

Symmetry analysis of hydrogen related structural transformations in Laves phase intermetallic compounds

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Abstract

Absorption of hydrogen in the intermetallic compounds of Rare Earths and Yttrium with 3-d metals causes structure distortions and transformations depending on hydrogen content and temperature. One of the most intriguing problems for the unsaturated hydrides is a tendency for ordering of hydrogen atoms. To find the explanation of the observed transformations and hydrogen ordering the symmetry analysis method in the frame of theory of space groups and their representations is applied for Laves phase hydrides RMn_2 (R = Rare Earth and Yttrium). There are analysed all possible transformations of the parent structure with symmetry space group $Fd-3m$ leading to the structures of lower symmetry, for $\mathbf{k} = (0,0,0)$ and selected transitions to the translation subgroup corresponding to $\mathbf{k} = (0,0,1)$. In such structures of lower symmetry the hydrogen interstitial positions split into subgroups with differentiated local symmetries and abundances. The hydrogen interstitial positions of A2B2 type and AB3 type are taken in to account. If one of such super-lattices is occupied by hydrogen and the others are empty, we receive effect of hydrogen ordering. All transformations allowed by symmetry rules are presented and discussed with the aim to analyse and understand the conditions determining phase transitions and hydrogen ordering.

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1. Introduction to the symmetry analysis

The method introduced at first by E.F. Bertaut and developed intensively recently [1], [2] works under the assumption that the symmetry change in phase transition preserves the group–subgroup relation (it means it is the continuous or “semi-continuous” phase transition) and that the “property” under consideration is localised on some sets of equivalent positions in the crystal initial phase.

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 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) $\vec{\Psi}_\lambda^{k_l, \nu}$ 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:

$$\vec{S} = \sum_{l, \nu, \lambda} c_\lambda^{k_l, \nu} \vec{\Psi}_\lambda^{k_l, \nu} \quad (1)$$

l is the number of \mathbf{k} vectors, ν the number of IR's and λ is the number of dimensions of ν 's IR.

The form of BV-s is given by the theory and may be calculated for example, by the computer program MODY [3], or

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another computer programs [4,5,6,7]. The coefficients $C_{\lambda}^{k,v}$ of the linear combination of basis functions should be obtained from a refinement procedure. The number of these unknown coefficients depends only on the number of IR taken into the model and their respective dimensions.

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 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, while $P' = 0$ means that the subgroup orbit is empty after the ordering, while 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 symmetry equivalent set has to be zero, what 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 (from A2B2 to AB3 tetrahedra for example) is observed.

3. RM₂H_x structure details

The structure of RM₂H_x hydrides is investigated as a function of the concentration of hydrogen atoms and the temperature. The face-centred cubic structure, with symmetry space group $Fd\bar{3}m$ (O_h^7) and positions of atoms R-8a, M-16d, and interstitial sites for H-96g (the names of position orbits are in Wyckoff notation, according to International Tables for Crystallography) was found [8,9,10,11] as the parent structure for these compounds with M=Mn and R=Sm, Gd, Tb, Dy, Ho and Y for example. The possibility of hydrogen ordering over 32e sites are also regarded [12]. Some examples of structural phase transitions observed in hydrides of YMn₂H_x are quoted below.

3.1. YMn₂H_x hydrides ($0 < x < 1.15$) [11]

The tetragonal distortion with space group $I4_1/amd$ and positions of atoms H1: 16h, H2: 32i had been identified, and it was established that for $0 < x < 0.5$ coexistence of cubic (with parent symmetry) and tetragonal phase occurs, for $0.5 < x < 0.8$ a single tetragonal phase exists, and for $0.8 < x < 1.15$ again the coexistence of cubic and tetragonal phase appears.

3.2. YMn₂H_x hydride with $x=1.15$ [13]

At temperature >217 K the cubic, $Fd\bar{3}m$, ($a = 7.886 \text{ \AA}$) with atom positions as in the parent compound had been observed. At temperature $T < 217$ K the change of the structure to a cubic, but with $P\bar{4}3m$ symmetry space group, with positions of atoms: Y1: 1a, Y2: 3c, Y3: 4e, Mn1: 4e, Mn2: 12i was found. The positions of interstitial sites after deuteration had been identified as D1, D2, D3, D4: 12i; D5, D6: 24j.

3.3. YMn₂H_x hydrides with $x > 3.5$; [14,15]

The rhombohedral distortion had been reported and for $3.5 < x < 4$ coexistence of two phases (rhombohedral and cubic) has been found, for $4 < x < 4.3$ the rhombohedral single phase, with space group $R\bar{3}m$ and for $x = 4.5$ also rhombohedral, but with space group $R3m$ (in hexagonal setting positions of atoms are: Y1, Y2: 3a; Mn1: 3a; Mn2: 9b; D1, D2, D3, D4: 9b; D5, D6: 18c).

4. Results of the symmetry analysis

All the structures determined till now for cubic RM₂H_x ($x \leq 5$) Laves phases possess the symmetry of the parent $Fd\bar{3}m$ structure subgroup with $\mathbf{k} = (0,0,0)$ or $\mathbf{k} = (0,0,1)$. Observed changes of the structure are related with distortion of the parent structure. The open question is—may the ordering of hydrogen atoms take place, and if it appears, how the hydrogen atoms are ordered. The symmetry analysis is able to help in solving this problem.

The results of occupation probability changes in YMn₂H_x for 96g interstitial sites, leading to the new structures with the same as parent structure translational symmetry ($\mathbf{k} = (0,0,0)$), obtained from symmetry analysis have been described in Ref. [16]. Because the obtained probability changes do not depend on the kind of atoms located at 8a and 16d positions, the analysis made for YMn₂ hydrides is right for all compounds of the C15 Laves phases. 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 atomic displacements observed, those 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.

In this work, the additional symmetry analysis is given for possible types of hydrogen atoms ordering over the 32e interstitial sites (AB3 tetrahedra), and one of possibilities of hydrogen ordering with $\mathbf{k} = (0,0,1)$ following to the $P\bar{4}3m$ space group indicated by Latroche et al. [13].

For the positions 8a: 1-(0,0,0), 2-(1/4,1/4,1/4), and rest from centring translations (0,1/2,1/2), (1/2,0,1/2), (1/2,1/2,0) occupied by R atoms, the symmetry analysis with $\mathbf{k} = (0,0,0)$ in the

Table 1

Representation	Position 1	Position 2
$\tau_7 (c_1, c_2, c_3)$	(c_1, c_2, c_3)	$(-c_1, -c_2, -c_3)$
$\tau_7 (c, c, c)$	(c, c, c)	$(-c, -c, -c)$
$\tau_{10} (c, c, c)$	(c, c, c)	(c, c, c)
$\tau_{10} (c, 0, 0)$	$(c, 0, 0)$	$(c, 0, 0)$
$\tau_{10} (c, c, 0)$	$(c, c, 0)$	$(c, c, 0)$

displacement type transition allows as active the 3-dimensional irreducible representations τ_7 and τ_{10} , each of them once. Displacements of R atoms following from symmetry analysis, written as (x, y, z) components are given in Table 1. For the positions 16d: 1-(0.625, 0.625, 0.625), 2-(0.625, 0.375, 0.375), 3-(0.375, 0.625, 0.375), 4-(0.375, 0.375, 0.625), and the rest as obtained by centring translations, occupied by M atoms, the symmetry analysis in the displacement type transition allows as active the following irreducible representations: 1-dimensional τ_4 , 2-dimensional τ_6 , 3-dimensional τ_8 and τ_{10} . Possible displacements of M atoms are given in Table 2. Because of $\mathbf{k} = (0, 0, 0)$ the displacements of the rest positions of 8a and 16d are in the corresponding sequence as given in the Tables 1 and 2. For the $Fd-3m$ group with $\mathbf{k} = (0, 0, 0)$ vector and 96g positions (A2B2 tetrahedra) in which hydrogen can locate, the symmetry analysis allows the following irreducible representations as active in the ordering type transition: once 1-dimensional τ_1 and τ_4 , once 2-dimensional τ_5 and τ_6 , once 3-dimensional τ_8 and τ_9 and two times 3-dimensional τ_7 and τ_{10} . For ordering of hydrogen atoms over another possible tetrahedral—AB3, (the 32e positions), as active representations are allowed: once 1-dimensional τ_1 and τ_4 , once 3-dimensional τ_7 and τ_{10} . The results of symmetry analysis of possible hydrogen site occupation changes for positions 96g and 32e together with splitting of these positions to the corresponding subgroup orbits are given in the Table 4.

From the Tables 3 and 4 may be seen that for example, for the representation τ_8 and parameters $C_{8,1} = c_1 = C_{8,2} = c_2 = C_{8,3} = c_3 = c$ ($R32$ group) the probability change for 96g positions is possible as follows: for positions H1: $\Delta P = c$; for H2: $\Delta P = -c$; for H3: $\Delta P = 0$; for H4: $\Delta P = 0$.

Table 2

Representation	Position 1	Position 2	Position 3	Position 4
$\tau_4 (c)$	(1,1,1)	(1,-1,-1)	(-1,1,-1)	(-1,-1,1)
$\tau_6 (c e^{i\varphi}, c e^{i(\pi/3-\varphi)})$	$x = 2\cos \varphi$ $y = -2C \cos(\pi/3 - \varphi)$ $z = -2C \cos(\pi/3 + \varphi)$	$x = 2\cos \varphi$ $y = 2C \cos(\pi/3 - \varphi)$ $z = 2C \cos(\pi/3 + \varphi)$	$x = -2\cos \varphi$ $y = -2C \cos(\pi/3 - \varphi)$ $z = 2C \cos(\pi/3 + \varphi)$	$x = -2\cos \varphi$ $y = 2\cos(\pi/3 - \varphi)$ $z = -2C \cos(\pi/3 + \varphi)$
$\tau_6 (c, c e^{i\pi/3})$	$(2c, -c, -c)$	$(2c, c, c)$	$(-2c, -c, c)$	$(-2c, c, -c)$
$\tau_8 (c, c, c)$	(0,0,0)	(0,-1,1)	(1,0,-1)	(-1,1,0)
$\tau_8 (c, 0, 0)$	(0,1,-1)	(0,-1,1)	(0,-1,-1)	(0,1,1)
$\tau_8 (c, c, 0)$	(-1,1,0)	(1,-1,2)	(1,-1,-2)	(-1,1,0)
$\tau_{10} (c, c, c)$ ver. 1	(1,1,1)	(1,1,1)	(1,1,1)	(1,1,1)
$\tau_{10} (c, c, c)$ ver. 2	(1,1,1)	(-1,0,0)	(0,-1,0)	(0,0,-1)
$\tau_{10} (c, 0, 0)$ ver. 1	(1,0,0)	(1,0,0)	(1,0,0)	(1,0,0)
$\tau_{10} (c, 0, 0)$ ver. 2	(0,1,1)	(0,-1,-1)	(0,-1,1)	(0,1,-1)
$\tau_{10} (c, c, 0)$ ver. 1	(1,1,0)	(1,1,0)	(1,1,0)	(1,1,0)
$\tau_{10} (c, c, 0)$ ver. 2	(1,1,2)	(-1,-1,0)	(-1,-1,0)	(1,1,-2)

Table 3

Representation	Dimension	OP	Symmetry group
τ_1	1	c	$Fd-3m$ (227)
τ_4	1	c	$F-43m$ (216)
τ_5	2	(c_1, c_2) (c, c)	$Fddd$ (70) $I4_1/amd$ (141)
τ_6	2	(c_1, c_2) $(c, -c)$ (c, c)	$F222$ (22) $I-4m2$ (119) $I4_122$ (98)
τ_7	3	(c_1, c_2, c_3) (c, c, c) $(c, c, 0)$	$P-1$ (2) $R-3m$ (166) $C2/m$ (12)
τ_8	3	(c_1, c_2, c_3) (c, c, c) $(c, c, 0)$ $(0, 0, c)$	$P1$ (1) $R32$ (155) $Ima2$ (46) $I-42d$ (122)
τ_9	3	(c_1, c_2, c_3) (c, c, c) $(c, c, 0)$ $(c, 0, 0)$	$P-1$ (2) $R-3$ (148) $C2/m$ (12) $I4_1/a$ (88)
τ_{10}	3	(c_1, c_2, c_3) (c, c, c) $(c, c, 0)$ $(c, 0, 0)$	$P1$ (1) $R3m$ (160) $Ima2$ (46) $I4_1md$ (109)

(It means that two sublattices remain disordered, and only for hydrogen concentration $x=6$ and maximum value $c=1/2$ one sublattices is fully occupied and one is empty).

For the representation τ_8 and parameters $c_1 = c_2 = c, c_3 = 0$ ($Ima2$ group) the probability changes on 96g positions are:

For positions H1 : $\Delta P = c$; for H2 : $\Delta P = -c$; for H3 : $\Delta P = 0$; for H4, H5 : $\Delta P = -1/2c$; for H6, H7 : $\Delta P = 1/2c$

(For maximum value $c=1/2$ one sublattice 4b is fully occupied by the hydrogen atoms ($P'=1$), one 4b is empty ($P'=0$), one sublattice 8c remains disordered with $P'=1/2$ and hydrogen diffuses between two sets of positions 8c with $P'=1/4$ and between two other sets of positions 8c with $P'=3/4$). For hydrogen ordering over 32e positions the τ_8 representation is not allowed.

Table 4

Destination group	<i>Fd-3m</i> position	Position in destination group	ΔP ver. 1	ΔP ver. 2
<i>Fd-3m</i> (227)	32e	32e (0.39,0.39,0.39)	0	–
	96g	96g (0.546,0.546,0.262)	0	–
<i>F-43m</i> (216)	32e	16e (0.390,0.390,0.390)	c'	–
	96g	16e (0.860,0.860,0.860)	$-c'$	–
		48h (0.546,0.546,0.262)	c	–
	48h (0.704,0.704,0.988)	$-c$	–	
<i>Fddd</i> (70)	32e	32h (0.390,0.390,0.390)	–	–
	96g	32h (0.704,0.512,0.296)	2c	–
		32h (0.704,0.796,0.012)	$-c$	–
		32h (0.988,0.796,0.296)	$-c$	–
<i>I4₁/amd</i> (141)	32e	16h (0.000,0.780,0.390)	–	–
	96g	16h (0.0,0.092,0.262)	2c	–
		32i (0.284,0.808,0.546)	$-c$	–
<i>F222</i> (22)	32e	16k (0.860,0.640,0.140)	–	–
		16k (0.390,0.110,0.610)	–	–
	96g	16k (0.988,0.796,0.296)	p_1	–
		16k (0.704,0.512,0.296)	$-p_3$	–
		16k (0.704,0.796,0.012)	$-p_2$	–
		16k (0.262,0.954,0.454)	$-p_1$	–
		16k (0.546,0.238,0.454)	p_3	–
		16k (0.546,0.954,0.738)	p_2	–
<i>I-4m2</i> (119)	32e	8i (0.000,0.780,0.390)	0	–
		8i (0.000,0.720,0.860)	0	–
	96g	8i (0.092,0.0,0.738)	2c	–
		8i (0.408,0.0,0.012)	$-2c$	–
		16j (0.284,0.808,0.546)	$-c$	–
	16j (0.716,0.692,0.704)	c	–	
<i>I4₁22</i> (98)	32e	16g (0.000,0.780,0.390)	0	–
	96g	16g (0.000,0.092,0.262)	0	–
		16g (0.284,0.808,0.546)	$-c$	–
		16g (0.716,0.808,0.546)	c	–
<i>R-3m</i> (166)	32e	2c (0.265,0.265,0.265)	3c'	–
		6h (0.265,0.265,0.705)	c'	–
	96g	6h (0.137,0.137,0.705)	c	c
		6h (0.137,0.137,0.521)	$-c$	c
		12i (0.521,0.705,0.137)	0	$-c$

$$p_1 = C \cos(\phi), p_2 = C \cos(\phi + \pi/3), p_3 = C \cos(\phi - \pi/3).$$

Destination group	<i>Fd-3m</i> position	Position in destination group	ΔP	
<i>R32</i> (155)	32e	2c (0.265,0.265,0.265)	–	
		6f (0.705,0.265,0.265)	–	
	96g	6f (0.137,0.137,0.705)	0	
		6f (0.521,0.705,0.137)	c	
		6f (0.705,0.521,0.137)	$-c$	
		6f (0.137,0.137,0.521)	0	
<i>Ima2</i> (46) (τ_8)	32e	4b (0.250,0.515,0.780)	–	
		4b (0.250,0.515,0.220)	–	
		8c (0.530,0.265,0.000)	–	
	96g	4b (0.25,0.387,0.092)	2c	
		4b (0.25,0.387,0.908)	$-2c$	
		8c (0.842,0.137,0.000)	0	
		8c (0.558,0.421,0.284)	$-c$	
		8c (0.034,0.329,0.808)	$-c$	
		8c (0.466,0.329,0.192)	c	
		8c (0.942,0.421,0.716)	c	

Table 4 (Continued)

Destination group	<i>Fd-3m</i> position	Position in destination group	ΔP ver. 1	ΔP ver. 2		
<i>I-42d</i> (122)	32e	16e (0.000,0.780,0.390)	–	–		
	96g	16e (0.0,0.092,0.262)	0	–		
		16e (0.284,0.808,0.546)	c	–		
		16e (0.808,0.284,0.454)	$-c$	–		
<i>R-3</i> (148)	32e	2c (0.265,0.265,0.265)	–	–		
		6f (0.705,0.265,0.265)	–	–		
	96g	6f (0.137,0.137,0.705)	0	–		
		6f (0.521,0.705,0.137)	c	–		
		6f (0.705,0.521,0.137)	$-c$	–		
		6f (0.137,0.137,0.521)	0	–		
<i>I4₁/a</i> (88)	32e	16f (0.000,0.780,0.390)	–	–		
		16f (0.284,0.808,0.546)	c	–		
	96g	16f (0.808,0.284,0.454)	$-c$	–		
		16f (0.000,0.092,0.262)	0	–		
Destination group	<i>Fd-3m</i> position	Position in destination group	ΔP ver. 1	ΔP ver. 2		
<i>R3m</i> (160)	32e	1a (0.390,0.390,0.390)	3c'	–		
		1a (0.860,0.860,0.860)	$-3c'$	–		
		3b (0.390,0.390,0.830)	$-c'$	–		
		3b (0.860,0.860,0.420)	c'	–		
		96g	3b (0.137,0.137,0.705)	c	c	
			3b (0.137,0.137,0.521)	$-c$	c	
	96g	3b (0.863,0.863,0.295)	$-c$	$-c$		
		3b (0.863,0.863,0.479)	c	$-c$		
		6c (0.521,0.705,0.137)	0	$-c$		
		6c (0.479,0.295,0.863)	0	c		
		<i>Ima2</i> (46) (τ_{10})	32e	4b (0.250,0.015,0.530)	c'	–
				4b (0.250,0.015,0.970)	$-c'$	–
8c (0.470,0.235,0.750)	0			–		
96g	4b (0.25,0.887,0.842)		2c	0		
	4b (0.25,0.887,0.658)		$-2c$	0		
	8c (0.158,0.363,0.750)		0	0		
		8c (0.966,0.171,0.558)	c	c		
		8c (0.442,0.079,0.034)	c	$-c$		
		8c (0.058,0.079,0.466)	$-c$	c		
		8c (0.534,0.171,0.942)	$-c$	$-c$		
<i>I4₁md</i> (109)	32e	8b (0.000,0.780,0.390)	c	–		
		8b (0.000,0.720,0.860)	$-c$	–		
		8b (0.0,0.092,0.262)	0	c		
	96g	8b (0.0,0.408,0.988)	0	$-c$		
		16c (0.284,0.808,0.546)	c	0		
		16c (0.808,0.284,0.454)	$-c$	0		
Destination group	<i>Fd-3m</i> position	Position in destination group				
<i>Fd-3m</i> (227)	8a	8a				
	16d	16d				
<i>F-43m</i> (216)	8a	4a, 4c				
	16d	16e				
<i>Fddd</i> (70)	8a	8a				
	16d	16d				
<i>I4₁/amd</i> (141)	8a	4b				
	16d	8c				
<i>F222</i> (22)	8a	4a, 4c				
	16d	16k				
<i>I-4m2</i> (119)	8a	2a, 2d				
	16d	8i				

Table 4 (Continued)

Destination group	<i>Fd-3m</i> position	Position in destination group
<i>I4</i> ₁ 22 (98)	8a	4a
	16d	8f
<i>R-3m</i> (166)	8a	2c
	16d	3e, 1b
<i>R32</i> (155)	8a	2c
	16d	1b, 3b
<i>Ima2</i> (46) (τ_8)	8a	4b
	16d	4a, 4b
<i>I-42d</i> (122)	8a	4a
	16d	8d
<i>R-3</i> (148)	8a	2c
	16d	1b, 3e
<i>I4</i> ₁ / <i>a</i> (88)	8a	4a
	16d	8d
<i>R3m</i> (160)	8a	1a, 1a
	16d	1a, 3b
<i>Ima2</i> (46) (τ_{10})	8a	4b
	16d	4a, 4b
<i>I4</i> ₁ <i>md</i> (109)	8a	4a
	16d	8b

For the case of $\mathbf{k} = (0,0,0)$ the symmetry analysis indicates the possibility of displacements of M atoms following to the mentioned above symmetry groups as given in Table 2, and no displacements of R atoms, because the τ_8 representation is not allowed for these positions.

Table 5

Position in <i>Fd-3m</i>	Position in <i>P-43m</i>	Displacement ver. 1	Displacement ver. 2		
8a	1a	(0,0,0)	(0,0,0)		
		(0,1/2,1/2)	(0,0,0)		
		(1/2,0,1/2)	(0,0,0)		
	4e	(1/2,1/2,0)	(0,0,0)		
		(1/4,1/4,1/4)	(-c,-c,-c)		
		(1/4,3/4,3/4)	(-c,c,c)		
		(3/4,1/4,3/4)	(c,-c,c)		
		(3/4,3/4,1/4)	(c,c,-c)		
		16d	4e	(5/8,5/8,5/8)	(-c,-c,-c)
				(3/8,5/8,3/8)	(c,-c,c)
(5/8,3/8,3/8)	(-c,c,c)				
12i	(3/8,3/8,5/8)		(c,c,-c)		
	(5/8,7/8,7/8)		(c,0,0)		
	(5/8,1/8,1/8)		(c,0,0)		
	(3/8,7/8,1/8)		(-c,0,0)		
	(3/8,1/8,7/8)		(-c,0,0)		
	(7/8,7/8,5/8)		(0,0,c)		
	(7/8,1/8,3/8)		(0,0,-c)		
	(1/8,7/8,3/8)	(0,0,-c)			
	(1/8,1/8,5/8)	(0,0,c)			
	(7/8,5/8,7/8)	(0,c,0)			
	(7/8,3/8,1/8)	(0,-c,0)			
	(1/8,5/8,1/8)	(0,c,0)			
	(1/8,3/8,7/8)	(0,-c,0)			

Table 6

Destination group	<i>Fd-3m</i> position	Position in destination group	ΔP	
<i>P-43m</i> (215)	96g	12i (0.438,0.438,0.250)	3c	
		$\mathbf{k}_1 = (0,0,1)$	12i (0.188,0.188,0.000)	0
		$\mathbf{k}_2 = (0,1,0)$	12i (0.313,0.313,0.000)	0
		$\mathbf{k}_3 = (1,0,0)$	12i (0.938,0.938,0.250)	-c
		$\tau_3 (c,c,c,c,c,c)$	24j (0.813,0.688,0.500)	0
			24j (0.438,0.938,0.750)	-c

The structure indicated for $\text{YMn}_2\text{H}_{1.15}$ by Latroche et al. [13] with symmetry group *P-43m* occurs possible in the multi- \mathbf{k} phase transition, with all three arms of \mathbf{k} vector: $\mathbf{k}_1 = (0,0,1)$, $\mathbf{k}_2 = (0,1,0)$ and $\mathbf{k}_3 = (1,0,0)$. The representation active in this phase transition, and set of coefficients following to *P-43m* group are: two-dimensional IR τ_3 and $(c,c;c,c,c,c)$. The results of the symmetry analysis indicating splitting of Wyckoff positions in the initial structure to the orbits of final, ordered structure and corresponding changes of site occupations are given in the Table 6. The possible accompanying displacements of Y and Mn atoms are quoted in the Table 5.

In a similar way, as for τ_8 of $\mathbf{k} = (0,0,0)$, all results mentioned in the Table 4, and Table 6, for given hydrogen concentration may indicate possible types of hydrogen ordering.

For the case with $\mathbf{k} = (0,0,1)$ the comparison of experimental data interpretation for $\text{YMn}_2\text{H}_{1.15}$ [13] and results of the symmetry analysis indicate qualitative agreement. The splitting on the subgroup orbits and the number of orbits with high, middle and low hydrogen occupation are the same, but positions with these types of occupations are different.

5. Magnetic ordering for the case $\mathbf{k} = (0,0,1)$

The symmetry analysis of possible ordering of Mn magnetic moments, coexisting with structural changes leading to *P-43m* symmetry, was made together with discussion of hydrogen ordering. For positions 16d, all star of \mathbf{k} vector $(0,0,1)$ and representation τ_3 , which lead to *P-43m* group the

Table 7

Position in <i>Fd-3m</i>	Position in <i>P-43m</i>	Magnetic moments	
16d	4e	(5/8,5/8,5/8)	(0,0,0)
		(3/8,5/8,3/8)	(0,0,0)
		(5/8,3/8,3/8)	(0,0,0)
	12i	(3/8,3/8,5/8)	(0,0,0)
		(5/8,7/8,7/8)	(0,-m,m)
		(5/8,1/8,1/8)	(0,m,-m)
		(3/8,7/8,1/8)	(0,-m,-m)
		(3/8,1/8,7/8)	(0,m,m)
		(7/8,7/8,5/8)	(-m,m,0)
		(7/8,1/8,3/8)	(-m,-m,0)
		(1/8,7/8,3/8)	(m,m,0)
		(1/8,1/8,5/8)	(m,-m,0)
		(7/8,5/8,7/8)	(m,0,-m)
		(7/8,3/8,1/8)	(m,0,m)
		(1/8,5/8,1/8)	(-m,0,m)
		(1/8,3/8,7/8)	(-m,-0,-m)

symmetry analysis indicates the non-collinear and non-planar structure with magnetic moments localised on 12i positions and no magnetic moments on the 4e positions. This results stay in good agreement with supposition made in [13], that one should expect different moments localised on different orbits of Mn atoms, what was not confirmed experimentally. The detailed description of resulting magnetic structure is given in the Table 7.

6. Conclusions

In results of our analysis, we can prove that transition of the RMn_2H_x hydrides to $R\bar{3}m$ and $R3m$ and as well to $I4_1/amd$ structure types observed experimentally, result from our symmetry analysis with $\mathbf{k}=(0,0,0)$. Also the transition to $P\bar{4}3m$ group observed for $\text{YMn}_2\text{H}_{1.15}$ [13] is possible when a full star of $\mathbf{k}=(0,0,1)$ is used, with qualitative agreement of deuterium site occupation and ordering of magnetic moments.

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