The symmetry analysis of structural deformations related to the hydrogen implementation in borohydrides

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Abstract. The symmetry of magnesium borohydride Mg(BH\textsubscript{4})\textsubscript{2} has been analyzed. In particular, relations between space groups I\textsubscript{4}1/amd(IT 141), I-4m2(IT 119) and F\textsubscript{2}2\textsubscript{2}2(IT 22) have been derived. As a result of the analysis based on the theory of the space groups and their representations we found all transformations from the parent structure, described by the high symmetry group, to the structures with symmetries belonging to the appropriate subgroups. For a given transformation we obtained the displacements of the atoms from their initial positions, the ordering of the hydrogen atoms over the interstitial sites and the ordering of the magnetic moments. In the description the number of free parameters has been reduced to the necessary minimum.

1. Introduction

Metal hydrides are known as safe media to store hydrogen with high density. In order to use hydrogen as a fuel in the transport sector, we need not only a light, cheap, safe and reliable hydrogen storage methods, but also high hydrogen storage capacity, fast kinetics and favourable thermodynamics. A usable hydrogen storage candidate, which meets all these criteria, has yet to be discovered. In this context light metal borohydrides are attractive due to their high gravimetric and volumetric hydrogen densities compared to other complex hydrides. Magnesium borohydride, Mg(BH\textsubscript{4})\textsubscript{2}, is a very promising candidate for hydrogen storage materials due to its high hydrogen content -14.8 wt\% [1] and due to the low hydrogen binding enthalpy [2].

Magnesium borohydride has been known since the 1950s, but the ground-state structure of it is still under debate. The experimentally [3][4][5][6] and theoretically [7][8][9][10] proposed structures do not match. The main debated question is related to the lattice stability of the proposed structures.

Recently a project under which several computational methods have been combined to build and compute the lowest energy structure of magnesium borohydride, has been initiated by the Division Hydrogen and Energy of the Swiss Federal Laboratories for Materials Testing and Research (EMPA) [11]. It has been found that the building motif of the crystalline structure of the alkali and the alkaline-earth metal tetrahydroborates is dictated by the coordination of the metal atom. The present study is closely related to this project. In particular, we have found relations of the space groups with the structures of Mg(BH\textsubscript{4})\textsubscript{2} reported in [11].

2. An introduction to the symmetry analysis

The symmetry analysis based on the theory of groups and representations has been applied to the description of the magnetic ordering in crystals for the first time by E.F. Bertaut [12][13]. He obtained the symmetry-adapted ordering modes, derived from the representation analysis, by the calculation of
the basis vectors of the irreducible representations. This method of analysis has been later developed by many other theoreticians, like Izyumov [14] and others.

The superstructure, as an ordering of some property of the initial crystal structure, may occur as a result of a phase transition induced by temperature, magnetic field or pressure. Each of the properties of the crystal that is localised on the atom sites may be described by a Wannier function $S$ defined by a set of equivalent positions. It may be a scalar (the change of probability of site occupations), a polar vector (displacements of atoms from the equilibrium positions), an axial vector (the ordering of magnetic moments), a tensor (the ordering of the quadrupole moments). The presentation of this function in the commonly used frame of coordinates related to the crystallographic system takes advantage of the translation symmetry only. The other symmetry relations are lost in this description. As a consequence, the description of many crystal properties becomes unnecessarily complicated. The presentation of the model structures in terms of the basis vectors (BV) $\mathbf{v}_{k\lambda\rho}$ of the irreducible representations of the initial symmetry group rather than in the frame of the crystallographic system (x,y,z), properly reflects the symmetry of the problem and provides the simplest, i.e. requiring the lowest number of independent parameters, form of the description of the structure. Thus, the Wannier function is expressed as a linear combination of the BVs:

$$
\mathbf{S} = \sum_{l\nu\lambda} c_{l\nu\lambda}^{k\nu} \mathbf{v}_{k\lambda}^{l\nu}
$$

(1)

where $l$, $\nu$, and $\lambda$ - correspond, respectively, to the vectors $\mathbf{k}$, to the irreducible representations (IRs) of the group and to the dimensions of the IRs.

The symmetry group $G(\mathbf{k})$ of the $\mathbf{k}$ vectors is a subgroup of the space group $G$. Consequently, the set of equivalent positions in the group $G$, the so-called orbit in $G$, may split to independent sets of equivalent positions in $G(\mathbf{k})$. Thus, one orbit in the group $G$ can lead to two or more orbits in the subgroup $G(\mathbf{k})$. The symmetry analysis uncovers the relations between the old sets of the equivalent positions (in the parent group) and the new sets of the equivalent positions (in the resulting subgroup).

The form of the basis vectors and the information which of the representations are relevant for the phase transition under consideration are directly given by the theory of groups and representations. Here we derive this information using the computer programme MODY [15] based on this. 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 a given orbit in the elementary cell of the crystal as well as in the elementary cell translated by a lattice vector $\mathbf{t}$, which just corresponds to a multiplication by $e^{i\mathbf{k}\cdot\mathbf{t}}$. Let us note that the set of parameters $c_{l\nu\lambda}^{k\nu}$ is restricted by several conditions. In particular, the resulting magnetic moments related to all atoms should be real. The conditions influence the set of equations satisfied by $c_{l\nu\lambda}^{k\nu}$. As a consequence the number of the independent free parameters is reduced and strictly determined. Finally, the model contains clearly defined minimum number of the free parameters and supplies strictly defined relations between the quantities localised on different crystal sites and describing the considered property. Each choice of these free parameters uniquely determines one of the possible models of the new structure that may appear after the phase transition.

The representation $\tau_{\nu}$ and the coefficients $c_{l\nu\lambda}^{k\nu}$ uniquely determine the symmetry of the structure, independently on the kind of the property taken into account. The type of the phase transition and the property under consideration is encoded in the form of the basis vectors.

3. Calculations:

On the request of the EMPA group we investigated whether there are some relations between the space groups: $I4_1/amd(141)$, $I4m2(119)$ and $F222(22)$. We performed the analysis using the programme MODY[15]. The programme gives relations between the parent groups and their
subgroups. It also calculates the basis vectors of the IRs and other characteristics of the groups which can be used for deriving the ordering modes. The results of the analysis are shown in Tables 1-7.

The subgroups of the parent group $I4_1/amd(141)$ related to the IRs $\tau_j$, $j=1,2,\ldots,10$ and ordering parameters $c_{k,l}^{j,v}$ for $k=(0,0,0)$, are listed in Table 1. As we can see, the destination group $I-4m2(119)$, relevant for the case under consideration, corresponds to the representation $\tau_8$.

### Table 1. Destination group - $I4_1/amd$ (141), Rep.- representations; Param. – free parameter $c_{k,l}^{j,v} = c_j$

| Rep. | Param | Destination groups |
|------|-------|---------------------|
| $\tau_1$ | $c_1$ | $I4_1/amd$ (141) |
| $\tau_2$ | $c_2$ | $I4_2$ (98) |
| $\tau_3$ | $c_3$ | $I4_1/a$ (88) |
| $\tau_4$ | $c_4$ | $I4 md$ (109) |
| $\tau_5$ | $c_5$ | $I4ma$ (74) |
| $\tau_6$ | $c_6$ | $I4md$ (74) |
| $\tau_7$ | $c_7$ | $F222$ (22) |
| $\tau_8$ | $c_8$ | $I-4m2$ (119) |

#### Dimension 2

| Rep. | Param | Destination groups |
|------|-------|---------------------|
| $\tau_9$ | | $P1$ (2) |
| $\tau_{10}$ | | $C2/m$ (12) |
| | | $C2/c$ (15) |

Next we had to take as parent group – symmetry $I-4m2$ group. Destination groups for parent (119) are reported in Table 2. and now we can see, that group F222 (22) is a subgroup.

In the next step we took $I-4m2(119)$ as the parent group. The destination groups are collected in Table 2. As one can see, F222(22) appears as a subgroup for $\tau_4$.

### Table 2. Destination group - $I-4m2$ (119), Rep.- representations; Param. – free parameter $c_{k,l}^{j,v} = c_j$

| Rep. | Param | Destination groups |
|------|-------|---------------------|
| $\tau_1$ | $c_1$ | $I-4m2$ (119) |
| $\tau_2$ | $c_2$ | $I-4$ (82) |
| $\tau_3$ | $c_3$ | $Imm2$ (44) |
| $\tau_4$ | $c_4$ | $F222$ (22) |

| Dim 2 | | $P1$ (1) |
|-------| | $C2$ (5) |
|       | | $Cm$ (8) |
The most important results contained in Tables 1 and 2 may be summarized as:

$I_{4d}/amd$ (141) $\rightarrow$ $\tau_8$ $\rightarrow$ $I$-4m2 (119) $\rightarrow$ $\tau_4$ $\rightarrow$ F222 (22)

The splitting relations for the subgroups I-4m2 and F222 for all types of Mg(BH$_4$)$_2$ atoms are shown in Table 3. The Wyckoff positions in the group I4$_d$/amd: Mg - 4a and 4b, B - 16h and H - two sets of 16h and 32i. It should be mentioned that the F-type cell is 2 times larger as the I-type cell. This leads to the doubling of the multiplicity of corresponding Wyckoff positions.

Table 3. Symmetry analysis – splitting of Wyckoff positions

| atoms          | Wyckoff positions |
|----------------|-------------------|
|               | I4$_d$/amd (141)  | I-4m2 (119) | F222 (22) |
| Mg            |                   |             |            |
| 4a            | 2a                | 4a          |            |
| 4b            | 2b                | 4b          |            |
| 2d            | 4c                |             |            |
| B             | 16 h              | 8i$_1$      | 16k$_1$   |
|               | 8i$_2$            | 16k$_2$    |            |
|               | 1. 16 h           | 1. 8i$_1$  | 1. 16k$_1$|
|               | 1. 8i$_2$        | 1. 16k$_2$ |            |
| H             | 2. 16 h           | 2. 8i$_1$  | 2. 16k$_1$|
|               | 2. 8i$_2$        | 2. 16k$_2$ |            |
|               | 32 i              | 16 j$_1$   | 3. 16k$_1$|
|               | 16 j$_2$         | 3. 16k$_2$ |            |
|               |                   | 3. 16k$_3$ |            |
|               |                   | 3. 16k$_4$ |            |

All transformations of the parent structure corresponding to the group I4$_d$/amd(141) leading to the structures of lower symmetry, for $k$=(0,0,0), have been analysed. The active representations of the invariable lattice $k$=(0,0,0) for different positions and for different types of orderings (modes) are shown in the Table 4. The designations S, P and A of the mode types correspond, respectively, to scalar (the change of probability of site occupations), polar (displacement of atoms from the equilibrium positions in the high symmetry structure) and axial (ordering of the magnetic moments). The column corresponding to $\tau_8$ is boldfaced because this case is most relevant for our discussion – it leads to I-4m2 destination group.

Table 4. Active representations for all types of modes - I4$_d$/amd (141)

| position | type of mode | representation |
|----------|--------------|----------------|
|          |              | dimension 1    | dim 2   |
|          | $\tau_1$    | $\tau_2$      | $\tau_3$ | $\tau_4$ | $\tau_5$ | $\tau_6$ | $\tau_7$ | $\tau_8$ | $\tau_9$ | $\tau_{10}$ |
| 4a (0,0,0)| S            | 1              | -        | -        | -        | -        | 1        | -        | -        |             |
| 4b (0,0, ½)| P            | -              | -        | 1        | 1        | -        | -        | 1        | 1        |             |
|          | A            | -              | -        | 1        | -        | 1        | -        | -        | 1        | 1           |
| 16h (0,z,y)| P            | 2              | 1        | 1        | 2        | 2        | 1        | 1        | 2        | 3           |
|          | A            | 1              | 2        | 2        | 1        | 2        | 2        | 1        | 3        | 3           |
| 32i (x,y,z)| S            | 1              | 1        | 1        | 1        | 1        | 1        | 1        | 2        | 2           |
|          | P            | 3              | 3        | 3        | 3        | 3        | 3        | 3        | 6        | 6           |
|          | A            | 3              | 3        | 3        | 3        | 3        | 3        | 3        | 6        | 6           |
Similar results for the group I-4m2(119) are collected in Table 5. Here the result for $\tau_4$ are most important – according to this representation the transformation to the F222 group is performed.

| Position | type of mode | Representation | $\tau_1$ | $\tau_2$ | $\tau_3$ | $\tau_4$ | $\tau_5$ |
|----------|--------------|----------------|----------|----------|----------|----------|----------|
| 2a (0,0,0) | S | 1 | - | - | - | |
| 2b (0,0,1/2) | P | - | - | 1 | - | 1 |
| 2c (0,1/2,1/4) | A | - | 1 | - | - | 1 |
| 2d (0,1/2,3/4) | S | 1 | - | 1 | - | 1 |

Using MODY for calculation of basis vectors, and corresponding mixing coefficients (Table 1) we can easily calculate many details concerning all types of modes. An example, corresponding to the position 16h (possible for B and H atoms) in 141 symmetry group, is shown in Table 6. The y and z quantities characterizing the 16h positions are taken from sets of data presented in [8]. $\Delta P_n$, $R_n$, $M_n$ characterize respectively change of probability of sites occupation, displacements of atoms from their equilibrium positions in the high symmetry structure and magnetic moments localized on these positions.

From our point of view the most important is the polar type displacement of the atoms.

| Wyckoff position | Type of modes | Results of calculations |
|------------------|---------------|-------------------------|
| h1 : (0,0,0, 485 0,230) | S | For atoms: h1, h4, h5, h8, h9, h12, h13, h16: $\Delta P_{hj}=+C$ |
| h2 : (0,0,0, 015 0,020) | $c^a=C$ | For atoms: h2, h3, h6, h7, h10, h11, h14, h15: $\Delta P_{hj}=-C$ |
| h3 : (0,0,0, 985 0,020) | $c^b=A$ | For atoms: h1, h2, h9, h10: $R_{hj}=(0,A,0)$ |
| h4 : (0,0,0, 515 0,230) | | |
| h5 : (0,515 0,000 0,770) | $P_1$-version | For atoms: h3, h4, h11, h12: $R_{hj}=-(0,A,0)$ |
| h6 : (0,515 0,500 0,480) | $c^x=A$ | For atoms: h5, h7, h13, h15: $R_{hj}=(A,0,0)$ |
| h7 : (0,485 0,500 0,480) | | |
| h8 : (0,485 0,000 0,770) | $P_2$-version | For atoms: h6, h8, h14, h16: $R_{hj}=(A,0,0)$ |
| h9 : (0,500 0,985 0,730) | $c^x=B$ | |
| h10 : (0,500 0,515 0,520) | | |
| h11 : (0,500 0,485 0,520) | | |
| h12 : (0,500 0,015 0,730) | | |
| h13 : (0,015 0,500 0,270) | | |
| h14 : (0,015 0,000 0,980) | | |
| h15 : (0,985 0,000 0,980) | | |
| h16 : (0,985 0,500 0,270) | | |
| c^a=M | For atoms: h3, h9, h11: $M_{hj}=(M,0,0)$ |
| A | For atoms: h2, h4, h10, h12: $M_{hj}=-(M,0,0)$ |
| c^b=M | For atoms: h5, h6, h13, h14: $M_{hj}=(0,M,0)$ |
| c^c=M | For atoms: h7, h8, h15, h16: $M_{hj}=(0,M,0)$ |
Likewise, Table 7 presents results for the position 8i in 119 group, for \( k=(0,0,0) \) and \( \tau_4 \).

| Wyckoff position | Type of modes | Results of calculations |
|------------------|---------------|-------------------------|
| 8i \( (x, 0, z) \) | S             | No active               |
| i1: (0.248 0,000 0.728) | S             | For atoms: i1, i5: \( \mathbf{R}_{ij} = (0,C,0) \) |
| i2: (0.752 0,000 0.728) | P             | For atoms: i2, i6: \( \mathbf{R}_{ij} = (0,-(C),0) \) |
| i3: (0.000 0,752 0.272) | \( c^4=C \)   | For atoms: i3, i7: \( \mathbf{R}_{ij} = (-C,0,0) \) |
| i4: (0.000 0.248 0.272) | \( c^4=A \)   | For atoms: i4, i8: \( \mathbf{R}_{ij} = (0,-(C),0) \) |
| i5: (0.748 0.500 0.228) | \( A_1\)-version | For atoms: i1, i5: \( \mathbf{M}_{ij} = (A,0,0) \) |
| i6: (0.252 0.500 0.228) | \( A_2\)-version | For atoms: i1, i2, i5, i6: \( \mathbf{M}_{ij} = (0,0,B) \) |
| i7: (0.500 0.252 0.772) | \( c^4 \)-version | For atoms: i3, i4, i7, i8: \( \mathbf{M}_{ij} = (0,-(A),0) \) |
| i8: (0.500 0.748 0.772) | \( c^4 \)-version | For atoms: i4, i8: \( \mathbf{M}_{ij} = (0,0,0) \) |

### 4. Summary

Using a computer programme MODY [15] we have derived all types of modes for all Wyckoff positions and for all active representations both for I41/amd (141) and for I-4m2 (119) space groups. Tables 1 - 7 indicate that the deformation of the structure from I41/amd to F222 is going in two steps. In each of them the Mg positions does not change while the B and H atoms move. This leads to the displacements and deformations of the BH4 tetrahedra surrounding the Mg atoms. The comparison of the predictions of the symmetry analysis will be compared with the predictions of the structure stability calculations and experimental data in a future.

### 5. Acknowledgments

The work was partially supported by Polish ministry of Science and Higher Education and CMA European Network for Excellence.

### References

[1] George L, Drozd V, Saxena S K, Bardaji E G and Fichtner M 2009 Structural Phase Transitions of Mg(BH4)2 under Pressure, *J. Phys. Chem. C* **113** 486-492

[2] Her J-H, Stephens P W, Gao Y, Soloveichik G L, Rijssenbeek J, Andrus M and Zhao J-C 2007 Structure of unsolvated magnesium borohydride Mg(BH4)2, *Acta Cryst. B* **63**: 561-568

[3] Riktor M D, Sørby M H, Chlopek K, Fichtner M, Buchter F, Züttel A and Hauback B C 2007 In situ synchrotron diffraction studies of phase transitions and thermal decomposition of Mg(BH4)2 and Ca(BH4)2, *J. Mater. Chem.* **17** 4939–4942

[4] Her J-H, Stephens P W, Gao Y, Soloveichik G L, Rijssenbeek J, Andrus M, and Zhao J-C 2007 Structure of unsolvated magnesium borohydride Mg(BH4)2, *Acta Cryst. B* **63**: 561–568

[5] Cerny R, Filinchuk Y, Hagermann H, and Yvon K 2007 Magnesium borohydride: Synthesis and crystal structure, *Angew. Chem.* **119** 5867–5869

[6] George L, Drozd V, Bardaji E G and Fichtner M and Saxena S K, 2009 Structural phase transitions of Mg(BH4)2 under pressure *Journal of Physical Chemistry: C* **113** 486-492

[7] Ozolins V, Majzoub E H and Wolverton C 2008 First-principles prediction of a ground state crystal structure of magnesium borohydride. *Phys. Rev. Lett.* **100** 135501

[8] Voss J, Hummelshj J S, Lodziana Z, and Vegge T 2009 Structural stability and decomposition of Mg(BH4)2 isomorphs- an ab initio free energy study, *J. Phys.: Condens. Matter* **21**

[9] Dai B, Sholl D S and Johnson J K 2008 First-principles study of experimental and hypothetical
Mg(BH4)2 crystal structures, J. Phys. Chem. C 112 4391–4395

[10] Zhou, Xiang-Feng; Qian, Quang-Rui; Zhou, Jian; Xu, Bo; Tian, Yongjun; Wang, Hui-Tian 2009 Crystal structure and stability of magnesium borohydride from first principles. Physical Review B 79 Issue 21, id. 212102

[11] Caputo R, Tekin A, Sikora W, Zuttel A 2009 First-principles determination of the ground-state structure of Mg(BH4)2 Chemical Physics Letters 480 203–209

[12] Bertaut E F in: Rado G T, Suhl H (Ed.) 1963 Treatise on Magnetism, 3, Academic Press, New York (Chapter. 4)

[13] Bertaut E F 1971 Magnetic structure analysis and group theory J. Phys.Colloques 32C1 462-470

[14] Izyumov Yu A, Syromyatnikov V N 1990 Phase Transitions and Crystal Symmetry (Dordrecht: Kluwer Academic Publishers) Chapter 2

[15] Sikora W, Bialas F, Pytlik L 2004 MODY: a program for calculation of symmetry – adapted functions for ordered structures in crystals, J. Appl. Cryst. 37 1015-1019 (Program available from: http://novell.ftj.agh.edu.pl/sikora/mody.htm)

[16] IZOTROPY (by Stokes and Hutch) http://www.physics.byu.edu/~stokesh/isotropy.html