The Influence of Hydrogen on Structural and Magnetic Transformations in RMn_2H_x Hydrides with Laves Phase C15 and C14 Structures—A Review

Supplementary material.

C14 and C15 type Laves Phases: Details of Crystal Structures

The AB2-type Laves phases compositions are a common type of topologically close-packed structures, with three polytypes typically observed: hexagonal C14 ($MgZn_2$), cubic C15 ($MgCu_2$), and dihexagonal C36 ($MgNi_2$) [1]. Laves phases exist at ratios of metallic radii (r_A/r_B) between ~1.05 and 1.68 with the ideal diameter ratio existing at ~1.225. Geometric analysis, the spatial arrangement of atoms in Laves phases is widely presented, for example, in [1,2,3]. The most important data on the crystal structure of Laves phases of C14 and C15 type of RMn_2 compounds (where, *R*—rare compounds) discussed in the paper are summarized below.

S1. C14-type Laves phase

The hexagonal structure of the C14 phase (type: $MgZn_2$) is described with the space group $P6_3/m\ 2/m\ 2/c$. The unit cell (Figure S1) contains 4 Mg atoms in the 4*f* positions and 8 (Zn) atoms: two Zn1 atoms in the 2*a* positions and six Zn2 atoms in the 6*h* positions. The number of stoichiometric particles is 4. A complete description of the positions of the atoms in the cell is provided in Table S1 [4].

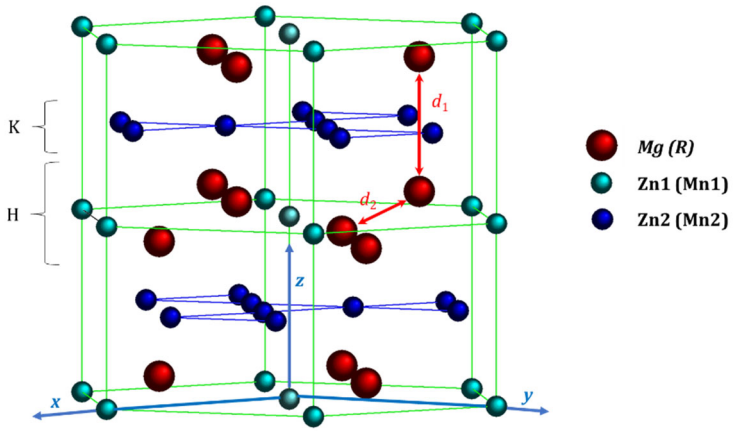

Figure S1. The arrangement of atoms in *C*14 Laves phase with hexagonal structure in $MgZn_2$ (Mg corresponds to *R*-rare earth and Zn to Mn, in the RMn_2, compounds).

Table S1. Atoms positions in C14-type Laves phase ($MgZn_2$): Space group: $P6_3/mmc, (D_{6h}^4)$ *Patterson symmetry: 6/mmm. No 194* [4, 5].

Atom	***Positions*** **Multiplicity, Wyckoff letter, Site symmetry**	**Coordinates of symmetrically equivalent points**	
Mg (R)	$4\,f\,(3\,m\,.)$	$\frac{1}{3},\frac{2}{3},z\quad \frac{2}{3},\frac{1}{3},\frac{1}{2}+z\quad \frac{2}{3},\frac{1}{3},\bar{z}\quad \frac{1}{3},\frac{2}{3},\frac{1}{2}+\bar{z}$	$z \approx \frac{1}{16}$
Zn1 (Mn1)	$2\,a\,(\bar{3}\,m\,.)$	$0,0,0\quad 0,0,\frac{1}{2}$	

Zn2 (Mn2)	6 *h* (*m m 2*)	$\pm\,(x, 2x, \frac{1}{4}\quad 2\bar{x}, \bar{x}, \frac{1}{4}\quad x, \bar{x}, \frac{1}{4})$	$x \approx -\frac{1}{6}$

In the cell of the C14 phase, a characteristic layered structure can be distinguished (Figure S1). The first layer (H) containing the *R* and Mn1 atoms is slightly folded—the rare earth atoms not fitting in the manganese plane were pushed out behind it by $z \approx 1/16$ [5, 6]. The second layer (K) consists only of Mn2 atoms arranged in the form of *kagomé* planes (Figure S1). Such a set of two layers (H+K) is the basic structural building block of the Laves phases of the AB_2 stoichiometric composition. Doublets of this type can fold relative to each other in different ways to create the highest density structure. Here, we can say that doublets (H and K) are arranged alternately along the z axis, i.e. each subsequent doublet (H + K) is created by rotating the previous one by 180° around the z axis and shifting it by a constant vector (½ of the cell height) along the z-axis. The distances between the nearest Mn atoms are:

$$d_{Mn2-Mn2} = a\,(3x^2+1/6)^{1/2},$$
$$d_{Mn1-Mn2} = (3x^2a^2+c^2/16)^{1/2};$$

where: *a* and *c* lattice parameters of the cell, and $x \approx -1/6$. These distances are equal only in the case of an ideal hexagonal structure, i.e. when $c/a = (8/3)^{1/2} \approx 1.633$. Then each Mn2 atom has 4 nearest neighbors (Mn2 atoms), and an Mn1 atom has 6 nearest neighbors (also Mn2 atoms).

In the case of *R* atoms, two distances d_1 and d_2 can be distinguished between the nearest *R* atoms (Figure S1), which are respectively:

$$d_1 = d_{R-R} = c\,(1/2 - 2z),$$
$$d_2 = d'_{R-R} = (a^2/3 + (2cz))^{1/2};$$

where: $z \approx 1/16$ means the displacement of the *R* atom beyond the plane determined by Mn1. Further distances between atoms are:

$$d_{R-Mn1} = (a^2/3 + c^2/16)^{1/2},$$
$$d_{R-Mn2} = (a^2/3 + x + 3\,x^2\,c^2(1/4 - z))^{1/2}.$$

S2. C15-type Laves phase

The crystallographic structure of the C15 phase of RMn_2 (prototype: $MgCu_2$) is a face-centred-cubic (*fcc*) lattice described with the space group $F4_1/d\,\bar{3}\,2/m$. The unit cell contains 16 Mn atoms and 8 R atoms (Figure S2) and the number of stoichiometric particles is 8. The positions of the atoms in the unit cell of the C15 phase are listed in Table S2.

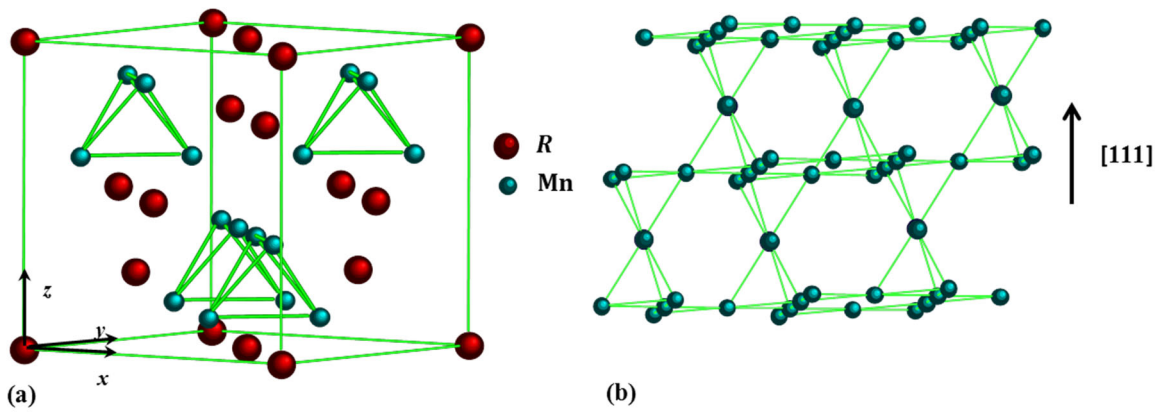

Figure S2. (**a**) The arrangement of atoms in C15 Laves phase with the *fcc* structure in the $MgCu_2$ (Mg corresponds to R-rare earth and Cu to Mn, in the RMn_2 compounds, respectively); (**b**) manganese sublattice for RMn_2.

Table S2. Positions of atoms in the unit cell of the C15 type phase, origin choice 1 [4, 7].

Atom	***Positions*** **Multiplicity, Wyckoff letter, Site symmetry**	**Coordinates of symmetrically equivalent points** $(0,0,0) + \left(0,\frac{1}{2},\frac{1}{2}\right) + \left(\frac{1}{2},0,\frac{1}{2}\right) + \left(\frac{1}{2},\frac{1}{2},0\right) +$
Mg (R)	8 a ($\bar{4}$ 3 m)	$0,0,0 \quad \frac{1}{4},\frac{1}{4},\frac{1}{4}$
Cu (Mn)	16 d (.$\bar{3}$ m)	$\frac{5}{8},\frac{5}{8},\frac{5}{8} \quad \frac{3}{8},\frac{7}{8},\frac{1}{8} \quad \frac{7}{8},\frac{1}{8},\frac{3}{8} \quad \frac{1}{8},\frac{3}{8},\frac{7}{8}$

Both the positions of the R and Mn atoms are crystallographically equivalent. Rare earth atoms form the skeleton of the *fcc* crystal structure - some of them are located inside the cell. In turn, Mn atoms form four manganese tetrahedra arranged in characteristic chains based on *kagomé* planes, along the main axis of the unit cell (Figure S2). The interatomic distances in the elementary cell of the C15 phase are:

$$d_{\text{R–Mn}} = a\,(11)^{1/2}/8 = 0.415\,a,$$
$$d_{\text{R–R}} = a\,(3)^{1/2}/4 = 0.433\,a,$$
$$d_{\text{Mn–Mn}} = a\,(2)^{1/2}/4 = 0.354\,a.$$

References

[1] Zhu, J.H.; Liu, C.T.; Pike, L.M.; Liaw P.K. *A thermodynamic interpretation of the size-ratio limits for laves phase formation.* Metall Mater Trans A. **1999**, *30*, 1449–1452 and references threrein. https://doi.org/10.1007/s11661-999-0292-5

[2]Thoma, D.J.; Perepezko, J.H. *A geometric analysis of solubility ranges in Laves phases*. Journal of Alloys and Compounds, **1995**, *224*, Pp. 330-341. https://doi.org/10.1016/0925-8388(95)01557-4

[3] Stein, F.; Leineweber, *A. Laves phases: a review of their functional and structural applications and an improved fundamental understanding of stability and properties*. J. Mater Sci. **2021** *56*, 5321–5427. https://doi.org/10.1007/s10853-020-05509-2

[4] Hahn,T. *International Tables for Crystallography*. **2002** Vol. A, 5th Edition.

[5] Materials explorer. https://next-gen.materialsproject.org/materials/mp-1124/

[6] Chojnacki, J. *Metalografia strukturalna*. **1966** Wydawnictwo „Śląsk", Poland.

[7] Materials explorer. https://next-gen.materialsproject.org/materials/mp-1038