

Contents list available at **IJND**  
**International Journal of Nano Dimension**

Journal homepage: [www.IJND.ir](http://www.IJND.ir)

---

## Comparison of metal additives and Boron atom on $MgH_2$ absorbing-desorbing characteristics using calculated NQCCs

---

### ABSTRACT

**M. A. Rafiee \***

*Department of Chemistry,  
Payame Noor University, P.O. BOX  
19395-3697, Tehran, Iran.*

---

Received 23 August 2014

Received in revised form

25 November 2014

Accepted 01 December 2014

Using ab initio calculations, the hydrogen desorption from Magnesium hydride ( $MgH_2$ ) was studied. We presented the calculated nuclear quadrupole coupling constants (NQCCs) of hydrogen atom in various systems of  $MgH_2$ . The effect of interactions of some metal atoms as well as Boron atom with  $MgH_2$  host matrix; ( $MgH_2+M$ ) nanostructures ( $M=Al, Ti, V, Fe, Ni$  and  $B$ ); were studied and  $^2H$ -NQCCs were calculated. From results, introduction of  $B$  decreased  $^2H$ -NQCC and consequently trend of decrease of charge density in the presence of  $B$  was observed. In the other hands introduction of  $B$  destabilized initial structure of  $MgH_2$ , But in ( $MgH_2+M$ ) nanostructures ( $M=Al, Ti, V, Fe$  and  $Ni$ ) the  $^2H$ -NQCCs were larger than those of pure  $MgH_2$  and consequently more difficult condition for hydrogen desorption were created. However at sufficiently low  $B$  concentration ( $Mg_{15}BH_{32}$ ); the calculation predicted existence of stable dopant system with greater  $^2H$ -NQCC. The electric field gradient (EFG) at the site of quadrupolar nuclei were calculated to obtain NQCC parameters at HF/3-21G level of theory.

**Keywords:** Nuclear quadrupole resonance (NQR); Magnesium hydride ( $MgH_2$ ); Hydrogen desorption; Ab initio calculations;  $^2H$ -NQCC.

---

### INTRODUCTION

Hydrogen is considered to be one of leading candidates for clean energy sources in the future. For safe and efficient hydrogen storage, developments of new hydrogen storage materials are currently being researched [1]. The hydrogen storage capacity per unit weight of typical metal alloys is very low (about 2.0 mass%) and not sufficient for use in a fuel cell vehicle. Among the metal hydrides, Magnesium hydride is one of the most promising candidates as a hydrogen storage media in the automotive industry due to its very high capacity (7.6 wt%) and low cost [1, 2]. Unfortunately, magnesium hydrides are thermodynamically stable, and the dehydrogenation of magnesium hydrides requires high temperatures ( $>277^\circ C$ ).

---

\* Corresponding author:

Marjan A. Rafiee

Department of Chemistry,  
Payame Noor University, P.O. BOX  
19395-3697, Tehran, Iran.

Tel +982136157111

Fax +982136114282

Email [rafiee.marjan@gmail.com](mailto:rafiee.marjan@gmail.com)

Therefore, the practical application is primarily limited by the slow kinetics and the high operating temperature. The possible reasons are that the hydrogen molecules do not readily dissociate on Mg surface and the high thermodynamic stability of Magnesium hydride [3, 4]. Experimentally, great efforts have been made to improve the H<sub>2</sub> absorption and desorption kinetics by mechanically milling MgH<sub>2</sub> and adding transition metals. High-energy ball milling is a suitable technique to affect both the particle size as well as the evolution of a particular crystallite size. Furthermore, different additives, such as liquid milling agents and hard particles, may also have a positive influence on the particle sizes during the milling process. An important group of additives enhancing significantly the absorption and desorption kinetics of nanocrystalline magnesium hydride is the group of a transition metal. Both the catalyst and the nanocrystalline structure with correspondingly high surface area are thought to play important roles in the improvement of hydrogen storage properties. [5–10]. These have been shown to work quite well to obtain the fast hydrogenation of Magnesium as reported by several groups [11–14]. However, in most case, it still requires at least 250 °C to liberate hydrogen from magnesium hydride [15], so the most of research efforts was put toward the ways of efficient and cost effective destabilization of MgH<sub>2</sub> matrix through various dopants introduction, mechanical or even ion beam modification [16-23]. In spite of the many experimental studies of dehydrogenation on MgH<sub>2</sub> surface, little is known about the surface properties and H<sub>2</sub> desorption in MgH<sub>2</sub> system. In order to improve the hydrogen desorption performance, it is clearly useful to understand the fundamental Mg–H bonding properties and the activation barrier for desorption starting from realistic Magnesium.

Nuclear Quadrupolar Resonance (NQR) spectroscopy [24] is a very sensitive technique for determination of electronic charge distribution around quadrupolar nuclei ( $I \geq 1$ ). This method can be used as a probe to obtain information about the environment of a given quadrupolar nuclei and consequently to determine the electronic structure of molecules and complexes.

Quantum mechanical approach has been shown to be a very effective method in determination of the charge distributions in molecules [25, 26].

It seems understanding the bonding nature of magnesium and hydrogen is essential in order to improve its fundamental dehydrogenation performance. Therefore in this work, attention has been focused on the details of the charge distribution on hydrogen atoms of MgH<sub>2</sub> in the presence of some heteroatoms in MgH<sub>2</sub> network; (MgH<sub>2</sub>+M) nanostructures (M=Al, Ti, V, Fe, Ni and B). For this purpose, we performed a theoretical investigation on the calculated NQCC parameters of these hydrogen atoms. It is evident that since the bond properties depend on electrons, it is possible to replace hydrogen atoms by deuterium, assuming no structural changes will occur.

These results may give a better understanding of their absorption strength based on their electronic structures.

## EXPERIMENTAL

Electric field gradients of Hydrogens were calculated using the Gaussian 03 program [27]. First, the three-dimensional structures of the above mentioned compounds were obtained from the Cambridge Crystallographic Database. Pure MgH<sub>2</sub> compound has crystal structure of rutile [28] (space group number 136, P4<sub>2</sub>/mnm, see Figure 1). (MgH<sub>2</sub>+M) nanostructures (M=Al, Ti, V, Fe, Ni and B) were obtained by substitution of one of two Mg atoms in original unit cell, thus lowering the symmetry (space group number 65, see Figure 2).

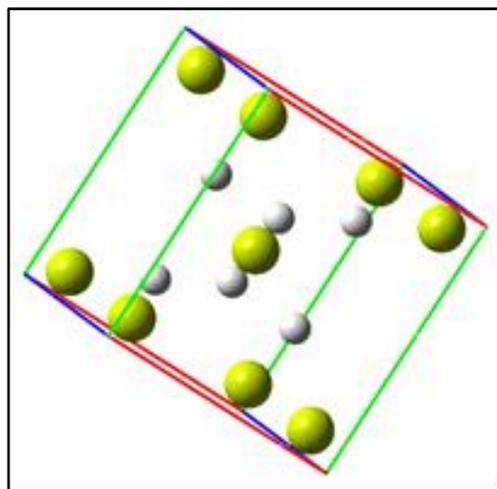


Fig. 1. One unit cell of MgH<sub>2</sub>.

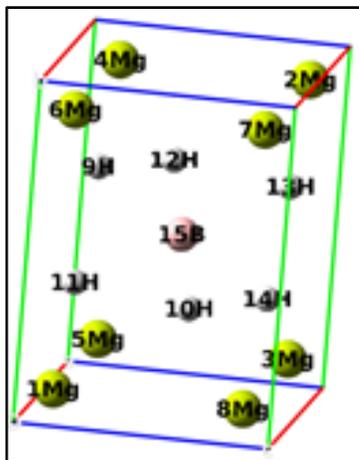


Fig. 2. One unit cell of (MgH<sub>2</sub>+M) systems.

After using experimentally established crystal-structure data as input, then an accurate molecular orbital method was applied to the most important part of the studies, i.e., electric field gradient (EFG) calculations. For the sake of CPU time, we apply HF/3-21G level of theory; this level can lead us to a qualitative results. In addition, since there is no experimental data on NQCCs of absorbed hydrogen in MgH<sub>2</sub> unit cells, HF/3-21G is able to lead us to the qualitative results using calculated NQCCs, which seems to be reasonable, because a qualitative prediction may be obtained faster.

### Evaluations of NQCCs

The formulation employed in the evaluation of NQR parameters can be found elsewhere [29]. Briefly, the EFG is a traceless, symmetric second-rank tensor that principal axes are chosen so that its components satisfy

$$|q_{zz}| \geq |q_{yy}| \geq |q_{xx}|, \quad (eq_{ij} = \frac{\partial^2 V}{\partial i \partial j}) \quad \text{where } i, j = X, Y, Z,$$

$e$  is electron charge and  $V$  is the external electronic potential [24]. The expression  $\chi = \frac{e^2 Q q_{zz}}{h}$  is

termed as nuclear quadrupole coupling constant and has the unit of frequency (Hz).  $h$  is the Planck's constant,  $Q$  is nuclear electric quadrupole moment and  $q_{zz}$  is the Z component of EFG tensor in principal axes system. Similar to the many previous studies [25, 26] here we assumed that the nuclear electric quadrupole moments act as a simple constant or scaling parameter, and we do not

parameterize it. Among the wide range of published standard values of quadrupole moments, we selected the recent value of  $Q(^2\text{H}) = 2.86 \text{ mb}$  reported by Pyykko [30].

From expression  $\chi = \frac{e^2 Q q_{zz}}{h}$ , it is obvious that NQCC of nuclei is directly proportional to  $q_{zz}$ .

There are two factors controlling the value of  $q_{zz}$  in a nucleus; charge density on the nucleus and symmetry of EFG around the quadrupolar nucleus. It is evident that an increase of the charge density causes the  $q_{zz}$  and consequently  $\chi$ , to increase. If charge distribution were such that the symmetry of EFG increased, then  $q_{zz}$  and consequently  $\chi$  will decrease.

## RESULTS AND DISCUSSION

MgH<sub>2</sub> is promising compound for hydrogen storage. Its relatively high stability has been the main obstacle for practical applications.

Quadrupolar parameters of nuclei can be used as a useful tool to understand the electronic structure of the compounds. Considering that MgH<sub>2</sub> is classified as ionic material with Mg and H in nearly 2+ and 1- states, respectively, for a strong Mg-H bond, charge transfer from Mg to H must be complete. In the other hands, larger <sup>2</sup>H-NQCC dictate: larger charge density on hydrogen and more complete charge transfer from Mg to H and consequently stronger Mg-H bond. Therefore, using calculated NQCCs of hydrogen atoms, the effect of some metal atoms (Al, Ti, V, Fe and Ni) in a unit cell of MgH<sub>2</sub> were compared with that of boron atom.

The results of Table 1 showed that in the presence of boron atom <sup>2</sup>H- NQCCs are smaller than those of MgH<sub>2</sub> unit cell (about 20 KHz). This point dictate that the bond strength of Mg-H in MgBH<sub>4</sub> is less than others and therefore desorption of hydrogen in this compound is easier. But in (MgH<sub>2</sub>+M) nanostructures (M=Al, Ti, V, Fe and Ni) the <sup>2</sup>H- NQCCs were larger than those of pure MgH<sub>2</sub> and consequently more difficult condition for hydrogen desorption are created. Therefore bond strength of Mg-H in MgBH<sub>4</sub> is less than the others and it is expected that desorption of hydrogen in this compound to be easier. But in

(MgH<sub>2</sub>+M) nanostructures (M=Al, Ti, V, Fe and Ni), the <sup>2</sup>H- NQCCs were larger than those of pure MgH<sub>2</sub> and consequently more difficult condition for desorption were created.

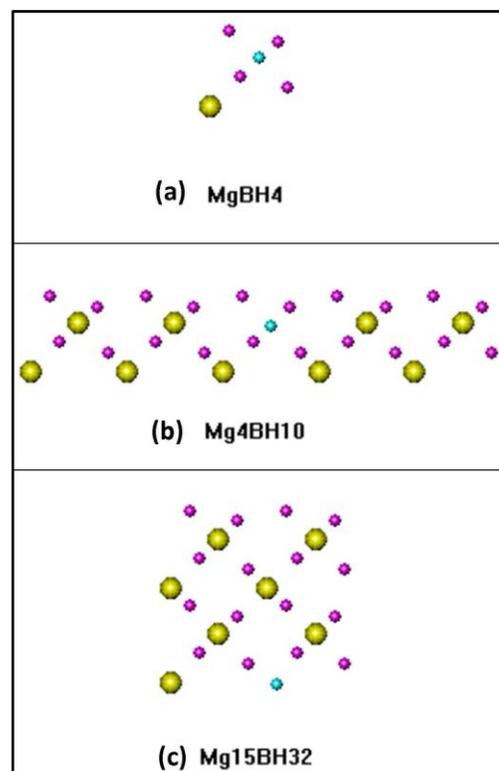
**Table 1.** The calculated <sup>2</sup>H- NQCCs in considered unit cells of MgH<sub>2</sub>+M systems.

MgH <sub>2</sub> +M systems	Calculated <sup>2</sup> H- NQCCs (KHz)					
	H9	H10	H11	H12	H13	H14
MgH <sub>2</sub>	49.68	53.98	49.68	53.98	46.21	47.55
MgH <sub>2</sub> +B	26.96	41.25	28.38	41.25	27.38	25.02
MgH <sub>2</sub> +Al	51.26	52.75	51.31	52.75	47.74	48.78
MgH <sub>2</sub> +Ti	61.00	51.62	52.65	51.62	57.52	49.81
MgH <sub>2</sub> +V	55.18	55.51	50.07	55.51	52.44	48.52
MgH <sub>2</sub> +Fe	49.94	55.66	50.00	55.66	46.62	48.19
MgH <sub>2</sub> +Ni	48.10	57.08	47.50	57.08	44.14	46.12

The destabilization of the magnesium hydride by boron atom was due to a weakened bonding between magnesium and hydrogen atoms. Hence the dehydrogenation properties of MgH<sub>2</sub> are expected to be improved to a different extent by the addition of boron atoms.

In continue we have performed ab initio charge density calculations of MgH<sub>2</sub>:B dopant systems with various concentrations of boron (Figure 3a). For construction of lower boron concentration structures, supercell approach was used. For Mg<sub>4</sub>BH<sub>10</sub> compound, supercell of five original unit cells was constructed, in structural arrangement 5×1×1 (space group number 136, P4<sub>2</sub>/mnm). The boron atoms are positioned at corners and at center of supercell (Figure 3b). Finally for Mg<sub>15</sub>BH<sub>32</sub> compound, supercell of eight unit cells was constructed, in structural arrangement 2×2×2 (space group number 65, Cmmm). The dopant atoms are positioned at center of two of supercell base planes (Figure 3c). Structural parameters for above mentioned compound are listed in Table 2.

The goal of our work in this part was to investigate the interaction of boron with MgH<sub>2</sub> host matrix, where boron acts as dopant at various concentrations, substituting Mg in its octahedral hydrogen environment. For comparison, <sup>2</sup>H-NQCC of pure MgH<sub>2</sub> system has been calculated as well.



**Fig. 3.** Unit cells of investigated MgH<sub>2</sub>:B dopant systems red balls: Hydrogen, blue balls: Boron, yellow balls: Magnesium; a: MgBH<sub>4</sub> (50 at% B); b: Mg<sub>4</sub>BH<sub>10</sub> (20 at% B); c: Mg<sub>15</sub>BH<sub>32</sub> (6.25 at% B).

**Table 2.** Some structural parameters of investigated systems.

structure	Cell parameters		Space group	
	$\alpha$ (A°)	$c$ (A°)	Number	Symbol
MgH <sub>2</sub>	4.518 <sup>a</sup>	3.022 <sup>a</sup>	136	P4 <sub>2</sub> /mnm
MgBH <sub>4</sub>	4.138	2.767	65	Cmmm
Mg <sub>4</sub> BH <sub>10</sub>	4.465	14.930	136	P4 <sub>2</sub> /mnm
Mg <sub>15</sub> BH <sub>32</sub>	8.930	5.972	65	Cmmm

The results in Table 3 showed that introduction of B decreases <sup>2</sup>H-NQCC and consequently trend of decrease of charge density in the presence of B was observed. In the other hands introduction of B destabilized initial structure of MgH<sub>2</sub>, however at sufficiently low B concentration (Mg<sub>15</sub>BH<sub>32</sub>); the calculation predicted existence of

stable dopant system with greater  $^2\text{H}$ -NQCC. It's still considerably high stability can be further decreases by slight increase of B concentration.

**Table 3.** The calculated  $^2\text{H}$ -NQCCs in compound with various concentration of Boron.

Compound	Calculated $^2\text{H}$ -NQCCs (KHz)			
	H1	H2	H3	H4
$\text{MgH}_2$	46.44	34.08	35.37	34.08
$\text{MgBH}_4$	38.17	4.14	2.80	4.14
$\text{Mg}_4\text{BH}_{10}$	36.52	9.30	5.82	35.81
$\text{Mg}_{15}\text{BH}_{32}$	50.10	44.78	48.64	54.27

This result is in agreement with previous findings that introduction of B destabilizes initial structure, and trend of sudden rise of enthalpy of formation with increase of B concentration is observed [31].

## CONCLUSIONS

According to the data obtained from charge distributions, it is concluded that:

- Quadrupolar parameters of nuclei can be used as a useful tool to understand the electronic structure of the compounds.

- The results showed that bond strength of Mg-H in  $\text{MgBH}_4$  is less than those of pure  $\text{MgH}_2$  and it is expected that desorption of hydrogen in this compound to be easier, in the other hands introduction of B destabilizes initial structure of  $\text{MgH}_2$ .

- At sufficiently low B concentration ( $\text{Mg}_{15}\text{BH}_{32}$ ); the calculation predicted existence of stable dopant system with greater  $^2\text{H}$ -NQCC.

## REFERENCES

[1] Aschlapbach L., Zuttel A., (2001), Hydrogen-storage materials for mobile applications. *Nature*. 414: 353-358.

- [2] Liang G., Huot J., Van Neste A., Schulz R., (1999), Catalytic effect of transition metals on hydrogen sorption in nanocrystalline ball milled  $\text{MgH}_2$  Tm (Tm=Ti, V, Mn, Fe and Ni) systems. *J. Alloys. Comp.* 292: 247-252.
- [3] Zaluska A., Zaluski L., Strom-Olsen J. O., (2001), Structure, catalysis and atomic reactions on the nano-scale: a systematic approach to metal hydrides for hydrogen storage. *Appl. Phys. A: Mater. Sci. Process.* 72: 157-165.
- [4] Von Zeppelin F., Reule H., Hirscher M., (2002), Hydrogen desorption kinetics of nanostructured  $\text{MgH}_2$  composite materials. *J. Alloys. Comp.* 330-332: 723-726.
- [5] Rivoirard S., de Rango F., Fruchart D., Charbonnier J., Vempaire D., (2003), Catalytic effect of additives on the hydrogen absorption properties of nano-crystalline  $\text{MgH}_2(\text{X})$  composites. *J. Alloys. Comp.* 356-357: 622-626.
- [6] Shang C. X., Bououdina M., Song Y., Guo Z. X., (2004), Mechanical alloying and electronic simulations of (MgH+M) systems (M=Al, Ti, Fe, Ni, Cu and Nb) for hydrogen storage. *Int. J. Hyd. Energy*. 29: 73-80.
- [7] Liang G., Huot J., Boily S., Schulz R., (2000), Hydrogen desorption kinetics of a mechanically milled  $\text{MgH}_2+5$  at.%V nanocomposite. *J. Alloys. Comp.* 305: 239-245.
- [8] Arico A. S., Bruce P., Scrosati B., Tarascon J. M., Van Schalkwijk W., (2005), Nanostructured materials for advanced energy conversion and storage devices. *Nat. Mater.* 4: 366-377.
- [9] Shao H., Felderhoffl M., Sch'uth F., Weidenthaler C., (2011), Nanostructured Ti-catalyzed  $\text{MgH}_2$  for hydrogen storage. *Nanotechnol.* 22: 235401-235408.
- [10] Hanada N., Ichikawa T., Fujii H., (2005), Catalytic effect of nanoparticle 3d-transition metals on hydrogen storage properties in magnesium hydride  $\text{MgH}_2$  prepared by mechanical milling. *J. Phys. Chem. B.* 109: 7188-7194.

- [11] Huot J., Pelletier J. F., Lurio L. B., Sutton M., Schulz R., (2003), Investigation of dehydrogenation mechanism of  $\text{MgH}_2\text{-Nb}$  nanocomposites. *J. Alloys. Comp.* 348: 319-324.
- [12] Zaluska A., Zaluski L., Strom-Olsen J. O., (1999), Synergy of hydrogen sorption in ball-milled hydrides of Mg and  $\text{Mg}_2\text{Ni}$ . *J. Alloys. Comp.* 289: 197-206.
- [13] Au M., Wu J., Wang Q. D., (1995), The hydrogen storage properties and the mechanism of the hydriding process of some multi-component magnesium-base hydrogen storage alloys. *Int. J. Hyd. Energy.* 20: 141-150.
- [14] Du A. J., Smith S. C., Yao X. D., Lu G. Q., (2005), The role of Ti as a catalyst for the dissociation of hydrogen on a Mg(0001) surface. *J. Phys. Chem. B.* 109: 18037-18041.
- [15] Au M., (2005), Hydrogen storage properties of magnesium based nanostructured composite materials. *Mater. Sci. Eng. B.* 117: 37-44.
- [16] Kurko S., Matovic Lj., Novakovic N., Matovic B., Jovanovic Z., Mamula B. P., Grbovic N., (2011), Changes of hydrogen storage properties of  $\text{MgH}_2$  induced by boron ion irradiation. *J. Int. J. Hydrogen Energy.* 36: 1184-1189.
- [17] Novakovic N., Grbovic-Novakovic J., Matovic Lj., Manasijevic M., Radisavljevic I., Paskaš-Mamula B., Ivanovic N., (2010), Ab initio calculations of  $\text{MgH}_2$ ,  $\text{MgH}_2\text{:Ti}$  and  $\text{MgH}_2\text{:Co}$  compounds. *Int. J. Hydrogen Energy.* 35: 598-608.
- [18] Matovic Lj., (2009), Structural destabilisation of  $\text{MgH}_2$  obtained by heavy ion irradiation. *Int. J. Hydrogen Energy.* 34: 7275-7582.
- [19] Ares J. R., Leardini F., Díaz-Chao P., Bodega J., Fernández J. F., Ferrer I. J., Sánchez C., (2009), Ultrasonic irradiation as a tool to modify the H-desorption from hydrides:  $\text{MgH}_2$  suspended in decan e. ultrason. *Sonochem.* 16: 810-816.
- [20] Montone A., Grbovic J., Bassetti A., Mirengi L., Rotolo P., Bonetti E., Pasquini L., Antisari M. V., (2006), Microstructure surface properties and hydrating behaviour of Mg-C composites prepared by ball milling with benzene. *Int. J. Hydrogen Energy.* 31: 2088-2096.
- [21] Greeley J., Norskov J. K., Mavrikakis M., (2002), Electronic structure and catalysis on metal surfaces. *Ann. Rev. Phys. Chem.* 53: 319-352.
- [22] Greeley J., Mavrikakis M., (2004), Alloy catalysts designed from first principles. *Nat. Mater.* 3: 810-814.
- [23] Vang, R. T., Honkala K., Dahl S., Vestergaard E. K., Schnadt J., Laegsgaard E., Clausen B. S., Norskov J. K., Besenbacher F., (2005), Controlling the catalytic bond-breaking selectivity of Ni surfaces by step blocking. *Nat. Mater.* 4: 160-162.
- [24] Graybeal J. D., (1998), Molecular Spectroscopy, McGraw-Hill: New York.
- [25] Rafiee M. A., (2012), The study of hydrogen storage in carbon nanotubes using calculated nuclear quadrupole coupling constant (NQCC) parameters (A theoretical ab initio study). *J. Comput. Theor. Nanosci.* 9: 2021-2026.
- [26] Rafiee M. A., Hadipour N. L., Naderimanesh H., (2004), The correlation study of quinoline derivatives and their pharmaceutical behavior by ab initio calculated NQR parameters. *J. Comput. Aided Mol. Des.* 18: 215-220.
- [27] Frisch M. J., Trucks G. W., Schlegel H. B., Scuseria G. E., Robb M. A., Cheeseman J. R., Zakrzewski V. G., Montgomery J. A., Stratmann R. E. Jr., Burant J. C., Dapprich S., Millam J. M., Daniels A. D., Kudin K. N., Strain M. C., Farkas O., Tomasi J., Barone V., Cossi M., Cammi R., Mennucci

- B., Pomelli C., Adamo C., Clifford S., Ochterski J., Petersson G. A., Ayala P.Y., Cui Q., Morokuma K., Malick D. K., Rabuck A. D., Raghavachari K., Foresman J. B., Cioslowski J., Ortiz J. V., Stefanov B. B., Liu G., Liashenko A., Piskorz P., Komaromi I., Gomperts R., Martin R. L., Fox D. J., Keith T., Al-Laham M. A., Peng C.Y., Nanayakkara A., Gonzalez C., Challacombe M., Gill P. M. W., Johnson B., Chen W., Wong M. W., Andres J. L., Gonzalez C., Head-Gordon M., Replogle E. S., Pople J. A., GAUSSIAN 03, Gaussian Inc. Pittsburgh, PA, 2003.
- [28] Yu R., Lam P. K., (1998), Electronic and structural properties of  $MgH_2$ . *Phys. Rev. B.* 37: 8730-37.
- [29] Cohen M. H., Reif F., (1957), Quadrupole effects in nuclear magnetic resonance studies in solid. *Solid State Phys.* 5: 321-438.
- [30] Pyykko P., (2001), Spectroscopic nuclear quadrupole moments. *Mol. Phys.* 99: 1617-1629.
- [31] Kurko S., Paskaš-Mamula B, Matovic Lj., Grbovic Novakovic J., Novakovic N., (2011), The influence of Boron doping concentration on  $MgH_2$  electronic structure. *Acta Phys. Pol. A.* 120: 238-241.

Cite this article as: M. A. Rafiee: Comparison of metal additives and Boron atom on  $MgH_2$  absorbing-desorbing characteristics using calculated NQCCs.

*Int. J. Nano Dimens.* 6 (3): 289-295, Summer 2015.

