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Electronic and optical properties of pressure induced phases of MgH_2

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Abstract

The electronic and optical properties of pressure-induced phases of MgH_2 are investigated using the full-potential linearized augmented plane wave method. The absorption features are investigated by means of the calculated complex dielectric function and the analysis are made based on the electronic structure. The phases as a whole exhibit a color neutral insulator behavior. The calculated band gap are in good agreement with earlier theoretical investigations. The absorption edges corrected by scissor operation matched quite well the experimental findings. The optical anisotropy has also been evaluated.

Keywords: Hydrogen storage; Magnesium hydride; Optical transmission; Semiconductors

1. Introduction

The compound MgH_2 has attracted considerable attention primarily for being a promising hydrogen storage material due to its light weight, low manufacture cost and high hydrogen storage capacity (7.6 wt.%). However, its slow hydrogen absorption/desorption kinetics and high dissociation temperature (nearly 300 °C) limit its practical applications for hydrogen storage [1]. Much of effort has been paid in order to overcome those limitations mainly by making nanocrystalline Mg [2] or by adding alloying elements [3–6].

The discovery of the optical transmission due to hydrogenation in rare-earth elemental metals [7] as well as in rare-earth-Mg [8–10] and MgNi [11] alloy thin films has turned the attention to investigations on the optical properties of MgH_2. It has been found that the absorption edges in the transmission spectra of these alloys are shifted to higher energies with increasing Mg concentration. Such a behavior is explained by considering the formation of MgH_2, which is expected to have a wide band gap. Recently, Isidorsson et al. [12] have provided a careful experimental study on magnesium hydride thin films developed by using spectrophotometry and ellipsometry techniques. They have found a band gap of 5.6 ± 0.1 eV for α-MgH_2. Materials with large band gap (color neutral insulator, $Eg > 3.0$ eV) in fully hydrogenated state and with reversible switching behavior upon hydrogenation are promising for applications in for instance “smart” windows.

Vajeestone et al. [13] using ab initio calculations have confirmed that MgH_2 undergoes several pressure-induced phase transitions [14,15]. They have found that the ground state α-MgH_2 (TiO_2-rutile-type) transforms into orthorhombic γ-MgH_2 (α-PbO_2-type) at 0.39 GPa and that the subsequent phase transformation from γ- to β-MgH_2 (Mod. CaF_2-type) occurs at 3.84 GPa. These phases can be found as a by-product in high-pressure syntheses of metal hydrides [16]. Thus, to figure out the role of MgH_2 in Mg-based alloys it is essential to determine the electronic and optical properties of their high-pressure phases.

In this work we present a theoretical investigation of the electronic and optical properties of α-, γ- and β-MgH_2. The calculations of the electronic structure were performed by using the full-potential linearized augmented plane wave (FP-LAPW) method [17]. The optical absorption as well as the optical anisotropy were investigated by means of the complex dielectric function. The latter were calculated from the joint density of states and the dipole matrix element [18]. In Section 2, we present the details of our computational method. Then, in Section 3, we present and discuss the electronic structure as well as the complex dielectric function. The main results are summarized in the conclusion.

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2. Computational method

The electronic structure was calculated within the framework of generalized gradient approximation (GGA) to the density functional theory (DFT) using the FP-LAPW method [17]. The calculation have been performed using the WIEN2K code [19]. The muffin-tin radius of hydrogen (magnesium) have been defined as 1.0, 1.2 and 1.05 au (2.65, 2.2 and 2.65 a.u.) in the α-, γ-, β-MgH_2, respectively. The basis set for the Hamiltonian matrix consisted of 865, 971 and 1357 plane waves in the interstitial region for α-, γ-, β-MgH_2, respectively. The maximum azimutal quantum number of $l_{\max} = 10$ has been used as the cutoff for the spherical harmonics in the atomic region. The integrations for the total energy have been carried out using 500 k-points in the irreducible part of brillouin-zone (IBZ), for all phases. The density of states as well as the imaginary part of dielectric function, however, has been calculated on a grid of 1500 k-points in the IBZ. In all calculations, self-consistency was achieved with a tolerance in the total energy of 1.36 meV.

The density of states were calculated by means of the modified tetrahedron method of Blöchl et al. [20]. The components of the imaginary part of the dielectric function, $\varepsilon_2(\omega)$, along the crystal axes were calculated directly from the electronic structure [18]. The total $\varepsilon_2(\omega)$ is thus obtained by performing the arithmetic average of its components. The real part of the dielectric function, $\varepsilon_1(\omega)$, was obtained from the Kramers–Kroning dispersion relations.

3. Results

The band structures near the fundamental band gap in γ- and β-MgH_2 are presented in Fig. 1. As one can see both γ and β phases have indirect band gap. The same sort of fundamental band gap has been obtained for α-MgH_2 [21].

In Fig. 2 we show the calculated partial density of states of the s- and p-states for Mg and H atoms in the different phases of MgH_2. In the energy interval between −6.5 and −4.5 eV in α-MgH_2, −6.7 and −5.5 eV in γ-MgH_2, and −8.0 and −6.4 eV in β-MgH_2 the valence band is primarily determined by hybridization between H 1s and Mg 3s states. The uppermost region however is composed mainly by hybridization between H 1s and Mg orbital with p character. The bottom of the conduction band, just above the Fermi energy, is composed mainly by the unoccupied Mg p and s states with a very small amount of unoccupied H s and p states.

Our results confirm that α-MgH_2 and their high-pressure modifications, considered in this work, exhibit insulating behavior. It is well known that the local-density theories underestimate the band gap of semiconductors in between 30 and 50%. Therefore the calculated band gap of 3.9 eV for α phase is 47% smaller than the experimental value of 5.6 eV [12]. The calculated band gap for γ and β phases are 3.6 and 2.5 eV, respectively.

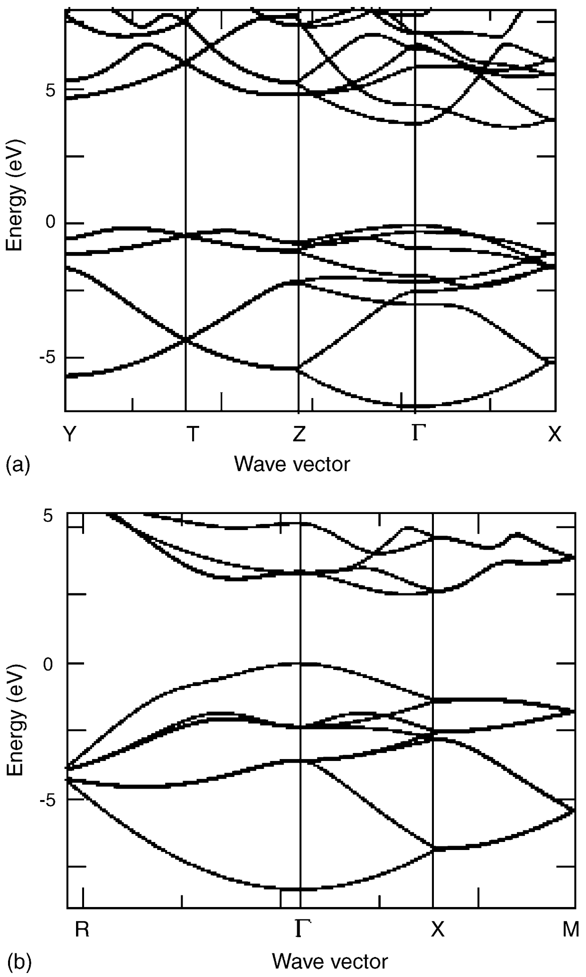

Fig. 1. Band structure of (a) γ- and (b) β-MgH_2.

The calculated complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ for α-, γ- and β-MgH_2 phases are shown in Fig. 3. The band gap underestimation was treated through a scissor operation which shift the calculated $\varepsilon_2(\omega)$ upwards in photon energy. We have used a band gap correction of Δ Eg=1.7 eV in order to match the experimental value of Eg= 5.6 eV [12] for the α phase. Assuming that the same value can be applied to γ and β phases, we expect an experimental gap of 5.3 eV for γ-MgH_2 and 4.2 eV for β-MgH_2.

For the α phase the $\varepsilon_2(\omega)$ show one primary peak at 7.6 eV and some weak shoulders at 7.2, 7.8 and 8.8 eV. For the γ phase there are two main peaks at 7.6 eV and 8.11 eV with some weak shoulders at 6.9, 7.1, 9.0, 9.7 and 10.3 eV. Whereas the β-MgH_2 has its principal peak at 7.3 eV, a very small peak at 4.9 eV and two shoulders at 6.6 and 8.5 eV. According to the electronic structure, the absorption features up to 7.6 eV in both α and δ phases and up to 7.3 eV in the β phase are mainly originated by the transitions from occupied Mg p states to unoccupied Mg s states, whereas the higher energy transitions are principally determined by Mg s to Mg p direct interband transitions.

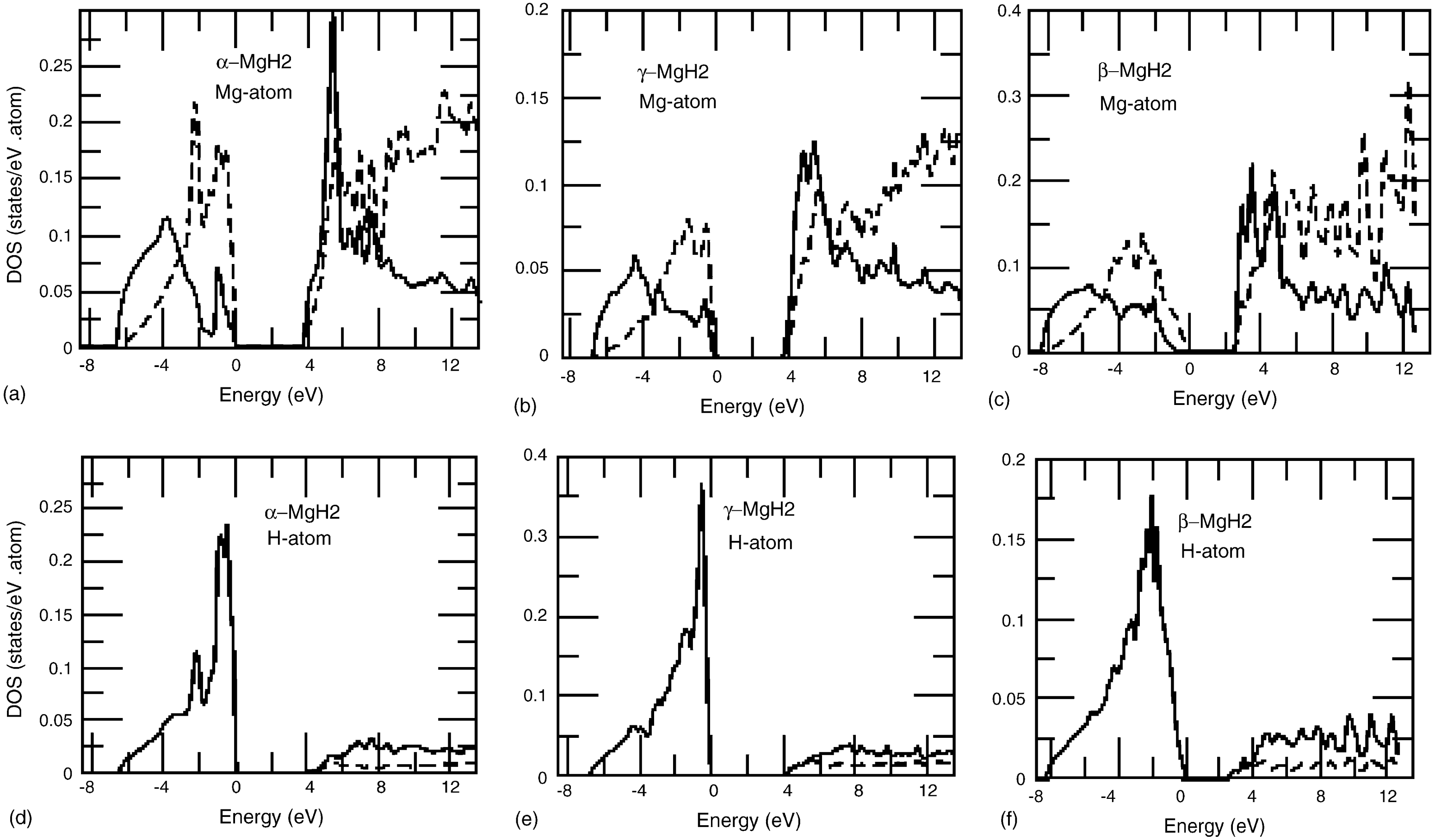

Fig. 2. Partial density of states (DOS) for a Mg-atom in (a) α-, (b) γ- and (c) β-MgH2 and for a H-atom in (d) α-, (e) γ- and (f) β-MgH_2. Solid and dashed lines represent s- and p-states, respectively. The band gap correction is not included and the Fermi level is set at zero energy.

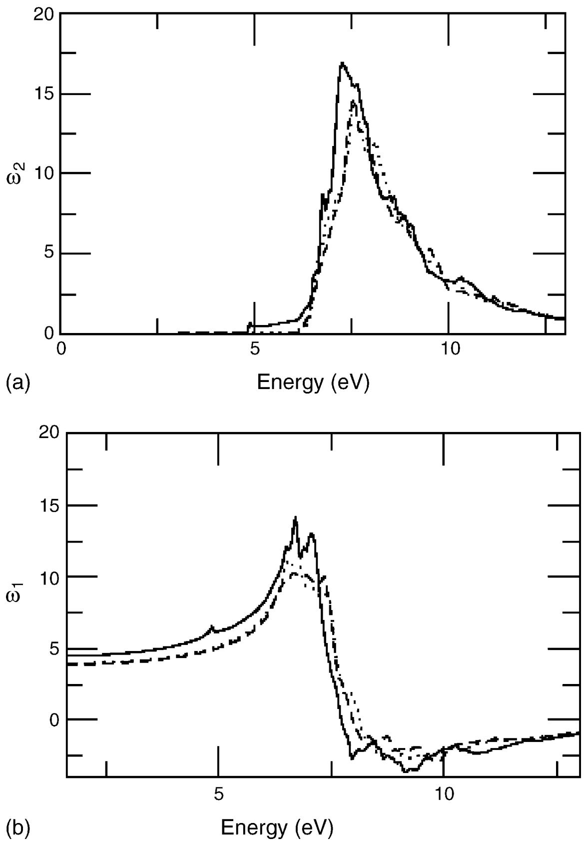

Fig. 3. (a) Imaginary and (b) real part of the dielectric function. Dashed, dotted and solid lines represent the α, γ and β phases, respectively. The corrections by scissor operation are included.

If one consider the ratio of $\varepsilon_1^c(0)/\varepsilon_1^a(0)$ as a measure for the average optical anisotropy, where $\varepsilon_1^c(0)$ and $\varepsilon_1^a(0)$ are the static components of the real part of the dielectric constant along the *c*- and *a*-axes of the crystal. Then, we can claim that neither α-MgH_2 ($\varepsilon_1^c(0)/\varepsilon_1^a(0) = 1.01$) nor γ-$MgH_2$ ($\varepsilon_1^c(0)/\varepsilon_1^a(0) = 1.04$) show high anisotropy.

4. Conclusion

In summary, we have investigated the electronic and optical properties of α-, γ- and β-MgH_2 within the framework of the GGA to DFT using the FP-LAPW method. The optical absorption as well as the optical anisotropy are investigated by means of the calculated complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The band structure near the fundamental band gap for the γ- and β-MgH_2 are presented. We have found that all phases exhibit insulating behavior with indirect band gap. If we consider the same band gap correction in the γ and β phases as in the α phase we expect a band gap of 5.3 eV for γ- MgH_2 and 4.2 eV for β- MgH_2. Thus, the latter is expected to be still color neutral insulator what is very important for applications in for instance smart windows. We have also found that neither α-MgH_2 nor γ- MgH_2 show high anisotropy.

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References

[1] F.E. Pinkerton, B.G. Wicke, Ind. Phys. 10 (2004) 20–23.
[2] A. Zaluska, L. Zaluski, J.O. Ström-Olsen, J. Alloys Compd. 288 (1999) 217.
[3] G. Liang, J. Huot, S. Boily, A. Van Neste, R. Schulz, J. Alloys Compd. 292 (1999) 247.
[4] Z. Dehouche, R. Djaozandry, J. Huot, S. Boily, J. Goyette, T.K. Bose, R. Schulz, J. Alloys Compd. 305 (2000) 264.
[5] J.F. Pelletier, J. Huot, M. Sutton, R. Schulz, A.R. Sandy, L.B. Lurio, S.G.J. Mochrie, Phys. Rev. B 63 (2001) 052103.
[6] Y. Song, Z.X. Guo, R. Yang, Phys. Rev. B 69 (2004) 094205.
[7] J.N. Huibert, R. Griessen, J.H. Rector, R.J. Wijngaarden, J.P. Dekker, D.G. De Groot, N.J. Koeman, Nature (London) 380 (1996) 231.
[8] P. Van der Sluis, M. Ouwerkerk, P.A. Duine, Appl. Phys. Lett. 70 (1997) 3356.
[9] M. Ouwerkerk, Solid State Ionics 431 (1998) 113–115.
[10] I.A.M.E. Giebels, J. Isidorsson, R. Griessen, Phys. Rev. B 69 (2004) 205111.
[11] T.J. Richardson, J.L. Slack, R.D. Armitage, R. Kostecki, B. Farangis, M.D. Rubin, Appl. Phys. Lett. 78 (2001) 3047.
[12] J. Isidorsson, I.A.M.E. Giebels, H. Arwin, R. Griessen, Phys. Rev. B 68 (2003) 115112.
[13] P. Vajeeston, P. Ravidran, A. Kjekshus, H. Fjellvag, Phys. Rev. Lett. 89 (2002) 175506.
[14] J.P. Bastide, B. Bonnetot, J.M. Létoffé, P. Claudy, Mater Res. Bull. 15 (1980) 1215.
[15] M. Bortz, B. Bertheville, G. Böttger, K. Yvon, J. Alloys Compd. 287 (1999) 4.
[16] D.G. Nagengast, A.T.M. van Gogh, E.S. Kooij, B. Dam, R. Griessen, Appl. Phys. Lett. 75 (1999) 2050.
[17] S. Cottenier, Density Functional Theory and the family of (L)APW-method: a step-by-step introduction (Instituut voor kern- en Stralingsfysica, K.U. Leuven, Belgium), 2002. ISBN 90–807215-1–4 (to be found at http://www.wien2k.at/reg-user/textbooks).
[18] C. Ambrosch-Draxl, J.A. Majewski, P. Vogl, Phys. Rev. B 51 (1995) 9668.
[19] P. Blaha, K. Schwarz, J. Luitz, Computer code WIEN2K, University of Technology, Vienna, 2000.
[20] P.E. Blöchl, O. Jepsen, O.K. Andersen, Phys. Rev. B 49 (1994) 16223.
[21] R. Yu, K. Lam, Phys. Rev. B 37 (1988) 8730.