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Hydrogen Ordering in Hexagonal Intermetallic AB_5 Type Compounds

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Dedicated to Professor Jerzy Janik on the occasion of his 80th birthday

Intermetallic compounds AB_5 type (A = rare-earth atoms, B = transition metal) are known to store reversibly large amounts of hydrogen and as that are discussed in this work. It was shown that the alloy cycling stability can be significantly improved by employing the so-called non-stoichiometric compounds AB_{5+x} and that is why analysis of change of structure turned out to be interesting. A tendency for ordering of hydrogen atoms is one of the most intriguing problems for the unsaturated hydrides. The symmetry analysis method in the frame of the theory of space group and their representation gives opportunity to find all possible transformations of the parent structure. In this work symmetry analysis method was applied for AB_{5+x} structure type ($P6/mmm$ parent symmetry space group). There were investigated all possible ordering types and accompanying atom displacements in positions 1a, 2c, 3g (fully occupied in stoichiometric compounds AB_5), in positions 2e, 6l (where atom B could appear in non-stoichiometric compounds) and also 4h, 6m, 6k, 12n, 12o, which could be partly occupied by hydrogen as a result of hydrides. An analysis was carried out of all possible structures of lower symmetry, following from $P6/mmm$ for $\boldsymbol{k} = (0, 0, 0)$. Also the way of getting the structure described by the $P6_3mc$ space group with double cell along the z-axis $\boldsymbol{k} = (0, 0, 0.5)$, as it is suggested in the work of Latroche et al. is discussed by the symmetry analysis. The analysis was obtained by computer program MODY. The program calculates the so-called basis vectors of irreducible representations of a given symmetry group, which can be used for calculation of possible ordering modes.

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1. Introduction to the symmetry analysis

The symmetry analysis based on the theory of groups and representations was at first introduced by Bertaut [1, 2] in the description of magnetic ordering in crystals. He obtained the symmetry-adapted ordering modes, derived from

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the representation analysis by calculation of the basis vectors of irreducible representations (IRs). Later that line of analysis has been developed by many other theoreticians, like Izyumov [3] and others.

The superstructure as the ordering of some "property" of the initial crystal structure may occur as the result of phase transition under the action of temperature, magnetic field, or pressure. Each of the properties of the crystal localised on atom sites may be described by a Wannier function $\boldsymbol{S}$ defined on some set of equivalent positions. It may be a function type scalar — describing for example change of probability of sites occupation, a vector-polar type describing for example displacements of atoms from equilibrium positions, an axial-type describing for example ordering of magnetic moments, or a tensor-type describing for example ordering of quadrupole momentum. The presentation of this function in the usually used frame of coordinates related to the crystallographic system takes advantage of translation symmetry only. The other symmetry relations are lost in this description and as a consequence the description of many crystal properties is not as simple as possible. The presentation of model structures in the frame of basic vectors of irreducible representations of the initial symmetry group $(BV)\boldsymbol{\Psi}_{\lambda}^{k_l,\nu}$, instead of that in the frame of crystallographic system (x, y, z), is the best matching to the symmetry of the problem and it provides the simplest (requiring the lowest number of independent parameters) form of the structure description

$$\boldsymbol{S} = \sum_{l,\nu\lambda} c_{\lambda}^{k_l,\nu} \boldsymbol{\Psi}_{\lambda}^{k_l,\nu} \tag{1}$$

(l — number of $\boldsymbol{k}$ vectors, ν — number of IRs, λ — number of dimensions of ν's IR). The symmetry group $G(\boldsymbol{k})$ of the $\boldsymbol{k}$ vectors is a subgroup of the space group G. From this fact follows that the set of equivalent positions in the group G, the so-called orbit in G, may split into independent sets of equivalent positions in $G(\boldsymbol{k})$. Thus, one orbit in the group G can lead to two or more orbits in the $G(\boldsymbol{k})$ subgroup. The symmetry considerations are able to indicate the relations between the old sets of equivalent positions (in the parent group) and the new sets of equivalent positions (in resulting subgroup).

The form of the basis vectors and the information which of the representations take part in the phase transition under consideration are directly given by the theory of groups and representations. In this work we use the computer programme MODY [4] (there are also another computer programs [5–8]), which is based on the theory of groups and representations, to calculate this information. It is important to note that the basis vectors have the same translational properties as the Bloch functions. Therefore, the basis vectors may be defined *on positions of given orbit* in the elementary cell of the crystal as well as in the elementary cell translated by a lattice vector $\boldsymbol{t}$, which just corresponds to a multiplication by $\mathrm{e}^{\mathrm{i}k_1 t}$. Not all from the possible $\mathrm{c}_{\lambda}^{k_l,\nu}$ are allowed, because the parameters should be selected in such way that the resulting magnetic moments related to all atoms have real values. This condition influences the set of equations which the $c_{\lambda}^{k_l,\nu}$ have

to satisfy and as a result the number of independent free parameters is reduced and strictly determined. After such operation the final model contains clearly defined minimum number of free parameters and presents strictly defined relations between localised on different crystal sites quantities describing considered property. Each choice of these free parameters uniquely determines one of the possible models of new structure that may be realised after the phase transition.

The coefficients $c_\lambda^{k_l,\nu}$ form also good order parameters of phase transitions. The symmetry analysis allows us to find the symmetry group of the new structure, followed by a given representation, active in the phase transition. Basic vectors $\mathbf{\Psi}_\lambda^{k_l,\nu}$ transform under the action of elements of the parent symmetry group by the set of matrices of τ_ν representation. Because the coefficients $c_\lambda^{k_l,\nu}$ of the linear combination are the components of the analysed property in the frame of $\mathbf{\Psi}_\lambda^{k_l,\nu}$ vectors, they transform according to τ_ν^{-1} matrices. These symmetry elements which leave the set of components $c_\lambda^{k_l,\nu}$ invariant belong to the structure symmetry group after the phase transition.

The choice of representation τ_ν and the coefficients $c_\lambda^{k_l,\nu}$ uniquely determines the symmetry of the structure, independently of the kind of the property taken into account. The type of phase transition and the property under consideration is included in the form of basic vectors!

2. Symmetry analysis of order–disorder phase transitions and associated displacements of atoms

One of the cases of symmetry analysis is encountered for scalar physical quantities, represented by occupation probability of local ion sites in a given crystal structure. An essential physical assumption about the parent, high symmetry phase, states that in the high-symmetry phase the occupation probability P on all allowed interstitial sites should be the same. The actual value depends on the hydrogen concentration and the number of occupied symmetry equivalent sites.

The calculated values, describing the ordering of H atoms, always denote the change ΔP of the site occupation probability P from the equilibrium values mentioned above. Each subset of symmetry equivalent sites, called an orbit in the given subgroup, is occupied with the same probability P'. If $P' = 1$ the subgroup orbit is fully occupied. $P' = 0$ means that the subgroup orbit is empty after the ordering. The condition $0 < P' < 1$ means that the hydrogen diffusion takes place within the given orbit. There is one more physical assumption: the sum of ΔP over all sites of the initial symmetry equivalent set has to be zero, which actually represents a kind of "mass conservation law", and appears in the situation, when no diffusion of H atoms between different interstitial parent structure orbits is observed.

The relations between the obtained probability changes on different orbits of the new structure do not depend also on the total concentration of hydrogen atoms in the structure. The hydrogen concentration has the influence on the

quantity of possible C_λ parameters and a possibility of complete occupation of given subgroup orbits. Because of the strong coupling between the site position and site occupation probabilities there are often observed atomic displacements, which accompany the occupation probability changes. These atomic displacements can also be calculated by symmetry analysis, as the IR active in both transitions must be the same by the requirements of symmetry consistency. This method had been applied to the discussion of the structural changes followed by the hydrogenation of cubic intermetallic Laves phases [9, 10].

3. AB_5 structure details

The parent AB_5 structure (presented in Fig. 1) belongs to hexagonal system with symmetry space group $P6/mmm$ (191). Possible ordering type and accompanying atom displacements in positions A — 1a, B — 2c, 3g (fully occupied in stoichiometric compounds AB_5), in positions 2e, 6l (where atom B could appear in non-stoichiometric compounds AB_{5+x}) and also 4h, 6m, 6k, 12n, 12o (which could be partly occupied by hydrogen as a result of hydrides) have been investigated. Analysis of all possible structures on invariable lattice ($\boldsymbol{k}$ = 0,0,0) was carried out.

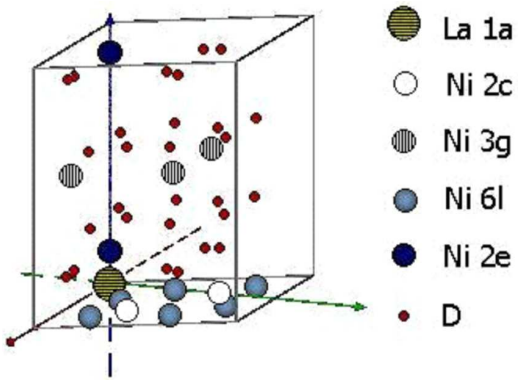

Fig. 1. The parent AB_5 structure.

4. Results of the symmetry analysis

There are analysed all possible transformations of the parent structure with symmetry space group $P6/mmm$ leading to the structures of lower symmetry, for $\boldsymbol{k} = (0, 0, 0)$. All possible active representations of invariable lattice ($\boldsymbol{k} = 0, 0, 0$) for different positions and for different types of orderings (modes) are shown in Table I. Types of modes are signed in this table as: S — scalar for describing change of probability of sites occupation; P — polar for describing displacement of atoms from equilibrium positions in high symmetry structure; A — axial for describing ordering of magnetic moments.

TABLE I

Active representations of invariable lattice ($\boldsymbol{k}$ = 0,0,0) for different positions and for different types of orderings (modes).

Position	Type of mode	Representation											
		dimension 1								dimension 2			
		τ_1	τ_2	τ_3	τ_4	τ_5	τ_6	τ_7	τ_8	τ_9	τ_{10}	τ_{11}	τ_{12}
1a	S	+	−	−	−	−	−	−	−	−	−	−	−
	P	−	−	−	+	−	−	−	−	−	+	−	−
	A	−	−	+	−	−	−	−	−	+	−	−	−
2c	S	+	−	−	−	−	−	−	+	−	−	−	−
	P	−	−	−	+	+	−	−	−	−	+	+	−
	A	−	−	+	−	−	+	−	−	+	−	−	+
3g	S	+	−	−	−	−	−	−	−	−	−	+	−
	P	−	−	−	+	−	+	−	+	−	+	−	+
	A	−	−	+	−	+	−	+	−	+	−	+	−
6l	S	+	−	−	−	−	−	−	+	−	+	+	−
	P	+	−	+	+	+	+	−	+	+	+	+	+
	A	−	+	+	+	+	+	+	−	+	+	+	+
2e	S	+	−	−	+	−	−	−	−	−	−	−	−
	P	+	−	−	+	−	−	−	−	+	+	−	−
	A	−	+	+	−	−	−	−	−	+	+	−	−
4h	S	+	−	−	+	+	−	−	+	−	−	−	−
	P	+	−	−	+	+	−	−	+	+	+	+	+
	A	−	+	+	−	−	+	+	−	+	+	+	+
6m	S	+	−	−	−	−	−	−	+	−	+	+	−
	P	+	−	+	+	+	+	−	+	+	+	+	+
	A	−	+	+	+	+	+	+	−	+	+	+	+
12n	S	+	−	−	+	−	+	+	−	+	+	+	+
	P	+	+	+	+	+	+	+	+	+	+	+	+
	A	+	+	+	+	+	+	+	+	+	+	+	+
12o	S	+	−	−	+	+	−	−	+	+	+	+	+
	P	+	+	+	+	+	+	+	+	+	+	+	+
	A	+	+	+	+	+	+	+	+	+	+	+	+

The symmetry analysis gives opportunity to calculate subgroups of the parent $P6/mmm$ group following from active IRs and ordering parameters $c_\lambda^{k_l,\nu}$. The result of the analysis for $\boldsymbol{k} = (0,0,0)$ is shown in Table II.

In such structures of lower symmetry the hydrogen interstitial positions belonging to one orbit in the high symmetry group split into suborbits with differ-

TABLE II

Subgroups of $P6/mmm$ group following from active IRs with $\boldsymbol{k} = (0,0,0)$ and ordering parameters $c_\lambda^{kl,\nu}$.

Representation	Parameters $c_\lambda^{kl,\nu}$	Destination groups	
τ_1	c	$P6/mmm$	(191)
τ_2	c	$P622$	(177)
τ_3	c	$P6/m$	(175)
τ_4	c	$P6mm$	(183)
τ_5	c	$P\text{-}3m1$	(164)
τ_6	c	$P\text{-}62m$	(189)
τ_7	c	$P\text{-}31m$	(162)
τ_8	c	$P\text{-}6m2$	(187)
τ_9	(c,c)	$C2/m$	(12)
	$(c,-c)$	-‖-	
	$(c,c\mathrm{e}^{\mathrm{i}\pi/3})$	-‖-	
	(c,c_2)	$P\text{-}1$	(2)
τ_{10}	(c,c)	$Amm2$	(38)
	$(c,-c)$	-‖-	
	$(c,\pm c\mathrm{e}^{\pm\mathrm{i}\pi/3})$	-‖-	
	(c_1,c_2)	Pm	(6)
τ_{11}	(c,c)	$Cmmm$	(65)
	$(c,-c)$	$P2/m$	(10)
	$(c,c\mathrm{e}^{\mathrm{i}\pi/3})$	-‖-	
	(c_1,c_2)	-‖-	
τ_{12}	(c,c)	$C222$	(21)
	$(c,-c)$	$Cmm2$	(35)
	$(c,c\mathrm{e}^{\mathrm{i}\pi/3})$	-‖-	
	(c_1,c_2)	$P2$	(3)

entiated local symmetries and abundances. If one of such sublattices has different hydrogen site occupation P' than the others, we receive effect of hydrogen ordering.

The possible site occupation changes ΔP, calculated in the frame of the symmetry analysis method for all possible cases (except monoclinic ones) following from parent group $P6/mmm$ (191), are quoted in Table III. The τ_2 and τ_3 IRs are active in the S-type phase transitions for none positions (see Table I), thus they do not appear in the table. In Table III the splittings of $P6/mmm$ equivalent positions to the corresponding subgroup orbits are also given. Calculated ΔP quantities correspond to the splitting on suborbits. At each position belonging to given suborbit ΔP is the same, thus only the representatives of the subgroup orbits are noted in the table.

TABLE III

The possible site occupation changes ΔP. The splitting of $P6/mmm$ equivalent positions to the corresponding subgroup orbits.

Destination group	Wyckoff position in $P6/mmm$	representatives of Wyckoff position in destination group		ΔP
τ_1	1a	1a	(0, 0, 0)	C_a
$P6/mmm$ (191)	2c	2c	(1/3, 2/3, 0)	C_c
	2e	2e	(0, 0, z)	C_e
	3g	3g	(1/2, 0, 1/2)	C_g
	6l	6l	(x, $2x$, 0)	C_l
	4h	4h	(1/3, 2/3, z)	C_h
	6m	6m	(x, $2x$, 1/2)	C_m
	12n	12n	(x, 0, z)	C_n
	12o	12o	(x, $2x$, z)	C_o
τ_4	2e	$1a_1$	(0, 0, z)	C_a
$P6mm$ (183)		$1a_2$	(0, 0, $-z$)	$-C_a$
	4h	$2b_1$	(1/3, 2/3, z)	C_h
		$2b_2$	(1/3, 2/3, $-z$)	$-C_h$
	12n	$6d_1$	(x, 0, z)	C_n
		$6d_2$	(x, 0, $-z$)	$-C_n$
	12o	$6e_1$	(x, $2x$, z)	C_o
		$6e_2$	(x, $2x$, $-z$)	$-C_o$
τ_5	4h	$2d_1$	(1/3, 2/3, z)	C_h
P-3m1 (164)		$2d_2$	(1/3, 2/3, $-z$)	$-C_h$
	12o	$6i_1$	(x, $2x$, z)	C_o
		$6i_2$	($-x$, x, z)	$-C_o$
τ_6	12n	$6i_1$	(x, 0, z)	C_n
P-62m (189)		$6i_2$	(x, x, z)	$-C_n$
τ_7	12n	$6k_1$	(x, 0, z)	C_n
P-31m (162)		$6k_2$	(x, x, z)	$-C_n$
τ_8	2c	1c	(1/3, 2/3, 0)	C_c
P-6m2 (187)		1e	(2/3, 1/3, 0)	$-C_c$
	6l	$3j_1$	(x, $2x$, 0)	C_l
		$3j_2$	($-x$, x, 0)	$-C_l$
	4h	2h	(1/3, 2/3, z)	C_h
		2i	(2/3, 1/3, z)	$-C_h$
	6m	$3k_1$	(x, $2x$, 1/2)	C_m
		$3k_2$	($-x$, x, 1/2)	$-C_m$
	12o	$6n_1$	(x, $2x$, z)	C_o
		$6n_2$	($-x$, x, z)	$-C_o$

TABLE III (cont.)

τ_9 (c_1, c_2)		12n	$2e_1$	$(x,\ 0,\ z)$	C_{n1}
P-1	(2)		$2e_2$	$(x,\ x,\ z)$	C_{n2}
			$2e_3$	$(0,\ x,\ z)$	C_{n3}
			$2e_4$	$(-x,\ 0,\ z)$	$-C_{n1}$
			$2e_5$	$(-x,\ -x,\ z)$	$-C_{n2}$
			$2e_6$	$(0,\ -x,\ z)$	$-C_{n3}$
		12o	$2e_1$	$(x,\ 2x,\ z)$	C_{o1}
			$2e_2$	$(-x,\ x,\ z)$	C_{o2}
			$2e_3$	$(-2x,\ -x,\ z)$	C_{o3}
			$2e_4$	$(-x,\ -2x,\ z)$	$-C_{o1}$
			$2e_5$	$(x,\ -x,\ z)$	$-C_{o2}$
			$2e_6$	$(2x,\ x,\ z)$	$-C_{o3}$
$\tau_{10}(c, \pm c e^{\pm i\pi/3})$		6m $(x,2x,1/2)$	$2b_1$	$(1/2,\ 0,\ x)$	$2C_m$
$Amm2$	(38)	$(-x,\ x,\ 1/2)$	$4e_1$	$(1/2,-3x/2,\ x/2)$	C_m
		$(-2x,\ -x,1/2)$	$4e_2$	$(1/2,-3x/2,-x/2)$	$-C_m$
		$(-x,-2x,1/2)$	$2b_2$	$(1/2,\ 0,-x)$	$-2C_m$
		6l $(x, 2x, 0)$	$2a_1$	$(0,0,x)$	
		$(-x, x, 0)$	$4d_1$	$(0,-3x/2, x/2)$	C_l
		$(-2x, -x, 0)$	$4d_2$	$(0, -3x/2, -x/2)$	$-C_l$
		$(-x, -2x, 0)$	$2a_2$	$(0,0,-x)$	$-2C_l$
		12n $(x, 0, z)$	$4c_1$	$(x, 0, z)$	$2C_n$
		(x, x, z)	$8f_1$	$(z, -x/2, x/2)$	C_n
		$(0, x, z)$	$8f_2$	$(z, -x/2, -x/2)$	$-C_n$
		$(-x, 0, z)$	$4c_2$	$(z, 0, -x)$	$-2C_n$
		12o $(x, 2x, z)$	$4c_1$	$(z, 0, x)$	$2C_o$
		$(-x, x, z)$	$8f_1$	$(z, -3x/2, x/2)$	C_o
		$(-2x, -x, z)$	$8f_2$	$(z, -3x/2, -x/2)$	$-C_o$
		$(-x, -2x, z)$	$4c_2$	$(z, 0, -x)$	$-2C_o$
$\tau_{11}(c', c')$		3g (1/2,0,1/2)	4f	(1/4,3/4,1/2)	C_g
$Cmmm$	(65)	(1/2,1/2,1/2)		(3/4,1/4,1/2)	C_g
$c' = c e^{i\pi/3}$				(1/4,1/4,1/2)	C_g
				(3/4,3/4,1/2)	C_g
		(0,1/2,1/2)	2c	(0,1/2,1/2)	$-2C_g$
				(1/2,0,1/2)	$-2C_g$
		6l $(x, 2x, 0)$	8p	$(x/2, 3x/2 + 1, 0)$	C_l
		$(1 + x, 2x, 0)$			
		$(-2x, -x, 0)$	4g	$(-x, 0, 0)$	$-2C_1$
		$(1 - 2x, -x, 0)$			
		6m $(x, 2x, 1/2)$	8q	$(x/2, 3x/2 + 1, 1/2)$	C_m
		$(-2x, -x, 1/2)$	4h	$(-x, 0, 1/2)$	$-2C_m$

TABLE III (cont.)

	12n $(x,0,z)$	16r	$(x/2,-x/2+1,z)$	C_n
	$(0,x,z)$	8n	$(0,x,z)$	$-2C_n$
	12o $(x,2x,z)$	16r	$(x/2,3x/2,z)$	C_o
		8o	$(-x,0,z)$	$-2C_o$
$\tau_{12}(c',c')$	12n $(x,0,z)$	$8l_1$	$(x/2,-x/2+1,z)$	$-C_n$
$C222$ (21)	(x,x,z)	$8l_2$	$(x/2,x/2,z)$	C_n
$c'=c\mathrm{e}^{\mathrm{i}5\pi/6}/\sqrt{3}$	$(0,x,z)$	$8l_3$	$(-x,0,z)$	0
	12o $(x,2x,z)$	$8l_1$	$(x/2,3x/2,z)$	$-C_o$
	$(-x,x,z)$	$8l_2$	$(2x,-x,z)$	C_o
	$(-2x,-x,z)$	$8l_3$	$(3x/2,1/2,z)$	0
$\tau_{12}(c',-c')$	12n $(x,0,z)$	$8f_1$	$(x/2,-x/2+1,z)$	C_n
$Cmm2$ (35)	$(0,x,z)$	$4e_1$	$(0,x,z)$	$-2C_n$
$c'=c\mathrm{e}^{\mathrm{i}5\pi/6}/\sqrt{3}$	$(x,0,-z)$	$8f_2$	$(x/2,-x/2+1,-z)$	$-C_n$
	$(0,-x,-z)$	$4e_2$	$(0,-x,-z)$	$2C_n$
	12o $(x,2x,z)$	$8f_1$	$(x/2,3x/2,z)$	C_o
	$(-2x,-x,z)$	$4d_1$	$(3x/2,1/2,z)$	$-2C_o$
	$(-x,-2x,-z)$	$8f_2$	$(2x,x,-z)$	$-C_o$
	$(-2x,-x,-z)$	$4d_2$	$(3x/2,1/2,-z)$	$2C_o$

Table I illustrates which atoms displacements and magnetic moments ordering may be associated with order–disorder type phase transitions. They should fulfil the condition of having the same active representation. As example, the displacements of atoms and magnetic moments orderings at different positions occupied in AB_5 deuterides, allowed by the τ_4 IR are presented in Table IV. The choice of this representation is given for comparison with experimental data presented in the paper of Latroche et al. [11]. The values of position parameters are taken from [11]. The detailed description of displacements and magnetic orderings of all possible cases is too much space consuming. For each case it may be fined by using the MODY program [4].

5. The experiment and theory

In the work [11] the deuterides of three intermetallic compounds $LaNi_{5+x}$ ($x = 0,\ 0.2,\ 0.4$) have been prepared and analysed by neutron powder diffraction at two different deuterium concentrations. Three different structural models were tested for the description of the deuterides.

— The first one keeps the cell and symmetry of the intermetallic compound $P6/mmm$. The deuterium atoms are distributed over 4 different crystallographic Wyckoff sites (orbits).

— The second model corresponds to the description in $P6mm$. The four D orbits of the $P6/mmm$ model split into seven ones.

TABLE IV

Displacements of atoms and magnetic orderings at different positions of $P6/mmm$ allowed by the 4 IR and $\boldsymbol{k} = (0, 0, 0)$.

Atom	Orbit	Positions	Magnetic ordering	Displacement ordering
La	1a (0,0,0)	1: (0.000 0.000 0.000)	–	R_{a1}=(0 0 B)
Ni	2c (1/3,2/3,0)	1: (0.333 0.667 0.000) 2: (0.667 0.333 0.000)	–	R_{c1}=(0 0 B)= R_{c2}
	3g (1/2, 0,1/2)	1: (0.500 0.000 0.500) 2: (0.500 0.500 0.500) 3: (0.000 0.500 0.500)	–	R_{g1}=(0 0 B)= R_{g2}=R_{g3}
	6l $(x, 2x, 0)$ $x = 0.2$	1: (0.200 0.400 0.000) 2: (0.800 0.200 0.000) 3: (0.600 0.800 0.000) 4: (0.800 0.600 0.000) 5: (0.200 0.800 0.000) 6: (0.400 0.200 0.000)	M_{l1}=(A 0 0)= – M_{l4} M_{l2}=(A A 0)= –M_{l5} M_{l3}=(0 A 0)= –M_{l6}	R_{l1}=(0 0 B)= R_{l2}=R_{l3}=R_{l4} = R_{l5}=R_{l6}
	2e(0, 0, z) $z = 0.12$	1: (0.000 0.000 0.120) 2: (0.000 0.000 0.880)	–	R_{e1}=(0 0 B)= R_{e2}
D	4h (1/3,2/3,z) $z = 0.36$	1: (0.333 0.667 0.360) 2: (0.667 0.333 0.360) 3: (0.667 0.333 0.640) 4: (0.333 0.667 0.640)	–	R_{h1}=(0 0 B)= R_{h2}=R_{h3}=R_{h4}
	6m ($x = 0.15$, $2x, z = 0.5$)	1: (0.150 0.300 0.500) 2: (0.850 0.150 0.500) 3: (0.700 0.850 0.500) 4: (0.850 0.700 0.500) 5: (0.150 0.850 0.500) 6: (0.300 0.150 0.500)	M_{m1}=(A 0 0)= –M_{m4} M_{m2}=(A A 0)= –M_{m5} M_{m3}=(0 A 0)= –M_{m6}	R_{m1}=(0 0 B)= R_{m2}=R_{m3}=R_{m4}= R_{m5}=R_{m6}
	12n ($x = 0.46$, 0, $z = 0.12$)	1: (0.460 0.000 0.120) 2: (0.460 0.460 0.120) 3: (0.000 0.460 0.120) 4: (0.540 0.000 0.120) 5: (0.540 0.540 0.120) 6: (0.000 0.540 0.120) 7: (0.540 0.540 0.880) 8: (0.000 0.540 0.880) 9: (0.460 0.000 0.880) 10: (0.460 0.460 0.880) 11: (0.000 0.460 0.880) 12: (0.540 0.000 0.880)	M_{n1}=(A 2A 0)= –M_{n4}=M_{n9}=– M_{n12} M_{n2}=(–A A 0)= –M_{n5}=–M_{n7}=M_{n10} M_{n3}=(–2A –A 0)= –M_{n6}=–M_{n8}=M_{n11}	(wer 1): $R_{n'1}$=(B 0 0)= –$R_{n'4}$=–$R_{n'9}$=$R_{n'12}$ $R_{n'2}$=(B B 0)= –$R_{n'5}$=$R_{n'7}$=– $R_{n'10}$ $R_{n'3}$=(0 B 0)= –$R_{n'6}$=$R_{n'8}$=–$R_{n'11}$ (wer 2): R_{n1}=(0 0 E)= R_{n2}=R_{n3}= . . . =R_{n12}
	12o ($x = 0.2$, $2x$, $z = 0.35$)	1: (0.200 0.400 0.350) 2: (0.800 0.200 0.350) 3: (0.600 0.800 0.350) 4: (0.800 0.600 0.350) 5: (0.200 0.800 0.350) 6: (0.400 0.200 0.350) 7: (0.800 0.200 0.650) 8: (0.600 0.800 0.650) 9: (0.800 0.600 0.650) 10: (0.200 0.800 0.650) 11: (0.400 0.200 0.650) 12: (0.200 0.400 0.650)	M_{o1}=(A 0 0)= –M_{o4}=– M_{o9}=M_{o12} M_{o2}=(A A 0)= –M_{o5} =M_{o7}=–M_{o10} M_{o3}=(0 A 0)= –M_{o6}=M_{o8}=–M_{o11}	(wer 1): R_{o1}=(B 2B 0)= –R_{o4}=R_{o9}=–R_{o12} R_{o2}=(–B B 0)= –R_{o5}=–R_{o7}=R_{o10} R_{o3}=(–2B –B 0)= –R_{o6}=–R_{o8}=R_{o11} (wer 2): $R_{o'1}$=(0 0 E)= $R_{o'2}$= $R_{o'3}$= . . .=$R_{o'12}$

— The third model corresponds to a cell twice larger obtained from a doubling of the z-axis in space group $P6_3mc$. The four D sites of the original cell split into 12 different structural positions.

The analysis of all possible structures following from $P6/mmm$ parent group, with invariable lattice ($\boldsymbol{k}$ = 0,0,0) was presented in the previous Section. It has been shown that structure with $P6mm$ symmetry group follows according to τ_4 IR. Another possible structure suggested in work [11], with the $P6_3mc$ symmetry space group, requires double cell along the z-axis in comparison with initial $P6/mmm$. In the symmetry analysis it corresponds to IRs belonging to $\boldsymbol{k} = (0, 0, 1/2)$. As follows from the calculations, the structure with such group is not allowed independently of our parent structure. It must be getting in two steps. At first the structure $P6_3/mmc$ should appear following from $P6/mmm$ by τ_5 IR and $\boldsymbol{k} = (0, 0, 1/2)$, and next — as the result of transition from $P6_3/mmc$ according to τ_4 IR and $\boldsymbol{k} = (0, 0, 0)$ — $P6_3mc$ structure may be realised.

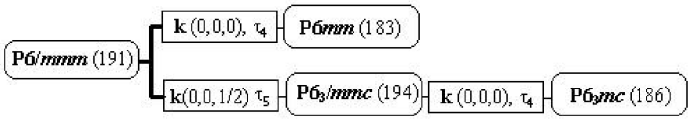

Fig. 2. The ways of structural phase transitions indicated in the experiment [11], allowed by the symmetry.

Atoms La (position 1a) and Ni (positions 2c, 3g, 6l, 2e) in new suggested subgroups (which result from the experiment and the symmetry considerations) are splitted like we see in Table V.

TABLE V

Positions of atoms La and Ni in new suggested subgroups.

$P6/mmm$ (191)	$P6_3mc$ (186)	$P6mm$ (183)
La 1a (0, 0, 0)	La 2a (0, 0, z)	La 1a (0, 0, z)
Ni 2c (1/3, 2/3, 0)	Ni $2b_1$ (1/3, 2/3, 0)	Ni 2b (1/3, 2/3, z)
	Ni $2b_2$ (1/3, 2/3, 1/2)	
Ni 3g (1/2, 0, 1/2)	Ni 6c (1/2, 0, 1/4)	Ni 3c (1/2, 0, z)
Ni 6l (x, $2x$, 0)	Ni $6c_1$ (x, $2x$, 0)	Ni 6e (x, $2x$, z)
	Ni $6c_2$ (x, $2x$, 1/2)	
Ni 2e (0, 0, z)	Ni $2a_1$ (0, 0, $z/2$)	Ni $1a_1$ (0, 0, z)
	Ni $2a_2$ (0, 0, $-z/2$)	Ni $1a_2$ (0, 0, $-z$)

Comparison of the splitting and occupation sites given by the experiment for the saturated deuterides with the results of the symmetry analysis method are

quoted below, in Table VI (results for $P6mm$ space group), and in Table VII (for $P6_3mc$).

TABLE VI

Splittings and sites occupations given in the experiment [11], and calculated by the symmetry analysis (results for P6mm space group).

Experimental data			The symmetry analysis method (Table III)
$La_{0.95}Ni_{5.11}D_{5.45}$	Model $P6mm$	Parent space group $P6/mmm$	Splitting, ΔP $P6mm$
$n = 0$	$2b_1$	4h	$2b_1 \quad -C_h$
$n = 0.56$	$2b_2$		$2b_2 \quad +C_h$
$n = 1.96$	6e	6m	6e $\quad C_m = 0$
$n = 2.48$	$6d_1$	12n	$6d_1 \quad +C_n$
$n = 0$	$6d_2$		$6d_2 \quad -C_n$
$n = 0$	$6e'_1$	12o	$6e_1 \quad -C_o$
$n = 0.59$	$6e'_2$		$6e_2 \quad +C_o$

n — occupancy parameters are given in atom per cell

TABLE VII

Splittings and sites occupations given in the experiment [11], and calculated by the symmetry analysis (results for $P6_3mc$ space group).

Experimental data				The symmetry analysis method			
$LaNi_5D_{6.5}$	$La_{0.97}Ni_{5.06}D_{5.9}$	Model $P6_3mc$	Parent space group $P6/mmm$	Splitting, ΔP $P6_3/mmc$		Splitting ΔP $P6_3mc$	
$n = 0$	$n = 0$	$2b_1$		4f	$+C_h$	$2b_1$	$-D_h$
$n = 0$	$n = 0$	$2b_2$	4h			$2b_2$	$+D_h$
$n = 1.28$	$n = 0.88$	$2b_3$		4f′	$-C_h$	$2b'_1$	$+D'_h$
$n = 0.29$	$n = 0.42$	$2b_4$				$2b'_2$	$-D'_h$
$n = 3.2$	$n = 3.6$	$6c_1$	6m	12k (1-6)	$+C_m$	$6c_1$	$+D_m$
$n = 0.7$	$n = 1.04$	$6c_2$		(7-12)	$-C_m$	$6c_2$	$-D_m$
$n = 5.36$	$n = 5.26$	$12d_1$	12n	24l (1-6)	$+C_n$	$12d_1$	$+D_n$
				(7-12)	$+C_n$		
$n = 0$	$n = 0$	$12d_2$		(13-18)	$-C_n$	$12d_2$	$-D_n$
				(19-24)	$-C_n$		
$n = 0$	$n = 0$	$6c'_1$		12k (1-6)	$-C_o$	$6c_1$	$+D_o$
$n = 0$	$n = 0$	$6c'_2$	12o	(7-12)	$-C_o$	$6c_2$	$-D_o$
$n = 0$	$n = 0.38$	$6c'_3$		12k′ (13-18)	$+C_o$	$6c_3$	$-D''_o$
$n = 2.3$	$n = 0.79$	$6c'_4$		(19-24)	$+C_o$	$6c_4$	$+D''_o$

n — occupancy parameters are given in atom per cell, numbering of atoms according to MODY program

As may be seen, it is possible to choose such parameters for calculated site occupation changes ΔP, which follow to good agreement with experimental data.

The displacements of atoms from initial positions (in the parent, high symmetry phase), calculated by the symmetry analysis method, following to the new positions in the final lower symmetry phase occur, in general, in good agreement with the positions indicated by experimental data given in [11]. The difference appears only at positions $6m$ occupied by D atoms, for which from the symmetry analysis follows the possibility of appearing of the displacements only along the z axis, while the experimental data indicates the displacements along the x axis with z component fixed in the refinement. Because the displacements of atoms followed by introducing the hydrogen are small, the differences which appear as the result of structure deformation in the diffraction pattern are small. Thus more than one model of structure deformation may give the same result of data refinement. In such situation the symmetry analysis may help to make the choice, which model from symmetry point of view seems to be more probable.

6. Conclusions

Based on our analysis we can prove that transition of the parent space group $P6/mmm$ to $P6mm$ structure types observed experimentally is possible using the symmetry analysis method $\boldsymbol{k} = (0, 0, 0)$ and τ_4 IR. The discussion of phase transition from $P6_3/mmc$ to $P6_3mc$ structure indicate two steps required by the symmetry restrictions: from $P6/mmm$, τ_5 IR and $\boldsymbol{k} = (0, 0, 1/2)$ to the structure $P6_3/mmc$, and next — from $P6_3/mmc$, τ_4 IR and $\boldsymbol{k} = (0, 0, 0)$ to the $P6_3mc$. Results of the experimental data and results of theory show the similar hydrogen ordering. The results presented in this work, calculated for all positions and all allowed irreducible representations can be applied to interpretation of experimental investigations of order–disorder phase transitions not only for AB_5 hydrates, but also in many other compounds with $P6/mmm$ parent symmetry group.

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