Classification of hydrides according to features of band structure

S. Zh. Karazhanov[1*], U. Sheripov[2], and A. G. Ulyashin[1**]

[1]Institute for Energy Technology, P.O. Box 40, NO-2027 Kjeller, Norway

[2]Physical-Technical Institute, 2B Mavlyanov St., 700084 Tashkent, Uzbekistan

In this work band structure of hydrides has been studied by the density functional calculations. From analysis of band structures it is found that similar to semiconductors some hydrides possess open fundamental band gap and those hydrides can be classified based on the following three characteristic features. The first one is based on value of the fundamental band gap and therefore the hydrides have been classified as narrow band gap and wide band gap materials. The second one is based on relative location in k space of the bottommost conduction band and topmost valence band compared to each other. Therefore the hydrides can be classified also as direct band gap and indirect band gap materials. The third one is based on the origin of the topmost valence and depends on the dominant contribution of s-, p-, and d-electrons to the topmost VB. According to this criterion the hydrides can be classified as type-s, -p, -d or hybridised materials. The classifications can be useful for applications of hydrides for the construction and processing of electronic devices in frame of the recently invented "hydride electronics".

Keywords: classification, metal hydrides, semiconductors, electronic materials, first-principles calculations.

[*]Corresponding author: smagul.karazhanov@ife.no

[**]Present address: SINTEF, Forskningsveien 1, P.O. Box 124 Blindern, NO-0314 Oslo

1. Introduction

Hydrides have found recently wide range applications as the hydrogen storage materials [1] and smart windows [2, 3]. For these applications hydrogen content, reversible and fast kinetics of the cyclic process of hydrogen adsorption and desorption without degradation of the material, etc. are extremely important. However, for the hydrides it is not important to posses the band gap or electrical conductivity. Based on these requirements and according to the nature of the bonding to other atoms of the host lattice, hydrides have been classified into three distinct classes: (i) covalent or volatile, (ii) saline or ionic, and (iii) metallic [4].

Recently, novel application of hydrides has been suggested in semiconductor electronics [5, 6], photovoltaics [7] and optoelectronics [8]. For these applications weight percent of hydrogen in the compound, fast kinetics of hydrogen absorption and desorption are not preferable. Here an air- and moisture-stable hydrides with as slow as possible kinetics of hydrogenation/dehydrogenation processes, present considerable interest. So far, such hydrides have been left out of attention, since they are not useful for the hydrogen-storage purposes. However, such materials are extremely important for the above-mentioned novel applications. It is important to note also that in order to be suitable for the novel applications, the hydrides should have open fundamental band gap and be capable to conduct electrical current. Verifications of such possibility is the most important issue, which has to be studied in details for each concrete case of a given hydride material.

It should be mentioned that from the studies of hydrogen storage materials some preliminary results, concerning electronic structure, electrical and optical properties of metal hydrides have already been obtained, which would be the basic information to initiate investigations on the novel application in semiconductor electronics. Namely, it is found that the fundamental band gap of semiconducting hydrides can be varied in wide energy range from ~0.6 to 7.0 eV (see, e.g., [4, 9-11]). It is necessary to note also that some hydrides with an open band gap are found to conduct

electrical current [9, 11, 12]. It has to be mentioned also that after the invention of "hydride electronics" [7], comparative analysis of electronic structure and optical properties of hydrides and semiconductors has been performed [4-6]. In particular it is found [8], that electronic structure and optical properties of cubic and monoclinic modifications of Mg_2NiH_4 are similar to that of crystalline and hydrogenated amorphous Si, respectively. It was reported [13] that the band gap of SrAlSiH is close to that of Ge. Application of hydrides as antireflection coatings has been suggested [14], etc.

The studies on the novel applications of hydrides have been specified into a scientific field called "hydride electronics" [8]. It has been formed at the intersection of two scientific fields such as "physics of semiconductors" and "hydrogen storage materials". Number of the hydrides suitable for the novel applications, will increase with time and creates the necessity to classify them. The aim of this paper is to perform classification of hydrides, based on features of their band structures. Three different characteristic features of semiconductors such as (i) narrow band gap/wide band gap, (ii) direct band gap/indirect band gap as well as (iii) the origin of the topmost valence band, which depends on the contribution of s-, p- or d- electrons (type-s, -p, and -d, respectively) have been used in this work for this purpose.

2. Computational details

Band structure calculations have been performed using the Vienna *ab initio* simulation package (VASP) [15, 16]. Generalized-gradient approximation (GGA) has been used following the Perdew-Bueke-Ernzerhof scheme (PBE) [17] for the exchange-correlation functional. Non-norm-conserving pseudopotentials have been used generated in accordance to the projector-augmented-wave (PAW) method [18, 19]. It allowed us to construct orthonormalized all-electron-like wave functions for the atoms of the hydrides. Lattice relaxation was performed by using the conjugate

gradient method. The plane-wave cutoff energy of 500 eV was used for all the calculations. The convergence was achieved when the forces acting on the atoms were smaller than 20 meV $Å^{-1}$ and the total energy difference between two consecutive iterations were $< 10^{-6}$ eV. The convergence criteria and more details about the optical calculations were discussed in Ref. [20]. Structural and positional parameters used in the present calculations for the hydrides have been obtained from Refs. [4, 10, 21-26].

3. Results and discussions

Depending on band gap values hydrides studied in this work can be classified as narrow band gap and wide band gap materials. It is established that fundamental band gap of semiconducting hydrides analysed in the present work can be in the wide range from infrared to ultraviolet parts of the energy interval. Table 1 shows energy band gaps for a number of hydrides studied in this paper along with those determined experimentally and/or calculated by other authors using the *ab initio* methods. It is well known that in DFT calculations band gaps of solids are systematically underestimated. Commonly, the calculated band gaps are ~30-50% smaller than the experimentally determined ones. We did not use the rigid shift technique, quasiparticle or other corrections to reduce the DFT related band gap error. Thus, the real values of the band gaps of hydrides studied can be larger than the calculated ones presented in Table I. Systematic experimental studies are needed to clarify the question.

Analysis of Table 1 shows that fundamental band gap of the hydrides can be varied in wide range from infrared to ultraviolet. Among the 40 hydrides considered in this work 20 of them possess the fundamental band gap in the ultraviolet range (~2.8-7.0 eV). In principle these hydrides could be classified as insulators. However, this classification can be done not only based on the fundamental band gap value, but also on band dispersion, which can determine carrier effective

mass and mobility, as well as dopability of the hydride. For example, despite its large fundamental band gap of ~5.5 eV [27] diamond is considered as semiconductor, because its electronic properties are even better than the other wide band gap semiconductors, such as, e.g. GaN or SiC, with smaller band gaps 3.44 eV and 3.00 eV [28], respectively, than the diamond. In particular, diamond benefits of high carrier mobilities (μ_n=2400–4500 cm^2/V s and μ_p=2100–3400 cm^2/V s at room temperature [27]. However, SiNx:H with band gap ~4.7-4.9 eV [29] is considered as insulator, because the compound is hardly dopable and its electrical conductivity is extremely small. Here it should be noted that such a comprehensive experimental study is not yet available for hydrides. Consequently, for the classification suggested in this work we are using the general terminology "wide band gap". More detailed classifications as to whether the semiconducting hydride is insulator or wide band gap semiconductor can be done only after comprehensive experimental studies.

From Table 1 it is seen that fundamental band gaps of eleven hydrides are in the visible range (~1.8-2.8 eV). Moreover five hydrides possess fundamental band gaps in the near infrared (~1.20-1.8 eV) range. The hydrides with band gaps in the above ranges can be classified as wide band gap hydrides. The rest four hydrides have small band gap (~0.19-1.2 eV) corresponding to the infrared range. Such hydrides with band gaps in the energy range 0.01-1.2 eV can be classified as narrow band gap hydrides. Here it should be noted that number of the semiconducting hydrides is much larger than that presented in Table I.

Following the analogy with semiconductors, hydrides with open fundamental band gap can be classified as direct band gap and indirect band gap depending on relative location of bottommost conduction band (CB) and topmost valence band (VB) in *k*-space compared to each other. A material can be called direct band gap if both topmost VB and bottommost CB are located at one and the same *k*-point and indirect bad gap if they are located at different *k*-points. By *ab initio* studies it is possible to perform this classification. Such analysis has been performed for the

hydrides listed in Table I. It is found that 18 hydrides possess direct band gap and 24 hydrides possess indirect gap.

Figure 1 shows band structure for Mg_2FeH_6, CsH, Na_3AlH_6, which possess direct fundamental band gaps. It is seen that both bottommost CB and topmost VB for CsH, Na_3AlH_6 are well dispersed. Hence, if high doping levels can be achieved, these hydrides are expected to possess good n-and p-type electrical conductivities. Although bottommost CB of Mg_2FeH_6 is well dispersed, its topmost VB is almost flat, which indicates that hole effective masses are large. Hence, hole mobility and conductivity are expected to be small. Consequently, one can suggest that if doping by shallow level impurities would be possible, Mg_2FeH_6 can possess good n-type electrical conductivity, while p-type conductivities expected to be smaller even if concentration of acceptors is larger than that of donors.

Analysis of band structures for hydrides shows that bottommost CB and topmost VB can be located not necessarily at Γ point, but at any k point of the Brillouin zone. They are located at X point for Mg_2FeH_6, at L point for CsH, and at Γ point for Na_3AlH_6. These hydrides are wide and direct band gap hydrides. Figure 2 shows examples of the hydrides with narrow and indirect fundamental band gaps. Analysis of Fig. 2 shows that bottommost CB of both Mg_2CoH_5 and SrAlSiH is at located M point. Topmost VB of Mg_2CoH_5 is located at the Γ point whereas that of SrAlSiH is located at the A point. Both topmost VB and bottommost CB of these hydrides are well dispersed. In these compounds one can expect n- and/or p-type electrical conductivity. Band structures of Mg_2CoH_5 and SrAlSiH are similar to that of Ge. Such a similarity has been reported before for Si and Mg_2NiH_4 [7].

Similar to semiconductors, hydrides with open fundamental band gap, depending on the origin of the topmost valence band, can also be classified as type-s, -p, and -d materials. Moreover a hybridization of s-p and s-d states can be expected. Thus, the classification is based on dominant

contribution of the *s*-, *p*-, or *d*-electrons to the top-most VB. Using this criterion the origin of the topmost valence band has been determined from the *ab initio* DFT studies (Table I). Analysis of Table I show that distinct from the commonly known semiconductors not only *p*- and *d*-, but also *s*-electrons contribute to the topmost valence band of hydrides. This is demonstrated in Fig. 3, which shows the orbital and site projected density of states (PDOS) for Na_3AlH_6. It is seen in Fig. 3 that dominant contribution to the top-most VB comes from the *s*-electrons of H atoms. This can be considered as one of the distinguishing features of hydrides with open fundamental band gap compared to well-known semiconductors. Analysis of the Table I show that most of the hydrides considered in the paper posses the feature and can be called as type-*s* materials. Binary saline hydrides can belong to this class.

Similar to the well-known semiconductors such as Si, GaAs etc., in some hydrides dominant contribution to the topmost VB can be provided by *p*-electrons. Figure 4 demonstrates it for the case of the SrSiAlH material. Analysis of Table I show that among the hydrides considered in the present article SrSiAlH is the only candidate, which possess the type-*p* feature. This kind of hydrides can be called as type-*p* hydrides. Analysis of band structure of some hydrides shows that similar to TiO_2 [30], contribution of *d* electrons to the topmost VB can also be dominant. This is demonstrated in Fig. 5 for Mg_2FeH_4. It is seen in Table I that a lot of hydrides possess this feature. Following analogy with TiO_2 [30], such hydrides can be called as type-*d* hydrides.

The classifications as type-*s*, -*p*, and -*d* can be applied when the topmost VB consists of pure *s*-, *p*-, and *d*-electrons or when one of them is dominant, so that contribution of other electrons can be neglected. However, often the topmost VB can be originated from hybridized *s-d* and/or *s-p* states. This is demonstrated in Table I for the hydrides with more or less well hybridized topmost VB. This kind of hydrides can be classified as hybridized ones.

4. Conclusion

In conclusion, by density functional calculations we have classified the hydrides with open fundamental band gap using their three different characteristic features, similar to those commonly used for semiconductors. The first one is based on fundamental band gap of hydrides and can be called as wide band gap/narrow band gap materials. The second one uses relative location in k space of the topmost valence band and bottommost conduction band compared each other. According to this criterion hydrides have been classified as direct and indirect band gap. The third one is based on relative contribution of s, p, and d electrons to the topmost valence band. This criterion allows to classify hydrides as type-s, -p, and -d as well as hybridised materials. The proposed classification can be useful for the novel applications of hydrides for the construction and processing of electronic devices in frame of recently invented "hydride electronics" [4-6].

References

[1] L. Schlapbach, A. Zuttel, Nature 414 (2001) 353-358.

[2] J. N. Huiberts, R. Griessen, J. H. Rector, R. J. Wijngaarden, J. P. Dekker, D. G. d. Groot, N. J. Koeman, Nature 380 (1996) 231-234.

[3] F. J. A. den Broeder, S. J. van der Molen, M. Kremers, J. N. Huiberts, D. G. Nagengast, A. T. M. van Gogh, W. H. Huisman, N. J. Koeman, N. I. Koeman, B. Dam, J. H. Rector, S. Plota, M. Haaksma, R. M. N. Hanzen, R. M. Jungblut, P. A. Duine, R. Griessen, Nature 394 (1998) 656-658.

[4] P. Vajeeston, Theoretical Modelling of Hydrides, in: '(Ed.)'^'(Eds.)', PhD thesis "Theoretical Modelling of Hydrides". Department of Physics, Faculty of Mathematics and Natural Sciences, vol ISSN 1501-7710, No 390. The University of Oslo, Oslo, 2004, p.^pp.

[5] S. Z. Karazhanov, A. G. Ulyashin, P. Ravindran, P. Vajeeston, Euro Phys. Lett. 82 (2008) 17006.

[6] S. Z. Karazhanov, A. G. Ulyashin, P. Ravindran, P. Vajeeston, Philos. Mag. 88 (2008) 2461-2476.

[7] S. Z. Karazhanov, A. Ulyashin, Euro Phys. Lett. 82 (2008) 48004.

[8] S. Z. Karazhanov, P. Ravindran, P. Vajeeston, A. G. Ulyashin, Phys. Stat. solidi (a) 204 (2007) 3538-3544.

[9] W. Lohstroh, R. J. Westerwaal, A. C. Lokhorst, J. L. M. van Mechelen, B. Dam, R. Griessen, J. Alloys Compd. 404-406 (2005) 490-493.

[10] A. Klaveness, PhD thesis "Quantum mechanical modelling and complex hydrides", in: '(Ed.)'^'(Eds.)', PhD thesis "Quantum mechanical modelling and complex hydrides". Faculty of mathematics and Natural Sciences, vol ISSN 1501-7710, No 629). The University of Oslo, Oslo, Norway, Oslo, 2007, p.^pp.

[11] W. Lohstroh, R. J. Westerwaal, B. Noheda, S. Enache, I. Giebels, B. Dam, R. Griessen, Phys. Rev. Lett. 93 (2004) 197404.

[12] S. Enache, T. Leeuwerink, A. F. T. Hoekstra, A. Remhof, N. J. Koeman, B. Dam, R. Griessen, J. Alloys Compd. 397 (2005) 9-16.

[13] T. Björling, D. Noréus, K. Jansson, M. Andersson, E. Leonova, M. Edén, U. Hålenius, U. Häussermann, Angew. Chem. Int. Ed. 44 (2005) 7269-7273.

[14] S. Z. Karazhanov, A. Ulyashin, J. Phys. D: Appl. Phys. (2008) Submitted.

[15] G. Kresse, J. Hafner, Phys. Rev. B **47** (1993) 558-561.

[16] G. Kresse, J. Furthmüller, Phys. Rev. B **54** (1996) 11169-11186.

[17] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. **77** (1996) 3865-3868.

[18] V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyzyk, G. A. Sawatzky, Phys. Rev. B 48 (1993) 16929.

[19] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, A. P. Sutton, Phys. Rev. B 57 (1998) 1505.

[20] S. Z. Karazhanov, P. Ravindran, A. Kjekshus, H. Fjellvag, B. G. Svensson, Phys. Rev. B **75** (2007) 155104.

[21] T. Sato, D. Noreus, H. Takeshita, U. Haussermann, J. Solid State Chem. 178 (2005) 3381-3388.

[22] S. V. Halilov, D. J. Singh, M. Gupta, R. Gupta, Phys. Rev. B 70 (2004) 195117.

[23] M. J. van Setten, G. A. de Wijs, G. Brocks, Phys. Rev. B 76 (2007) 075125-075128.

[24] M. J. van Setten, V. A. Popa, G. A. de Wijs, G. Brocks, Phys. Rev. B **75** (2007) 035204.

[25] Inorganic Crystal Structure Database, in: '(Ed.)'^'(Eds.)', Inorganic Crystal Structure Database, vol Gmelin Institut, Karlsruhe, 2001, p.^pp.

[26] A. Klaveness, O. Swang, H. Fjellvag, Euro Phys. Lett. 76 (2006) 285-290.

[27] J. B. Cui, J. Ristein, L. Ley, Diamond Relat. Mater. 9 (2000) 1036-1040.

[28] J. Zhang, K. Sugioka, S. Wada, H. Tashiro, K. Toyoda, K. Midorikawa, Appl. Surf. Sci. 127-129 (1998) 793-799.

[29] R. D. Carson, S. E. Schnatterly, Phys. Rev. B 33 (1986) 2432 LP - 2438.

[30] Y. Furubayashi, N. Yamada, Y. Hirose, Y. Yamamoto, M. Otani, T. Hitosugi, T. Shimada, T. Hasegawa, J. Appl. Phys. 101 (2007) 093705.

Figure captions

Fig. 1. Band structure for Mg_2FeH_6, CsH and Na_3AlH_6 with direct fundamental band gap.

Fig. 2. Band structure for indirect band gap hydrides Mg_2CoH_5 and SrAlSiH.

Fig. 3. Orbital and site projected DOS for Na_3AlH_6.

Fig. 4. Orbital and site projected DOS for SrAlSiH.

Fig. 5. Orbital and site projected DOS for Mg_2FeH_6.