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ELECTRONIC STRUCTURE AND STABILITY OF MAGNESIUM DIHYDRIDE PHASES

With the help of band calculations in the framework of the full-potential linearized augmented-plane-wave model, information on the energy characteristics, the charge states of atoms, the nature of chemical bonds, the structure of valence bands, and the conductivity bands of polymorphous modifications of magnesium dihydride has been obtained. It is found that all magnesium dihydride phases are nonmagnetic insulators, with the electronic states of the metal and hydrogen atoms being hybridized within the whole energy interval of both the valence and conduction bands. It is shown that a reduction in the total charge of electrons in the interatomic region leads to a decrease in the cohesive energies of high-pressure magnesium dihydride phases, which are factors favoring the improvement of their hydrogen desorption kinetics.

Keywords: band calculations, magnesium dioxide, polymorphism, electronic structure, phase stability.

1. Introduction

Searching for ecologically clean energy sources is one of the determinative directions in the development of the modern society. Among the corresponding promising developments, there are considered devices in which hydrogen is applied as fuel. Hydrogen has been chosen as the most widespread element on the Earth. Besides, it has a high combustion heat, and the product of its combustion is water, which becomes finally introduced into the natural cycle.

Conventionally, hydrogen fuel sources can be divided into two large classes [1]: some of them use hydrogen in its gaseous (high-pressure devices) or liquid (cryogenics) state, whereas the other class is associated with absorbing media and materials that reversibly release hydrogen itself. Operational requirements for such sources are rather high and, in many respects, are not satisfied by the modern development of science and technology. In particular, they include, first of all, the application safety (this especially concerns devices belonging to the first mentioned class) and the list of requirements to the temperatures and pressures acceptable for the storage of hydrogen, as well as the effective kinetics of hydrogen absorption and desorption by various substances. The most important operational parameters characterizing such media are the content of the hydrogen absorbed by them and their cheapness as raw materials.

Magnesium and magnesium-based compounds are considered as one of the most promising materials for such purposes [2, 3]. It occurs, because magnesium is a quite widespread (the magnesium content in the lithosphere is about 2.1 wt.%), cheap, and light material, and the application of intermetallides on its basis does not pollute the environment. The concentration of hydrogen in magnesium dihydride (MgH_2) equals 7.67%, which is a rather high indicator. However, the thermodynamic stability of the so-called α-phase of magnesium dihydride at atmospheric pres-

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sure are such that there arise certain difficulties, when it is applied in practice. First, the process of hydrogen desorption from this phase is associated with rather high (>3000 °C) heating temperatures [4], and this circumstance limits its use, e.g., in fuel cells. Second, the saturation kinetics of the initial metal and, as a result, its hydride is weak. As it turned out, the latter circumstance is associated with a low dissociation level of molecular hydrogen at the MgH_2 surface [5] and the formation of an oxide layer on it, which prevents the hydrogen diffusion into the hydride "bulk" [6].

There are several approaches to overcome those difficulties. The kinetics of magnesium hydrogenation can be improved by the annealing of magnesium hydride specimens [7] or using catalysts [8]. In turn, the low level of hydrogen desorption kinetics from magnesium dihydride is considered [9–11] to be a result of the rutile-like structure of the discussed phase, i.e., of the "strength" of hydrogen chemical bonds in the metal matrix. It is clear that their transformation and their possible weakening must originate from changes in the structural features of magnesium dihydride itself. It is most likely that, just for this reason, the attempts to obtain this substance in other polymorphic modifications have been started. Currently, there are six such structural forms; five of them are generated under high-pressure conditions [12–14].

In the works cited above, as well as in others [15–17], the methods for synthesizing the initial α-phase of magnesium dihydride were discussed, whereas the structural, thermodynamic, and optical parameters of its high-pressure modifications were studied partially, and the total and partial electron densities of states in the α and γ phases were calculated without their detailed discussion and analysis [18, 19]. However, a number of comparative characteristics concerning the electronic structure of all phases of magnesium dihydride still remain unexamined in the framework of the general and systematic approach. For example, there is no important information that would shed light on the properties of the whole range of polymorphic MgH_2 forms, namely, on their energy characteristics, atomic charge states, the nature of interatomic chemical bonds, the structure of the valence and conduction bands, and the size and structure of forbidden gaps in the electronic state spectrum. The most important is the fact that the issue concerning the relation of all indicated characteristics to the specific features in the spatial structures of the magnesium dihydride phases themselves, the formation of which directly depends on the external pressure, remains open in many aspects. This work is aimed at finding answers to those questions.

2. Experimental Technique

The initial α phase of MgH_2 (α-MgH_2) is formed in the $P4_2/mnm$ symmetry (Fedorov space group No. 136) [12, 13]. In work [13], a detailed study of the nucleation processes of other polymorphic MgH_2 modifications was performed and, which is most important, the measurements of their structural parameters were carried out under high-pressure conditions. It turned out that the pressure P, when growing to a level of 5.5 GPa, stimulates the appearance of γ phase (No. 60 *Pbcn*) in magnesium dihydride specimens. Then, up to pressures of 9.35 GPa, the both indicated polymorphic forms coexist. At higher pressures, in a narrow pressure interval from 9.35 to 10.36 GPa, the polymorphic β modification with the *Pa-3* symmetry (No. 205) is generated in the MgH_2 specimens in addition to the available phases. As the pressure exceeds a threshold of 10 GPa, all those three phases transform into a single δ' modification with the symmetry *Pbca* (No. 61), which exists up to the experimentally reached pressure value $P = 16$ GPa.

If the pressure decreases, hysteresis phenomena are observed. In particular, at a pressure of 9.85 GPa, the δ' phase transforms into the β modification, which dominates down to a pressure of 6.23 GPa. Then, down to a pressure of 1.79 GPa, the α and γ phases coexist. Below this pressure, only the γ modification survives and remains intact even at atmospheric pressure. In this case, the γ modification is accepted to be considered metastable with respect to the α phase, because its total energy decreases by 0.81 meV in comparison with that for the α phase [13]. The coexistence of the α and γ phases in various MgH_2 specimens under atmospheric pressure was also pointed out in work [12]. In the cited work, as well as in work [13], the *Pbca* phase was detected at a pressure of 13.9 GPa. In addition, the so-called HP1 phase with the $Pbc2_1$ symmetry was also revealed at the same pressure. A detailed theoretical group analysis performed in this work showed that this phase should be considered as a modification with the $Pca2_1$ symmetry (No. 29). At the pressure elevation to 21.9 GPa, a new HP2 phase with the *Pnma* lattice symmetry (No. 62) was found [12].

In this work, band calculations of the electronic structure of all indicated phases of magnesium dihydride were carried out. In the calculations, the structural data reported in works [12, 13] were used. The band calculations were performed in the framework of the density functional theory (DFT) using the full-potential linearized augmented-plane-wave (FLAPW) model [20] with the gradient approximation of the electron density of states (the Gga-generalized gradient approximation) in the form given in work [21]. The well-known software package Wien2k [22] was used to calculate the electronic structure parameters.

The radii $R_{\rm mt}$ of the muffin-tin (MT) spheres (the intraatomic regions I of unit cells) were chosen to minimize the size of the intersphere region II in the *Pnma* phase, where the unit cell volume is minimum. For all examined MgH_2 phases and all atoms in those compounds, the following $R_{\rm mt}$ values were taken: $R_{\rm mt} = 2.20a_0$ for magnesium and $R_{\rm mt} = 1.18a_0$ for hydrogen, where $a_0 = 5,2918 \times 10^{-11}$ m is the Bohr radius.

The electronic structure parameters for the $P4_2/mnm$, *Pbcn, Pa-3 Pbca*, $Pca2_1$, and *Pnma* phases of magnesium dihydride were calculated using 120, 125, 119, 126, 125, and 140 points, respectively, in the nonreducible parts of their Brillouin zones.

The LAPW bases [22] were applied to approximate the electron wave functions for all atoms. The basis set size was obtained from the product $R_{\rm mt}K_{\rm max} = 3.0$, where $K_{\rm max}$ is the maximum magnitude of the reciprocal cell vector. When choosing the maximum orbital quantum number for partial waves in the MT spheres, the values $l = 10$ and $l = 4$ were used to calculate the non-muffin-tin matrix elements.

The cohesive energies were calculated as the difference between the total energy of the unit cell in the specific MgH_2 phase and the sum of the total energies of composing atoms located at "infinity" from one another [23], with the required values being obtained according to the recommendations of work [24].

A trial series of calculations in the spin-polarized version showed that all polymorphic forms of magnesium dihydride are non-magnetic. Therefore, all parameters discussed below were obtained in the framework of the scalar-relativistic approach [22].

3. Discussion of Obtained Results

Let us analyze the results obtained in this work. Figure 1 illustrates some characteristics calculated for all discussed polymorphic forms of magnesium dihydride. The pressure P values are indicated at which the discussed phases can exist. One can see that such parameters as the cohesive energy and the atomic charge states vary, in effect, symbatically with the pressure, whereas the behavior of the curves characterizing the cell volume V and the charges in the interatomic region II is opposite to the pressure(P)-

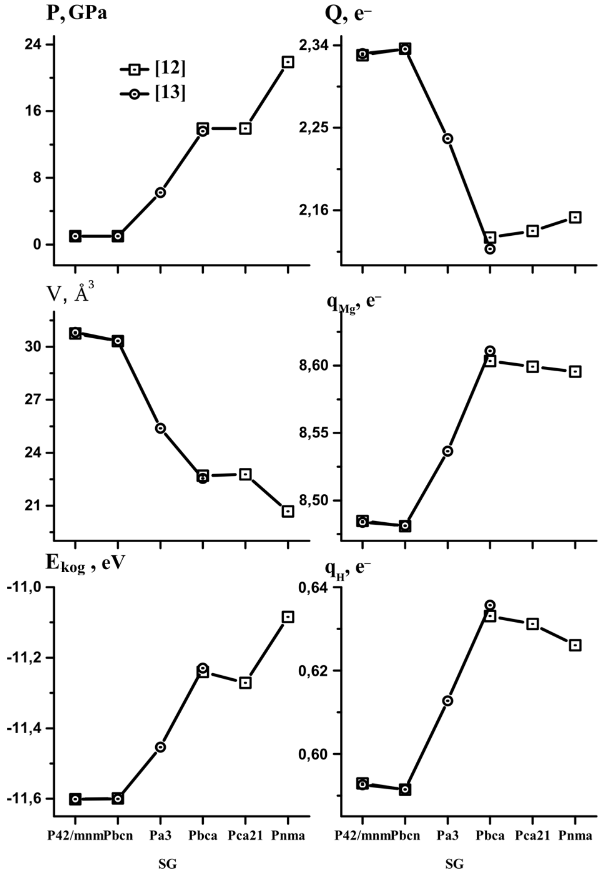

Fig. 1. Dependences of the volume V, cohesive energy $E_{\rm kog}$, and charges Q (e^- is the electron charge) per MgH_2 formula unit in the interatomic regions II, and the charges of valence electrons in magnesium ($q_{\rm Mg}$, – taking into account the Mg 2s-electrons) and hydrogen ($q_{\rm H}$) atoms on the phase composition (SG, Space Group) of magnesium dihydride. P is the pressure at which the corresponding polymorphic form exists. Hereafter, the parameter values obtained on the basis of the structural data taken from works [12, 13] are marked by the corresponding symbols (see the legend in the upper-left panel) and connected by lines for illustrative purpose

versus-symmetry group (SG) dependence. It is quite expected and reasonable that the reduction of the volume V at the transition between the extreme "points" $P4_2/mnm$ and $Pnma$ reaches a rather large value of 10.10 Å^3, whereas the volume reduction between the nearest point $P4_2/mnm$ and $Pbcn$ equals 0.46 Å^3. The pressure constancy in the pairs $P4_2/mnm$-$Pbcn$ and $Pbca$-$Pca2_1$ transforms into almost a "plateau' between the indicated pairs of modifications for other parameters presented in Fig. 1.

Really, the cohesive energy of the $P4_2/mnm$ phase exceeds that of the $Pbcn$ polymorphic form by 2.1 and 0.61 meV according to the values obtained on the basis of structural data taken from works [12] and [13], respectively. On average, this excess equals 1.36 meV, which suggests that the $Pbcn$ phase can be considered as metastable [13] and existing under atmospheric pressure conditions. At the same time, the increase of the cohesive energy value in the $Pca2_1$ phase in the pair of modifications $Pbca$-$Pca2_1$ reaches a much larger value of 30.3 meV. In general, the transition to high-pressure phases is accompanied by a drastic drop in the cohesive energy values, namely, the energy "distance" between the "extreme" pair of $Pnma$ and $P4_2/mnm$ states becomes substantially larger and equals 517.2 meV.

The mechanism governing the loss of the chemical bond stability in the high-pressure phases can be elucidated by analyzing the values of the charges Q in the interatomic region II. Indeed, using the logic of the theory of chemical bonds [25], the presence of electrons in the region between the atoms points to the covalent character of chemical bonds: the higher the total electron charge here, the stronger the interatomic interaction. On this basis, it can be asserted that a drastic decrease of the interspherical charge along the sequence of polymorphic forms $Pbcn \rightarrow$ $\rightarrow Pa\text{-}3 \rightarrow Pbca$ leads to an overall weakening of the covalent component in their interatomic chemical bonds, which correlates with the monotonic decrease of their cohesive energies. The transition from the $Pbca$ phase to the $Pca2_1$ one does not contradict this approach: here, the growth of the cohesive energy in the latter modification occurs due to the increase of Q values, i.e., the strengthening of interatomic covalent bonds in it.

However, the transition pairs $P4_2/mnm \rightarrow Pbcn$ and $Pca2_1 \rightarrow Pnma$ are not described by the above picture. It turns out that the growth of the interspherical charge Q in the former pair is small: only about $0.005e^-$, where e^- is the electron charge, whereas the increase of Q in the latter pair reaches a more appreciable value of $0.015e^-$. In the former case, the small difference between the Q values can be somehow justified by the accuracy of their determination ($0.001e^-$) at calculations, but no origin of inconsistency for the cohesive energy and the interspherical charge data was revealed in the latter case.

At the same time, since the total charge of valence electrons per MgH_2 formula unit is constant, the very transformation of Q values is rigidly related to the changes in the charge states of the atoms entering the composition of examined phases. Indeed, as follows from Fig. 1, the charges of the magnesium and hydrogen atoms vary synchronously and in the opposite way to the charges in the interatomic region II. The weakening of the covalent interatomic bonds and the accompanying decrease in the cohesive energy of the high-pressure MgH_2 phases would undoubtedly improve their kinetics of hydrogen desorption in practice, if there were a possibility to transform those phases into a state that would be thermodynamically stable under normal atmospheric pressure.

The picture of interatomic bonds in the magnesium dihydride phases can be appended with information on the structure of their electronic state spectra. The relevant data are presented in Figs. 2 and 3. Several important conclusions follow from them. First, the spectra of all MgH_2 phases contain wide forbidden-energy gaps that separate the valence and vacant states. Hence, all polymorphic phases of magnesium dihydride turned out to be insulators. For the initial α-$P4_2/mnm$ phase, this conclusion is confirmed by optical measurements carried out in work [17], where a value of 5.6 ± 0.1 eV was obtained for the energy gap. Second, the states of metal and hydrogen atoms turned out hybridized within the entire energy interval of both the valence and conduction bands in manganese dihydride. Third, for most phases, the states of hydrogen atoms dominate in their valence bands, whereas the states of magnesium atoms dominate in the conduction band. The spectral composition of electronic states (Fig. 3) testifies that the bottom of the valence band in the MgH_2 phases is mainly formed by the densities of states of Mg s-electrons, which are genetically related to $3s$-electrons of Mg atom. Its middle region is mainly formed by Mg p-valence elec-

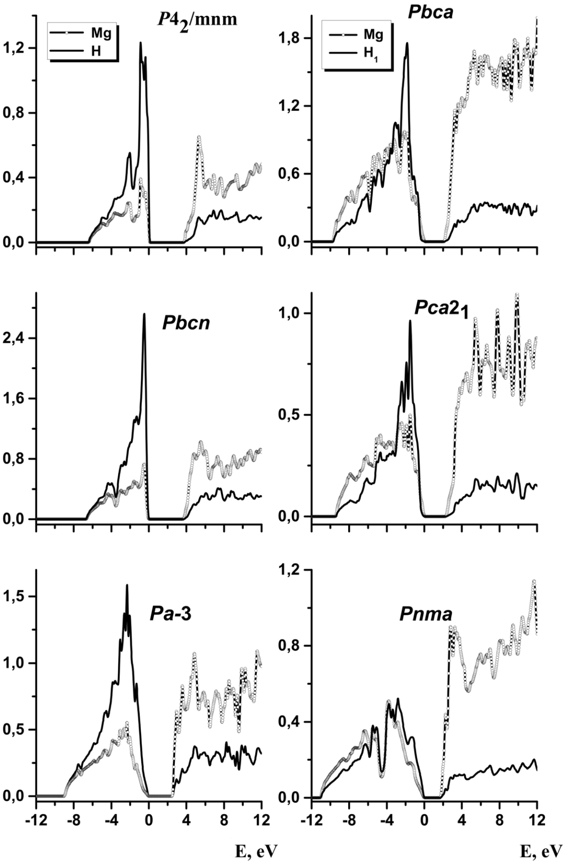

Fig. 2. Total densities of electronic states in atoms of magnesium dihydride phases. For the atomic types, see the legends. The energy distributions of states in different hydrogen atoms (H_1 and H_2) in the polymorphic forms *Pbca, Pca*2_1, and *Pnma* turned out quite similar; therefore, the total densities of states for only the H_1 atom in those phases are exhibited. The results for the *nïSnïSnïS*2_1 and *Pnma* phases were obtained using the structural data from work [12]; the results for other phases were obtained using the structural data from work [13]. The energies are reckoned from the Fermi level

trons, which originate from the unoccupied $4p$-states of free and unexcited magnesium atoms. In turn, the valence band top is mainly formed by s-electrons of hydrogen atoms with a small admixture of Mg $3d$-electrons. A detailed analysis shows that, on average, the contribution of Mg $3d$-electrons does not exceed 1.1% of the total charge of MgH_2 valence electrons. As concerning the spectral composition of the conduction bands, the s- and p-electron states of metal atoms dominate in them, whereas the density of states of d-electrons turned out low. The contribution of the partial s-states of hydrogen atoms to the formation of conduction band is also insignificant.

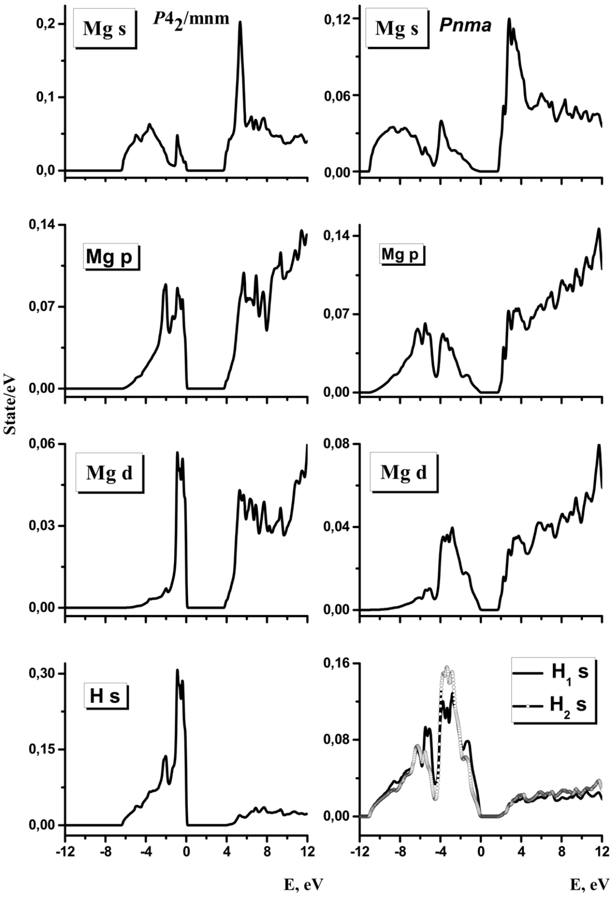

Fig. 3. Partial electron state densities in the atoms of magnesium dihydride phases calculated using the structural data taken from works [12, 13]. The energies are reckoned from the Fermi level

So, which are the most illustrative quantitative changes of the parameters that could characterize the discussed distributions at the transition to the high-pressure phases of magnesium dihydride? Even a quick glance at the energy distributions of atomic states (Figs. 2 and 3) allows one to understand that the successive motion along the sequence *P*$4_2/mnm$ → *Pbcn* → *Pa*-3 → *Pbca* → *Pca*2_1 → → *Pnma* leads to an appreciable decrease of the forbidden gap width E_g and an increase of the valence band width W in those states. Quantitative data illustrating this remark are shown in Fig. 4. Here, similarly to Fig. 1, the behavior of both curves is "governed" by the external pressure P. Really, the depen-

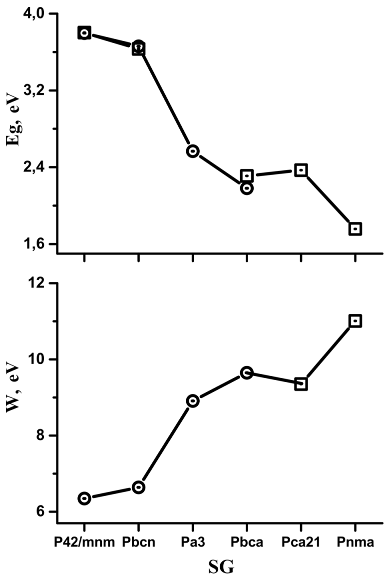

Fig. 4. Forbidden, E_g, and valence, W, band widths in magnesium dihydride phases

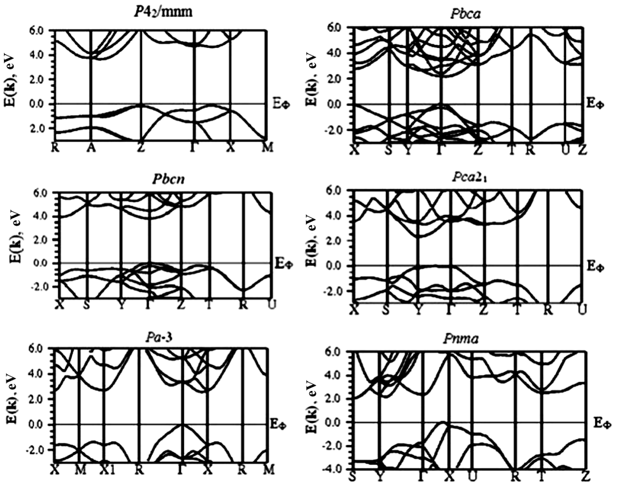

Fig. 5. Dispersion dependences $E(\mathbf{k})$ for MgH_2 phases near the corresponding Fermi energy E_F

dence W (SG) actually repeats the dependence on the external pressure, whereas the gap widths in the magnesium dihydride phases change with the pressure in the opposite way, almost synchronously with the volume V per MgH_2 formula unit (see Fig. 1). A reduction of the E_g values along the discussed sequence of polymorphic MgH_2 forms increases the probability of exciting electrons to their conduction band [23], i.e., it facilitates the possibility of the formation of typical homogeneous semiconductors among the high-pressure phases. The same can also be evidenced by the regular increase of the valence band width W in the high-pressure phases, since the value of W is directly proportional to the integral of electron hopping between lattice sites in the Hubbard model [26].

Let us analyze the structure of the forbidden bands themselves and consider the energy band structures $E(\mathbf{k})$ in magnesium dihydride (see Fig. 5). The direct gap of the minimum energy, which is located at the point H of the Brillouin zone, is characteristic only of the γ-*Pbcn* phase. For other polymorphic forms of magnesium dihydride, the minimum energy gaps turned out indirect. For instance, for the β-*Pa*-3 modification, the valence band maximum is located at the point Γ, and the conduction band minimum is located in the segment Γ-X near the point X. As for the valence band top and the conduction band bottom, which participate in the formation of forbidden gap energy in the δ'-*Pbca* modification of MgH_2, the former is located at the center of the Brillouin zone (the point Γ), and the latter is located in its vicinity in the direction toward the point Z. In the $Pca2_1$ phase, those extreme points are located near the middle of the segment Y-Γ and at the point Y itself. In the maximum-pressure phase *Pnma*, the both extreme points are located near the points X (the interval Γ-X) and Y (the segment Γ-Y), respectively. The indirect energy gap in the α-$P4_2/mnm$ phase, which exists under atmospheric pressure, is formed by the extremum points in the space of reciprocal wave vectors $\mathbf{k}$'s that are located in the intervals Γ-X and A-Z. An optical gap of 4.6 eV is determined at that by the values of the wave vector $\mathbf{k}$ corresponding to the conduction band bottom (the segment A-Z). This value is approximately 1.0 eV less than the experimentally measured value of the previously mentioned gap. This fact is not surprising because it reflects the general shortcoming of band calculations when determining the values of forbidden bands in the energy spectrum of insulator states, which consists in that traditionally implemented calculation schemes give, as a rule, underestimated values for E_g.

4. Conclusions

1. All polymorphic phases of magnesium dihydride are non-magnetic insulators. The minimum direct en-

ergy gap, which is located at the point Γ of the Brillouin zone, is characteristic of only the γ-*Pbcn* phase. In other polymorphic forms of magnesium dihydride, the minimum energy gaps turned out indirect.

2. The electronic states of the metal and hydrogen atoms are hybridized within the whole energy interval of both the valence and conduction bands of polymorphic MgH_2 forms. The bottom of their valence bands is mainly formed by the Mg s-electrons, and the middle region of the bands mainly by the Mg valence p- electrons; mainly the H s-electrons and Mg d-electrons are located near their top. The electron s- and p-states of metal atoms dominate in the conduction band.

3. The cohesive energy, the atomic charges, and the valence band width in the magnesium dihydride phases change symbatically with the pressure within the pressure intervals of their existence. The cell volume and the charges in the interatomic region II per MgH_2 formula unit MgH_2, as well as the band gap widths in the polymorphic forms of magnesium dihydride change in the opposite way.

4. A decrease of the interspherical charge gives rise to an accompanying weakening of covalent interatomic chemical bonds and, as a result, to a reduction of the cohesive energy in the high-pressure phases of magnesium dihydride, which are factors that favorably improve the hydrogen desorption kinetics of those phases.

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ЕЛЕКТРОННА БУДОВА І СТАБІЛЬНІСТЬ ФАЗ ДИГІДРИДУ МАГНІЮ

За допомогою зонних розрахунків в моделі FLAPW (the full-potential linearized augmented-plane-wave) отримано інформацію про енергетичні характеристики, зарядові стани атомів, характер хімічних зв'язків, структуру валентних смуг і смуг провідності поліморфних модифікацій дигідриду магнію. Виявлено, що всі фази дигідриду магнію є немагнітними ізоляторами, а електронні стани атомів металу та водню виявились гібридизованими на всьому протязі як їхніх валентних смуг, так і смуг провідності. Показано, що зниження сукупного заряду електронів у міжатомній області приводить до зменшення когезійних енергій фаз високого тиску дигідриду магнію – чинників, які сприяють поліпшенню кінетики десорбції водню.

Ключові слова: зонні розрахунки, дигідрид магнію, поліморфізм, електронна будова, стабільність фаз.