It characterizes the properties of the given lattice. Combining expressions (2.2), (2.3), (2.5a), (2.5b) and (2.9) we obtain

$$g_\mathbf{k} = \left(-\frac{\partial f_\mathbf{k}^0}{\partial \varepsilon_\mathbf{k}} \right) \tau (\mathbf{v_k} \cdot e\boldsymbol{E}) \tag{2.10}$$

Then, following (2.4), the current density can be presented as [4,5]

$$\boldsymbol{J} = \sigma \mathbf{E} \tag{2.4'}$$

where conductivity σ is proportional to the relaxation time τ. Particularly, within the frames of the free-electron model it follows [5]

$$\sigma = n_e e^2 \frac{\tau}{m} \tag{2.11}$$

where n_e is the concentration of charge carriers and m is the electron mass. Resistivity R is defined as

$$R = \sigma^{-1} \tag{2.12}$$

If conduction electrons are scattered at different types of the ideal lattice imperfections (e.g. thermal vibrations of the lattice, point defects, impurities), then the effects of different type perturbations are summarized and the total resistivity R_tot can be

presented as a sum of corresponding ingredients. In the case of MH_{2+c} compounds conduction electrons are scattered on the thermal vibrations of metal lattice, denoted as R_{therm}(metal), on the optical vibrations of H_T- and H_O-atoms, denoted respectively as $R_{therm}(H_T)$ and $R_{thermt}(H_O)$, and on the disordered configurations of H_O-atoms, denoted as R_H. Thus, the total resistivity of MH_{2+c} compounds $R_{tot}(MH_{2+c})$ can be presented as

$$R_{tot}(MH_{2+c}) = R_{therm}(metal) + R_{therm}(H_T) \\ + R_{therm}(H_O) + R_H \quad (2.13)$$

We concentrate our attention on the R_H term. Let us consider the specific details of perturbation caused by the spatial redistribution of H_O-atoms. Perturbation potential $V'(\mathbf{r})$ acting on the conduction electron located in the point $\mathbf{r}$ is usually presented as a difference between the potentials caused by the real configuration of the perturbing centers in the lattice and caused by their averaged equilibrium distribution [4–6]. In the case of ordering $N_H = cN$ particles (H_O-atoms) perturbing the electron states in the conduction band created by the N trivalent metal atoms (and depleted by 2N H_T-atoms and cN H_O-atoms) we can write:

$$V'(\mathbf{r}) = \sum_i^{N_H} V^H(\mathbf{r} - \mathbf{R}_i) - \sum_i^{N} V^H(\mathbf{r} - \mathbf{R}_i)n(\mathbf{R}_i) \quad (2.14)$$

where the first sum is over the interstitial sites really occupied by H_O-atoms and the second sum includes all octahedral interstitial positions occupied in equilibrium by the hydrogen atoms with the probability $n(\mathbf{R}_i)$. In both sums $V^H(\mathbf{r} - \mathbf{R}_i)$ is the potential created at the point $\mathbf{r}$ by the hydrogen atom located in point $\mathbf{R}_i$.

The second sum in (2.14) can be presented as

$$\sum_i^{N} V^H(\mathbf{r} - \mathbf{R}_i)n(\mathbf{R}_i) = \sum_i^{N_0}\sum_p V^H(\mathbf{r} - (\mathbf{R}_i + \mathbf{R}_p))n(\mathbf{R}_p) \quad (2.15a)$$

where N_0 is the number of new unit cells in the ordered configuration, $p = 1, \ldots, 8$ numbers the nonequivalent positions within each unit cell (radius-vectors $\mathbf{R}_p$ are shown in Fig. 1), and $n(\mathbf{R}_p)$ are the equilibrium occupation numbers which are equal to n_1, n_2 or n_3, respectively.

For the first sum we have to assume that

$$\sum_i^{N_H} V^H(\mathbf{r} - \mathbf{R}_i) = \sum_i^{N_0}\sum_p V(\mathbf{r} - (\mathbf{R}_i + \mathbf{R}_p)) \quad (2.15b)$$

where p runs over eight nonequivalent positions within each unit cell, and $V(\mathbf{r} - (\mathbf{R}_i + \mathbf{R}_p))$ equals $V^H(\mathbf{r} - (\mathbf{R}_i + \mathbf{R}_p))$ or 0, depending on the real spatial distribution of H_O-atoms.

On calculating with the Bloch wave functions the square of the modulus of the corresponding matrix elements (induced by the perturbing potentials (2.13)–(2.15)), and averaging in a standard way over the set of the enlarged unit cells [4–6], we obtain

$$\left(\frac{\partial f_{\mathbf{k}}}{\partial t}\right)_{scatter} \sim \left(\frac{1}{\tau}\right) \sim \sum_l \nu_l n_l(1 - n_l), \quad l = 1, 2, 3 \quad (2.16)$$

Here, ν_l are the portions of octa-positions where the distribution function $n(\mathbf{R}_i)$ equals, respectively, to n_1, n_2 or n_3, defined by (1.3) ($\nu_1 = \nu_2 = 0.25$, $\nu_3 = 0.5$).

Integrating (2.16) over the $\mathbf{k}$-space and using relations (2.10)–(2.12), we can present the hydrogen-dependent part of the total resistivity by a *qualitative expression*:

$$R_H(c) = A\left(\frac{1}{n_e(c)}\right)\sum_l \nu_l n_l(T)(1 - n_l(T)), \quad l = 1, 2, 3 \quad (2.17)$$

Here, A is a factor depending on the conduction electron energy gradient integrated over the Fermi surface and in a wide concentration range is very weakly dependent on the temperature, hydrogen concentration and order parameters, while $n_e(c)$ is the real concentration of conduction electrons. The latter is hydrogen concentration dependent and decreases on filling the octa-positions by H-atoms:

$$n_e(c) \sim (1-c) \quad (2.18)$$

From (2.17) it follows that the temperature dependence of the hydrogen ordering induced part of resistivity R_H is determined mainly by temperature dependences of equilibrium occupation numbers $n_1(T)$, $n_2(T)$, and $n_3(T)$.

Let us determine now the equilibrium values of the sites occupation numbers n_l. The free energy function of the ordering subsystem $F(\eta_1, \eta_2, c, T)$ is defined in the restricted part of (η_1, η_2)-plane. The restrictions on the possible values of order parameters η_1 and η_2 are imposed by the conditions which have to satisfy the sites occupation numbers, that is $0 \leq n_1 \leq 1$, $0 \leq n_2 \leq 1$, $0 \leq n_3 \leq 1$. Coming from linear relations (1.3) and the condition of positive values of order parameters, the physically meaningful part of (η_1, η_2)-plane, containing all allowed values of η_1 and η_2 parameters forms a polygon, surrounded by η_1 and η_2 axes and the boundary lines $n_2 = 0$, $n_1 = 1$, $n_3 = 0$ (or $n_3 = 1$, if concentration $c > 0.5$). The form of this polygon (denoted hereafter as "region P") depends only on the concentration of H_O-atoms c (see Figs. 2(a) and 3(a)). The disordered state is located in the zero-point of coordinate axes, while the low-temperature limiting ordered state is associated with one of the corner points, b- or d-points. The ordering process described by the sequence of equilibrium values of order parameters is presented by a trajectory relating the zero-point with the corresponding corner point (for details see e.g. in [7,8]). It has to be noted that $\left[\frac{d\eta_1(T)}{dT}\right]$ and $\left[\frac{d\eta_2(T)}{dT}\right]$ along the trajectory are, generally, negative.

At the given values of concentration c and temperature T in equilibrium will be the ordered configurations characterized by the values of η_1 and η_2 parameters, which provide the absolute minimum of the free energy function $F(\eta_1, \eta_2, c, T)$.

The extrema of $F(\eta_1, \eta_2, c, T)$ are determined by the equations [3,7,8]:

$$\ln\left[\frac{n_1 n_2(1 - n_3)^2}{((1 - n_1)(1 - n_2)n_3^2)}\right] = -\frac{V_1}{kT} \quad (2.19a)$$

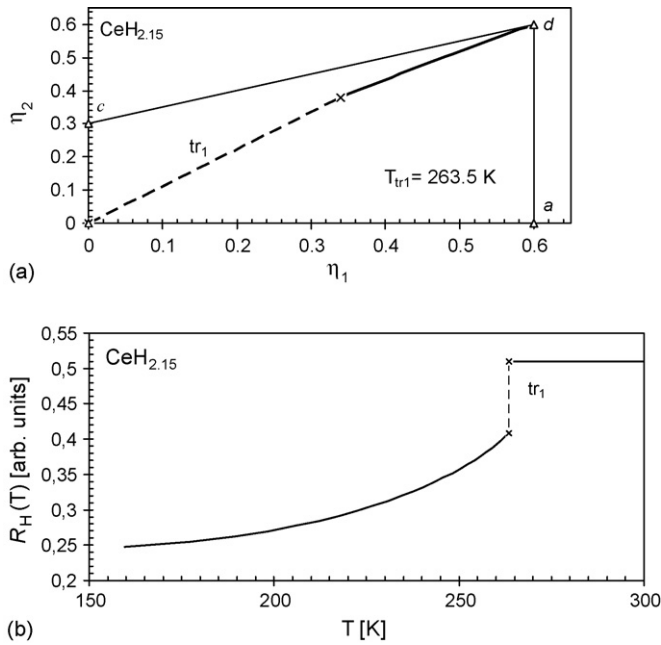Fig. 2. CeH$_{2.15}$; T_{tr} = 263.5 K. (a) Trajectory of the ordering process; (b) temperature dependence of the hydrogen redistribution induced resistivity (2.17). In (a) solid line indicates the sequence of equilibrium states and the dashed line the discontinuous disorder–order transition.

$$\ln\left[\frac{n_1(1-n_2)}{((1-n_1)n_2)}\right] = -\frac{V_2}{kT} \qquad (2.19b)$$

where V_1 and V_2 are the energy constants (different for different rare-earths [3]), while the occupation numbers n_l are determined by (1.3). The absolute minimum of the free-energy function corresponds to its lowest extremum.

3. Results of calculations

In this section, results of calculations of equilibrium ordering processes in compounds LaH$_{2+c}$ and CeH$_{2+c}$, and of the corresponding temperature dependences of hydrogen redistribution induced part of resistivity $R_H(T)$ are presented.

Calculations of $R_H(T)$ of MH$_{2+c}$ compounds were performed basing on expression (2.17). The needed temperature dependent equilibrium values of occupation numbers n_1, n_2, and n_3 were determined using relation (1.3) and Eq. (2.19).

The development of the equilibrium ordered states can be presented as a set of temperature dependences of occupation numbers $\{n_1(T), n_2(T), n_3(T)\}$(Fig. 4(a)), or as trajectories of the ordering processes on the (η_1, η_2)-plane (Figs. 2(a), 3(a) and (b)).

In the CeH$_{2+c}$ compounds the high-temperature equilibrium state ($\eta_1 = 0$, $\eta_2 = 0$) at lowering temperatures transforms in the ($\eta_1 \neq 0$, $\eta_2 \neq 0$) state. At $c < 0.35$ this transition is discontinuous and it becomes continuous for concentrations $(0.35 < c < 0.65)$ [7]. The second, low-temperature order–order discontinuous transition arise only if $c > 0.35$ [7]. It is associated with the transfer of the free-energy absolute minimum from one local minimum to another (*bd*-transition in Fig. 3(a) and (b)) [7]. Typical trajectories of ordering processes for $c < 0.35$ and $c > 0.35$ are shown in Figs. 2(a) and 3(a), respec-
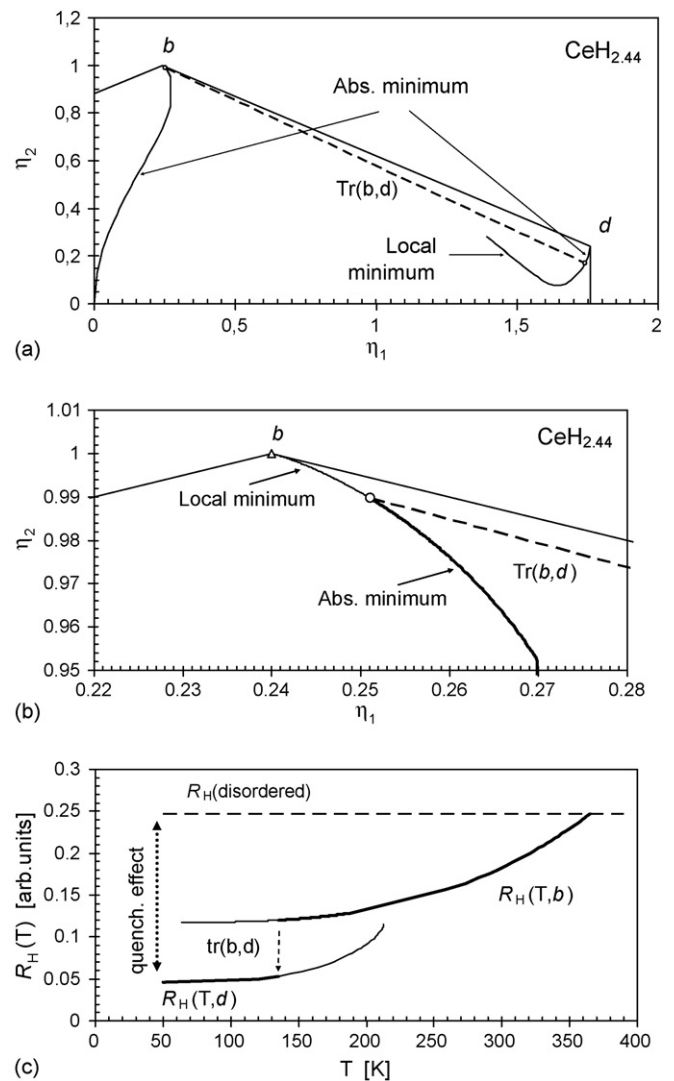

Fig. 3. CeH$_{2.44}$; T_{tr1} = 365 K, T_{tr2} = 135 K. (a) Trajectory of the ordering process; (b) details of the equilibrium trajectory; (c) temperature dependence of the hydrogen redistribution induced resistivity (2.17). In (a) and (b), solid lines indicate the sequences of equilibrium states, fine lines indicate the sequences of metastable states, and the dashed line the order–order *bd*-transition.

tively. Their influence on the resistivity $R_H(T)$ is illustrated by Figs. 2(b) and 3(c).

In case of LaH$_{2+c}$ compounds, the high-temperature disordered state of H$_O$-atoms ($\eta_1 = 0$, $\eta_2 = 0$) at lowering temperatures transforms subsequently in two different equilibrium states: ($\eta_1 \neq 0$, $\eta_2 = 0$) and ($\eta_1 \neq 0$, $\eta_2 \neq 0$), undergoing continuous disorder–order and order–order transitions, respectively. An example of development of the ordering process is shown in Fig. 4(a). This sequence of states is realized practically at all concentrations, $0.15 < c < 0.9$, except the region $c \approx 0.5$. The corresponding phase diagram can be seen in Fig. 4(c) [3,8], where besides the disorder–order and order–order transition temperature curves, are indicated the experimental transition temperature points cited in [8].

The reflections of ordering processes in the $R_H(T)$ curves are shown in Fig. 4(b). Concentration variations of the disorder–order and order–order transition temperatures, T_{tr1} and
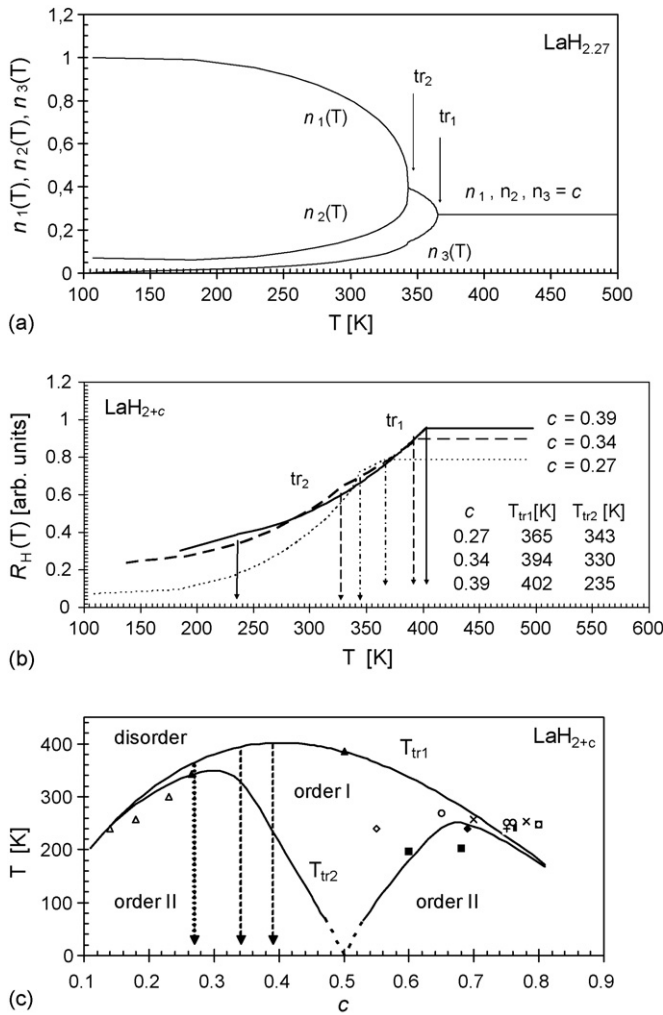
Fig. 4. LaH$_{2+c}$ compounds. (a) Temperature dependence of the sites occupation numbers $n_l(T)$. $c = 0.27$; (b) resistivity curves calculated following Eq. (2.17) at different concentrations; (c) phase diagram of LaH$_{2+c}$ [3,8].

T_{tr2}, are explained in Fig. 4(c), where the considered concentrations are indicated by dashed flashes.

In Fig. 5 concentration dependent residual resistivities associated with the low-temperature disordered (quenched) and ordered (relaxed) configurations of H$_O$-atoms are shown (dashed
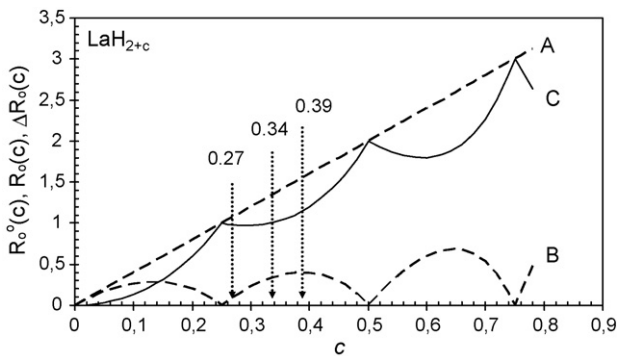

Fig. 5. Residual resistivity as a function of concentration in the disordered (quenched) state (A) and in the completely relaxed (equilibrium) state (B). Solid curve C – concentration dependence of the maximal possible quenching effect. Dashed flashes indicate the compounds considered in Fig. 4(b) and (c).

curves A and B, respectively). The difference between these two dependences, representing the maximal possible quenching effect (see below) is given by the solid curve C. Dashed flashes indicate compounds considered in Fig. 4(b) and (c).

It has to be noted that the equilibrium values of order parameters increase, as a rule, when temperature decreases, that is $\left(\frac{d\eta_1}{dT}\right) < 0$ and $\left(\frac{d\eta_2}{dT}\right) < 0$ (see Fig. 2(a) and the high-temperature part of Fig. 3(a)). But, as it follows from calculations of equilibrium ordered states [7], in some cases the ordering processes may contain the regions where one of the parameters changes the temperature derivative's sign. Such phenomenon is shown in details in Fig. 3(b) and will be discussed briefly below.

4. Discussion

Expression (2.17) is obtained in a traditional way based on the first-order perturbation theory describing the scattering of conduction electrons on point scatterers (H$_O$-atoms, in our case). The adequacy of this approximation is not established yet and, consequently, expression (2.17) can be treated as a qualitative relation only. Nevertheless, it can provide some meaningful physical results.

First of all, introducing in (2.17) expressions (1.3) we can represent it as

$$R_H(c, T) = R_H(\eta_1, \eta_2) = A \left(\frac{1}{n_e(c)} \right)$$
$$\times \left[c(1 - c) - \gamma^2 (\eta_1^2(T) + 2\eta_2^2(T)) \right] \quad (2.17')$$

where $\eta_1(T)$ and $\eta_2(T)$ are equilibrium values of LRO parameters.

From (2.17') it follows that at the increasing of order in the hydrogen subsystem, the resistivity $R_H(c, T)$ gradually reduces. Due to this expression it is obvious as well that the discontinuities of $\eta_1(T)$ and $\eta_2(T)$ functions (in the phase transition points) will be revealed by corresponding discontinuities in the resistivity. Such anomalies of $R_H(T)$ curves are characteristic for CeH$_{2+c}$ compounds (see Figs. 2(b) and 3(c)).

In LaH$_{2+c}$ hydrides the disorder–order and order–order transitions are continuous at concentrations $0.15 < c < 1$ [8]. From Fig. 4(a) and (b) it follows that the phase transition points are associated with the kink-like anomalies of the smooth $R_H(T)$ curves. These kinks are induced by the discontinuities of derivatives: $\left(\frac{d\eta_1(T)}{dT}\right)$ at $T = T_{tr1}$ and $\left(\frac{d\eta_2(T)}{dT}\right)$ at $T = T_{tr2}$.

Measurability of these anomalies of $R_H(T)$ curves has to be considered.

It was mentioned already (see relation (2.13)) that the resistivity $R_H(T)$ is a part of the total resistivity of MH$_{2+c}$ compound, R_{tot}(MH$_{2+c}$), the main contributions to which come from the acoustic oscillations of the metal lattice, R_{therm}(metal). A remarkable role is played by the optical oscillations of H$_T$-atoms, R_{therm} (H$_T$), as it was shown [9] in the case of MH$_2$ dihydrides. Addition of optically oscillating H$_O$-atoms will increase the "thermal-component" of the total resistivity. In these conditions the anomalies of $R_H(T)$ curves associated with the spatial redistribution of H$_O$-atoms (discontinuities and/or kinks) will

be masked by the temperature-dependent contributions of other terms in (2.13).

Region	limits	$\gamma\eta_1(d)$	$\gamma\eta_2(d)$	$q_d(c)$	
I	$0 \le c \le 0.25$	c	c	$\dfrac{3c^2}{(1-c)}$	
II	$0.25 \le c \le 0.50$	c	$0.5 - c$	$\dfrac{(3c^2 + 0.5 - 2c)}{(1-c)}$	(2.25b)
III	$0.50 \le c \le 0.75$	$c - 1$	$c - 0.5$	$\dfrac{(3c^2 + 1.5 - 4c)}{(1-c)}$	
IV	$0.75 \le c \le 1.0$	$c - 1$	$1 - c$	$3(1 - c)$	

Nevertheless, the hydrogen redistribution processes in the MH$_{2+c}$ compounds can be registered directly in the measurements of quenching effects.

The maximal possible quenching effect for a given c $\Delta R_0(c)$ can be determined as

$$\Delta R_0(c) = R_0^0(c) - R_0(c) \tag{2.20}$$

where $R_0^0(c)$ and $R_0(c)$ are residual resistivities for the completely disordered and maximally ordered states, respectively. We have in all cases

$$R_0^0(c) = A\left(\frac{1}{n_e(c)}\right)c(1-c) \tag{2.21a}$$

$$R_0(c) = A\left(\frac{1}{n_e(c)}\right)\sum_l \nu_l n_l(j)(1 - n_l(j)) \quad l = 1, 2, 3 \tag{2.21b}$$

In (2.21b) j denotes the corner points (b and d points) of the "region P".

Basing on relations (2.17') and (2.21a), expression (2.20) can be presented as

$$\Delta R_0(c) = A\left(\frac{1}{n_e(c)}\right)\gamma^2[\eta_1^2(j) + 2\eta_2^2(j)] \tag{2.22}$$

or

$$\Delta R_0(c) = A'q(c) \tag{2.23}$$

where A' is independent of the hydrogen concentration c,

$$A' \equiv A\left[\left(\frac{1-c}{n_e(c)}\right)\right] \tag{2.24a}$$

$$q(c) = \gamma^2[\eta_1^2(j) + 2\eta_2^2(j)](1-c)^{-1} \tag{2.24b}$$

To obtain an algebraic expression of $\Delta R_0(c)$ we have to substitute in (2.24b) the coordinates of the corner points of the "region P" ($\eta_1(b), \eta_2(b)$), or ($\eta_1(d), \eta_2(d)$).

In the whole concentration range $0 \le c \le 1$ coordinates of the b-point are: $\gamma\eta_1(b) = 0.5 - c$ and $\gamma\eta_2(b) = 0.25$ [10] giving for $0 < c < 1$

$$q_b(c) = \frac{[0.375 - c(1-c)]}{(1-c)} \tag{2.25a}$$

The coordinates of the d corner point are known [10] to be different in the different concentration regions of the whole con-

centration range $0 \le c \le 1$. Basing on [10] and (2.24b) we can obtain the following results for $0 < c < 1$.

In the case of LaH$_{2+c}$ compounds, where within the main range of concentrations ($0.1 < c < 0.9$) the limiting low-temperature equilibrium states are associated with the corner point d, we shall have

$$q(c)[LaH_{2+c}] = q_d(c) \tag{2.26}$$

As it was mentioned above, dependences (2.21) for the disordered and ordered states are shown in Fig. 5 by the dashed lines (A and B, respectively), while the concentration dependence of the possible maximal quenching effect determined by (2.26) and (2.25b) is given in the same figure by a solid line (curve C).

In the compounds CeH$_{2+c}$ the low-temperature limiting state is located for some c in the corner b, and for the others in the corner d (for details see [7]). It follows that $q(c)$ [CeH$_{2+c}$] is presented correspondingly by (2.25a) or by (2.25b).

It has to be noted that quenching effects in the ordering rare-earth dihydrides were investigated experimentally more than a decade ago (see e.g. [11]).

Some words concerning the peculiar regions of the ordering process, such as the "turning point" shown in Fig. 3(b), where one of the order parameters changes its temperature derivative sign. In the corresponding part of the $R_H(T)$ dependence shown in Fig. 3(c) no anomalies can be seen. It means that at lowering temperature in this trajectory point the second order parameter increases so significantly that the temperature derivative sign of the total expression (2.17') remains unchanged.

5. Conclusions

1. The ordering of H$_O$-atoms reduces the resistivity of RH$_{2+c}$ compounds and provides the existence of observable quenching effects. The magnitude of these effects depends on the hydrogen concentration.
2. Phase transitions included in the ordering processes are reflected as kinks or discontinuities of the smooth $R_H(T)$ dependences. The order of the given phase transition determines the type of the corresponding anomaly: it is a kink for a second-order transition and a discontinuity for the transition of the first-order.
3. Dependence of the resistivity R_H upon the order parameters η_1 and η_2 (2.17') explains the inadequacy of resistivity measurements to register such details of the ordering process, as the mentioned above "turning points".

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