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Interstitial hydrogen in Laves phases – local electronic structure modifications from the first-principles

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Understanding the microscopic aspect of hydride formation process provides an insight into the experimentally observed properties of prospective hydrogen storage materials. In this paper, we have studied the local structural and electronic modifications induced by hydrogen absorption in cubic C15 Laves phases AB_2 (A = Zr; B = Cr, Mn, Ni), as well as the stability of formed hydrides, by means of density functional theory (DFT). To address the effect of hydrogen absorbed in one of three tetrahedral sites (96g, 32e, and 8b) on the electronic structure of its surrounding atoms, we have calculated the electric field gradient (EFG) on the position of Cr, Mn, and Ni in pure and hydrogenated compounds. EFG is associated with the hydrogen site-preference, and formation enthalpies of ZrB_2H hydrides are used to examine their formation feasibility. Obtained enthalpies reveal that $ZrMn_2H$ and $ZrNi_2H$ are both unstable regardless of the occupied site, and only attainable hydride is $ZrCr_2H$, with comparable occupational probability of sites 96g and 32e. EFG results indicate that a hydrogen distribution within the crystal depends on the level of induced electronic structure modifications; *i.e.*, hydrogen site-preference is governed by the condition of minimal divergence of the electronic charge from its initial distribution.

1. Introduction

Laves phases are a large class of intermetallic compounds that exhibit reasonably high hydrogen storage capacity and favourable absorption/desorption kinetics around room temperature and ambient pressures. Consequently, they are being extensively investigated as potential hydrogen storage materials, or electrodes for the Ni/MH batteries;[1-8] however, optimization of their performance and practical properties is still necessary for such applications. Formation enthalpies and binding energies of hydrides, and changes in the ground state structure that occur after hydrogenation are constantly being reported for various types of compounds, but linking the practical features of the material to its microscopic structure still remains a challenging issue. For example, subtle modifications in the electronic structure of hydrogen storage materials, induced by the absorbed hydrogen, can stabilize or destabilize initial compounds. Evaluating the cause of such behaviour contributes to better understanding of the hydride formation process and experimentally observed properties of hydrides. Consequently, it is of paramount importance to thoroughly investigate the effect that hydrogen has on the electronic structure of prospective hydrogen storage materials,

and this study represents a contribution in that regard. It deals with the local electronic structure modifications that occur in cubic Laves phase compounds $ZrCr_2$, $ZrMn_2$, and $ZrNi_2$, due to the formation of corresponding monohydrides $ZrCr_2H$, $ZrMn_2H$, and $ZrNi_2H$.

Due to the experimentally observed storage capability of $ZrCr_2$ and $ZrMn_2$, as well as of the alloys from Zr-Ni phase system; all selected compounds have been previously studied. So far, the research focus has been based on their electrochemical performance and tuning of thermodynamic and kinetic properties by partial substitution of host atoms with various transition metals (e.g., V, Cr, Mn, Fe, Ni) and rare earths (La, Ce). In that regard, their hydrogen absorption capacity and absorption/desorption kinetics have been studied in the case of both pure and multicomponent systems.[1,2,9,10] Pure and hydrogenated $ZrCr_2$ is easily synthesized in cubic C15 structure, with the maximum storage capacity of 3 hydrogen atoms per formula unit. Additionally, pressure–composition– temperature (PCT) measurements revealed its satisfactory thermodynamic properties regarding the needed electrochemical stability.[2,9] $ZrMn_2$ is found to readily crystallize in the hexagonal C14 structure, and is able to store up to 3.6 hydrogen atoms per formula unit;[10,11] however,

several theoretical studies indicate the possibility of existing structural degeneracy at low temperatures, and forming of cubic C15 $ZrMn_2$ compound and $ZrMn_2H_{0.5}$ hydride.[1,7] Furthermore, optimization of the synthesis process of compounds in the Zr-Ni phase system led to the potential discovery of C15 Laves phase $ZrNi_2$. Recently, Kumar et al.[12] studied the effect of various concentrations of Ni on the $ZrMn_{2-x}Ni_x$ phase transformation from hexagonal C14 $ZrMn_2$ to cubic C15 $ZrNi_2$ compound, and revealed the existence of cubic Laves phase $ZrNi_2$. Acknowledging the previous studies, we have decided to examine the possibility of $ZrMn_2H$ and $ZrNi_2H$ formation in cubic configuration by calculating their heats of formation.

2. Details of calculations.

2.1. Crystal structure of studied compounds and calculation methodology.

The cubic AB_2 Laves phase crystallizes in $MgCu_2$ structure with $Fd\overline{3}m$ (O_h^7) space group, with atom A located on 8a cubic site and atom B on 16d noncubic Wyckoff site. During the absorption process, hydrogen can occupy three interstitial positions – 96g, 32e, or 8b. Unit cell of this structure with emphasized interstitial tetrahedra is presented in Fig. 1; for the sake of clarity some atoms are omitted from this figure.
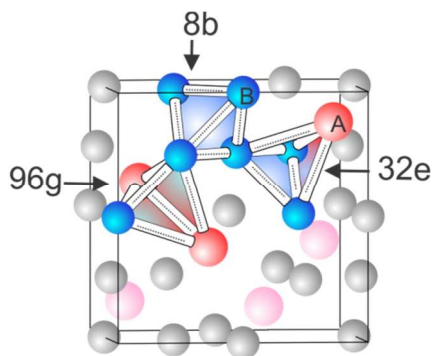

Fig. 1 Cubic C15 Laves phase unit cell, with indicated 96g (A_2B_2), 32e (AB_3), and 8b (B_4) tetrahedral interstitials. Some atoms are omitted for clarity.

Interstitial position 96g is a tetrahedral site formed by two A and two B atoms, A and B being the host atoms of AB_2 Laves phase. For simplicity, this site and respective hydride will be addressed as A_2B_2. In analogy to previous position, 32e site, which is constructed by one A and three B atoms, will be referred to as AB_3, and finally, 8b as B_4.

Depending on the size of the interstitial site, and type of A and B atoms, hydrogen preferably occupies A_2B_2 and/or AB_3 position, although, in some compounds B_4 site can also be occupied, but with considerably lower probability.[1,3,13] Considering that the foremost interest of this study is to observe the changes in electronic structure of atoms, in various tetrahedral arrangements, in the presence of hydrogen, and consequently provide an explanation for the hydrogen occupational site-preference, we have neglected the occupation probability and equally studied all three interstitial positions.

The used methodology assumed subsequent introduction of hydrogen into the A_2B_2, AB_3, or B_4 tetrahedral site, in order to construct AB_2H hydride. It was expected that due to different hydrogen's first coordination spheres (see Fig. 1.) the local crystal structure and electronic properties of host metals would be differently modified. Because the electric field gradient (EFG) directly reflects both geometrical and electronic aspects, induced modifications were studied by calculating it on the atomic site of Cr, Mn, and Ni, before and after hydrogenation.

EFG originates from the charge density deviation from spherical symmetry in the vicinity of observed nucleus, and it is extremely sensitive even to trivial changes in the electronic structure. Mathematically, it is defined as the second partial derivative of the electrostatic potential near nucleus ($V(\vec{r}), \vec{r} \rightarrow 0$) with respect to spatial coordinates $V_{zz} = \partial^2 V(0)/\partial x_i \partial x_j$.[14,15] It is designated as a traceless, symmetric second rank tensor, diagonal in the principal-axis coordinate system, and it is always present at the atomic site with the noncubic point group symmetry. According to a convention, its three nonzero components are ordered as $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$; however, it is completely described by its largest component, comparable with the experimental values. Furthermore, in full-potential formalism, used in present calculations, total EFG (V_{ii}^{tot}) equals a sum of the valence EFG (V_{ii}^{val}), which is a linear combination of partial valence electronic charge contributions ($V_{ii}^{val} = \sum_{ll'} V_{ii}^{ll'}$), and the lattice EFG ($V_{ii}^{lat}$).

The heats of formation were calculated by defining the energy difference between the total energy of studied hydrides and the total energy of the reactants; details can be found in our previous work.[16] Our calculations reflect the situation at 0 K, and do not incorporate the vibrational frequencies associated with zero point energy, since in various types of Laves phases they are significantly smaller then $\Delta H(AB_2H)$. In addition, their values in different interstitial sites are mutually comparable; therefore, they do not disrupt the calculated trend.[17]

2.2. Computational details.

The calculations were performed using a full-potential (linearized) augmented plane-wave ((L)APW) + local orbitals (lo) method, as implemented in WIEN2k,[14,18] a program package based on density functional theory (DFT).[19] WIEN2k describes the charge density without any shape restriction in the entire region of the crystal. Therefore, the charge density and the Coulomb potential are calculated very accurately in close proximity of the nucleus, as well as in the interstitial region between the atoms. Consequently, quantities like EFG are calculated very precisely.[14] The radii of the muffin-tin spheres, centred on the atomic nucleus, (R_{mt}) were set to 2.2 bohr for Zr, 1.95 bohr for Ni, Mn, and Cr, and 0.95 bohr for H. The number of basis functions used in the interstitial region was determined by $R_{mt}K_{max}$ parameter, which was set to 4.5; K_{max} signified the magnitude of the largest plane wave vector, while R_{mt} denoted the smallest MT radius in the unit cell. Inside the MT spheres wave functions were expanded in the spherical harmonics up to l_{max}=10. The cutoff energy that separated the core and valence states was −6 Ry for $ZrCr_2$ and $ZrNi_2$, and −7 Ry for $ZrMn_2$.

The exchange and correlation effects were included within the generalized gradient approximation (GGA), using the Perdew–Burke–Ernzerhof (PBE) scheme.[20] Brillouin zone integration was performed via the tetrahedron method, and depending on the occupied interstitial position, a mesh of 275 to 475 k points was used in the irreducible Brillouin zone. After testing the effect of spin polarization on studied values it was established that it has minor significance, as a result we have decided to neglect it. Self-consistency was achieved by demanding that the difference of integrated charge in successive iterations was less than 10^{-5} e. Relaxation of all atomic positions was performed until forces acting on all atoms were less than 1 mRy/bohr.

3. Results and Discussion

Lattice expansion, due to AB_2H monohydride formation, is calculated with respect to pure compounds. The optimized lattice constants are presented in Table 1. According to obtained results lattice expansion depends on the type of occupied interstitial site and the chemical nature of host metals (Cr, Mn, or Ni). Relative to the initial volumes, the expansion ranges from 5% to 15% per hydrogen atom, which is in accordance with previous studies.[1,3,13] Comparison of volume changes in series of monohydrides reveals nearly identical structural changes in all hydrogenated compounds. On the basis of this, it was difficult to evaluate to what extent hydrogen affects the studied structures. Therefore, we focused our research on observing the local crystal structure and electronic properties of atoms that surrounds the absorbed hydrogen.

Table 1. Calculated lattice parameters of AB_2 and AB_2H compounds.

|	$ZrNi_2$	$ZrMn_2$	$ZrCr_2$
C15	6.991	6.995	7.134
B_4	7.243	7.238	7.384
AB_3	7.155	7.147	7.318
A_2B_2	7.136	6.958	7.302

3.1. Electric field gradients on the atomic site of Cr, Mn, and Ni in pure and hydrogenated compounds.

EFG is considered to be a local property because it is determined by the electronic charge distribution of the selected atom, and by the spatial distribution of its neighbouring atoms. Subtle modifications of the local electronic structure induced by the absorbed hydrogen are sufficient to cause significant variations in the EFG value, and furthermore, to stabilize or destabilize a starting compound. Establishing the physical foundation of such correlation would be beneficial in providing the insight into the process of hydride formation, and experimentally observed properties of hydrogen storage materials.

Total EFGs on the atomic site of Cr, Mn, or Ni, the corresponding valence component, and partial orbital p (V_{zz}^{pp}) and d (V_{zz}^{dd}) contributions, have been calculated in pure and hydrogenated compounds and results are presented in Fig. 2.

In all compounds total EFG is entirely determined by its valence component $V_{zz}^{tot} \cong V_{zz}^{val}$, that is, by the charge density within the MT sphere. In pure and hydrogenated compounds value and sign of the EFG depend on the type of B atom, while in hydrides it also depends on the atom's spatial arrangement in the tetrahedral site itself.

In series of pure compounds, stable $ZrCr_2$ exhibits the lowest absolute EFG value, which indicates that compared to Mn or Ni a lesser charge deviation from the spherical symmetry occurs in the vicinity of Cr. In $ZrCr_2H_x$ and $ZrMn_2H_x$ (x=0,1) EFG exhibits an analogous increase of its absolute value throughout the series of tetrahedral sites. Established trend and its evident discrepancy in case of $ZrNi_2H_x$ can be understood in view of Cr, Mn, and Ni electronic configuration. However, to comprehend the importance of this, one should initially perceive that for all studied hydrides partial p and d terms predominantly contribute to the valence EFG in a form of linear combination $V_{zz}^{val} \cong V_{zz}^{pp} + V_{zz}^{dd}$ (see Fig. 2.). Atomic Cr and Mn have comparable electronic configuration (Cr: $4s^1 3d^5 4p^0$; Mn: $4s^2 3d^5 4p^0$), which differs from that of Ni ($4s^2 3d^8$). As a result of that, and their identical site symmetry, it can be expected that d and p charge in Cr and Mn are equivalently spatially distributed. Considering the spherical symmetry of s orbital, contribution from s states is negligible compared to V_{zz}^{pp} and V_{zz}^{dd}. Providing this explanation, it is relatively simple to understand the established trend and the lack of it in Ni-hydrides.
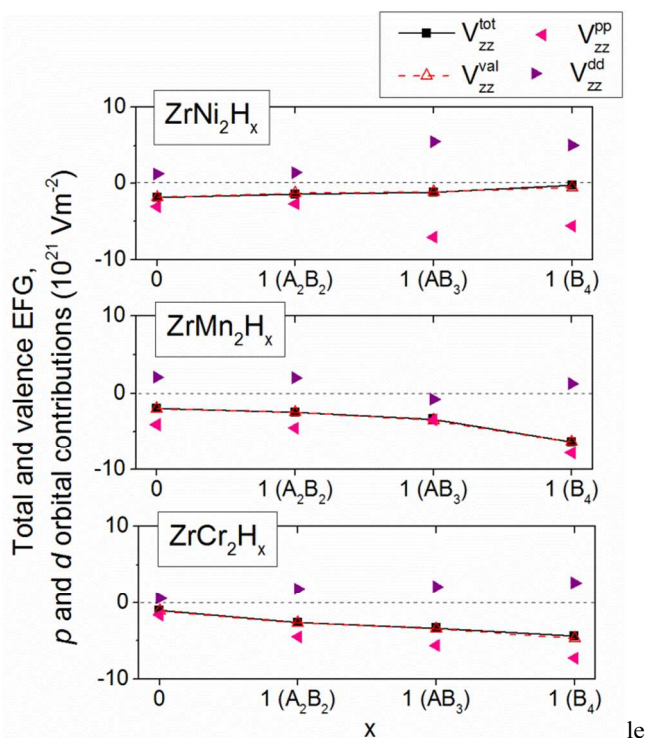
Fig. 2 Total EFG, valence EFG, and p and d orbital contributions calculated on the atomic site of Ni, Mn, or Cr, in pure and hydrogenated C15 Laves phases.

It was briefly mentioned that the governing factor in the occupation process is the volume of the interstitial position.

Accordingly, because it possesses the largest volume, A_2B_2 site will be preferably occupied and followed by the occupation of somewhat smaller AB_3 tetrahedra.[21] The smallest available B_4 site usually remains unoccupied; however, negative formation enthalpies for several B_4 hydrides have been reported.[13] At this point, we will correlate the obtained EFG values with the hydrogen occupational site-preference in studied compounds, and add a presumption to the "site-volume–site-preference" rule. According to our results, absorption of hydrogen in A_2B_2 site only slightly modifies the EFG values from the ones calculated in corresponding pure compounds. On the other hand, considerably pronounced divergence of the electronic charge from the original distribution is observed when hydrogen occupies B_4 tetrahedral site. On the basis of this, it can be argued that the interstitial positions of studied Laves phases are being occupied under the condition that the electronic charge of its surrounding atoms minimally diverges from the initial distribution.

3.2. Density of states (DOS) of studied compounds

Previous presumption can be supported by analysing the density of states (DOS) of hydrides and corresponding pure compounds, which is presented in Fig. 3. DOS is decomposed according to atoms of all studied structures, and given with respect to the Fermi level (E_F). In order to effectively signify hydrogen electron states, on the graphs of all hydrides are provided insets that represent the rescaled DOS in the equivalent energy range. The lowest conduction band in DOS graphs, which consists of hydrogen $1s$ states and overlapping host metal bands, is located in the energy range approximately from −5 eV to −11 eV (see insets in Fig. 3.). However, its relative position with respect to E_F depends on the occupied interstitial site. In comparison to A_2B_2 and AB_3, in B_4 hydride lowest conduction band is shifted further away from the E_F. Also, in all studied structures it is closest to the E_F in A_2B_2 hydride. This issue is addressed considering that several studies indicate that hydrides are more stable if hydrogen electrons states shift higher in energy; i.e., closer to E_F.[22,23] Furthermore, the shape of DOS, which corresponds to the distribution of occupied m-decomposed states, also depends on the type of the occupied interstitial site. DOS shape of A_2B_2 hydride, and to some extent of AB_3, is comparable with the DOS outline of pure compounds, while in B_4 hydrides it is significantly altered. This infers that compared to the hydrogen absorption in A_2B_2 or AB_3 site, energetically and spatially less favoured modification of the initial electronic structure occurs after its absorption in B_4 tetrahedral site. This confirms the aforementioned presumption, according to which modifications of the original electronic charge distribution of atoms surrounding the absorbed hydrogen should be minimal.

Further observation can be made regarding the correlation between the Fermi level position and the stability of studied structures. In pure $ZrCr_2$, Fermi level clearly separates the bonding from the antibonding states, while in $ZrMn_2$ it is shifted towards the antibonding area. This agrees with the pronounced stability of $ZrCr_2$, and infers that $ZrMn_2$ compound does not crystallize in cubic C15 structure.
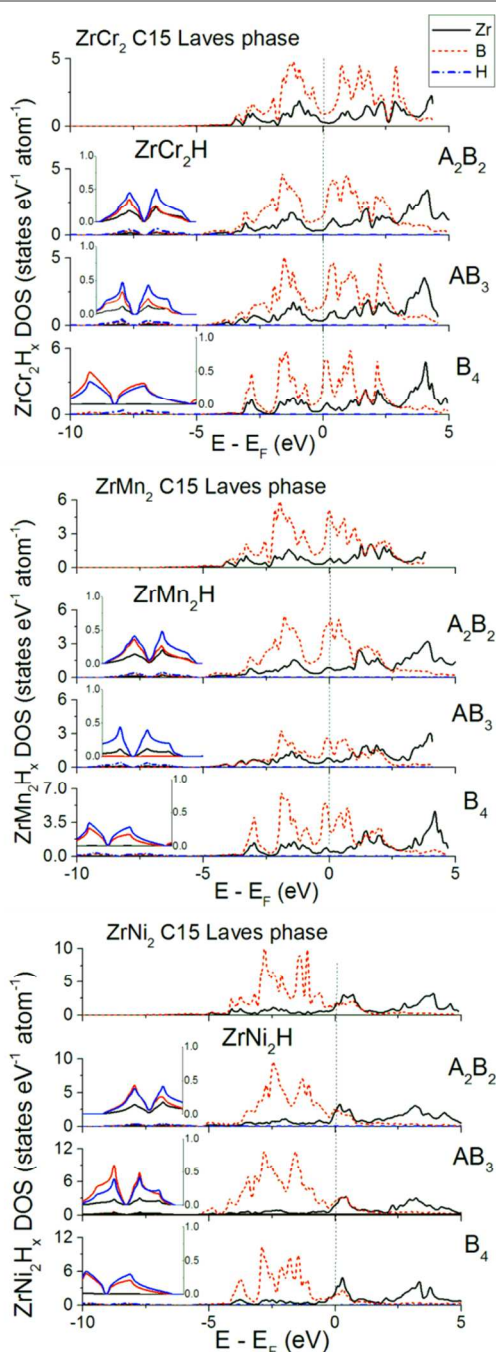

Fig. 3. Density of states of $ZrCr_2$, $ZrMn_2$, and $ZrNi_2$, as well as of their monohydrides, decomposed according to atoms. Insets: DOS rescaled to 1 eV^{-1}atom^{-1} to represent corresponding hydrogen states.

In addition, according to the position of E_F, all $ZrMn_2H$ interstitial hydrides are likely to be unstable. Position of E_F in DOS of $ZrCr_2H$ reveals the stability of A_2B_2 and AB_3 hydrides, and suggests the instability of B_4 hydride. DOS of $ZrNi_2$ and $ZrNi_2H$ does not afford such distinct assumptions, which is why in order to gain insight into its practical features formation enthalpies of this hydride have to be addressed.

3.3. Heats of formation of studied hydrides

In Fig. 4. are presented calculated formation enthalpies of all studied hydrides. It should be stressed out that the conditions under which the studied compounds are used are estimated according to a change in Gibbs free energy, not merely a change in enthalpy. However, several studies determined similar entropy changes in the solid hydride formation reactions, justifying the use of enthalpy change for the estimation of hydrides stability.[21]
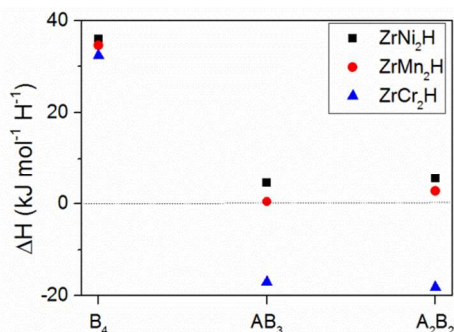

Fig. 4. Calculated formation enthalpies of studied hydrides.

According to the formation enthalpies of all three studied cubic Laves phase compounds the only stable monohydride is $ZrCr_2H$. $ZrNi_2H$ and $ZrMn_2H$ have positive formation enthalpies, which indicates that, regardless of the occupied interstitial site, all suggested hydrides are physically unattainable. When hydrogen is accommodated in A_2B_2 or AB_3 interstitial site of $ZrCr_2$, negative formation enthalpies are obtained, according to which both hydrides are stable. On the other hand, positive enthalpy of B_4 hydride suggests that occupation of this site destabilizes the initial compound. Calculated enthalpies of A_2B_2 or AB_3 hydrides are mutually comparable (-16.98 kJmol^{-1}H^{-1} for AB_3 and -18.17 kJmol^{-1}H^{-1} for A_2B_2) and lead to an assumption that in $ZrCr_2$ their occupation is competitive. To be able to directly compare our values with those from previous studies, experimental or computational, it would be beneficial to have the formation enthalpies for $ZrCr_2H_x$, with x=1. However, in lack of these results we can relate our values to the existing ones in respect to the range of available hydrogen concentrations. Previously studied concentrations ranged from 0.5 H/f.u. to ~3 H/f.u., and published formation enthalpies listed from the experimental value of -18 kJmol^{-1}H^{-1} for $ZrCr_2H_3$[10,24] to theoretical of -33.5 kJmol^{-1}H^{-1} for $ZrCr_2H_{0.5}$.[1–3] Our value for A_2B_2 hydride agrees excellently with the experimental one for 3 hydrogen atoms per formula unit.

Positive formation enthalpies of all $ZrNi_2H$ and $ZrMn_2H$ indicate that regardless of the occupied interstitial site these hydrides are always unstable. The obtained values suggest difficulties in any prospective synthesis attempt; nevertheless, hydrogenation of potentially synthesized cubic C15 $ZrMn_2$ or $ZrNi_2$ may also result in the phase transformation into hexagonal C14 Laves phase, or even some other stable

structure. Our results are in agreement with the experimental findings of Kumar and coworkers.[12] On the other hand, present computational and previous experimental results contradict the first-principles calculations conducted on hypothetical $ZrMn_2H_{0.5}$,[1] for which the authors obtained negative formation enthalpies. In addition, it is expected that the formation of hydrides in Zr-Ni system would be less probable with increasing Ni content, given that Ni, being the late transition metal, does not form stable binary hydride, while Zr does (ZrH_2). Baring in mind that $ZrNi_2$ forms a hydride of significantly decreased stability, with respect to the pronounced stability of ZrNi hydrides,[25,26] further investigation of $ZrNi_xH_y$ alloy system (1<x<2) could present a prospective way of tailoring the desired stability of the Zr-Ni hydrides.

4. Conclusions

First-principles calculations of the electronic structure of AB_2 cubic C15 Laves phases (A=Zr; B=Cr, Mn, Ni), and of their monohydrides, showed how the absorption of only one hydrogen atom substantially modifies the local electronic structure. Electronic charge distribution of hydrogen surrounding atoms was associated with the hydrogen formation process by calculating the electric field gradient (EFG) on Cr, Mn, or Ni, when hydrogen occupied one of three interstitial positions (A_2B_2, AB_3, B_4). Comparison of EFG values indicated that the hydrogen distribution within the crystal lattice is governed by the condition of minimal modification of the initial electronic charge distribution. Consequently, compared to the A_2B_2, or even AB_3 site, absorption of hydrogen in the B_4 interstitial site is not likely to occur in any of the studied compounds, as it considerably modifies the starting electronic structure of its surrounding atoms. This observation is in accordance with the previous results; in addition, it complements the former conclusion, according to which occupational site-preference of atomic hydrogen in cubic Laves phases is governed by the volume of interstitial tetrahedra ($A_2B_2{\rightarrow}AB_3{\rightarrow}B_4$). Furthermore, provided presumption was supported by the analysis of densities of states obtained before and after hydrogenation, which implied energetically less favoured modification of the electronic structure with respect to pure compounds in case of B_4 or AB_3 hydrides.

Calculated formation enthalpies indicated that of all studied hydrides only $ZrCr_2H$ is the stable one; with hydrogen occupying A_2B_2 or AB_3 interstitial site. Both $ZrMn_2H$ and $ZrNi_2H$ were found to be unstable, regardless of the occupied interstitial site. Our values agree with experimental results for all hydrides; however, they contradict the previously calculated formation enthalpies of Mn-hydride, according to which this hydride in cubic C15 structure can be stable.

Presented results suggest the existence of correlation between the electronic structure of atoms surrounding the absorbed hydrogen and hydride formation process in the cubic Laves phases. However, to provide a deeper insight into such correlation, and additionally study provided conclusions, it

would be beneficial if an extensive investigation is conducted on a broader class of prospective hydrogen storage materials.

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Notes and references

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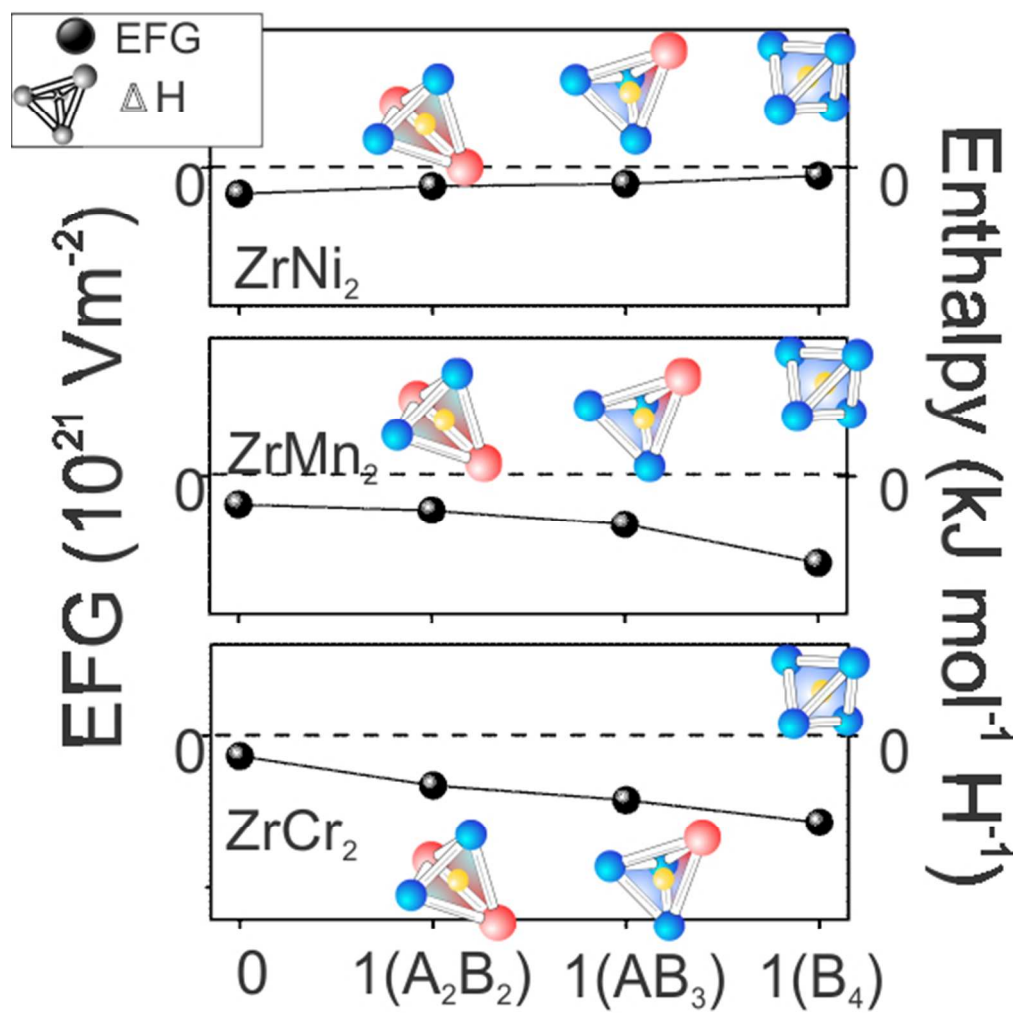
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