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# Ti-derived intermediate band in $MgH_2$

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This article deals with a study of electronic structure of Ti-doped $MgH_2$ by the first-principles calculations. We show that Ti impurity substituting Mg ($Ti_{Mg}$) forms an intermediate band in the band gap of $MgH_2$, which is partially filled with electrons. However, the intermediate bands are well localized around Ti impurity. So, the effective masses of electrons in this intermediate band can be said to be infinite, it means that the electrons in these bands are immobile, and $MgH_2$:Ti remains to be an insulator. The energy estimated from the topmost valence band (conduction band) to Fermi level is ≥2.8 eV. Since the band gap of $MgH_2$ is ~5.6 eV, the energy between the conduction band minimum and Fermi level is also 2.8 eV. So despite presence of the intermediate band $MgH_2$ remains to be transparent to the visible part of the solar spectra and slightly reflective to the infrared light with very low light absorption.

Исследована электронная структура $MgH_2$, легированного Ti с помощью расчетов из первых принципов. Показано, что примеси Ti, замещающие Mg ($Ti_{Mg}$), образуют частично заполненные электронами промежуточные зоны в запрещенной зоне $MgH_2$. Эти зоны локализованы вокруг примеси Ti. Соответственно, эффективные массы электронов в этих промежуточных зонах могут стать бесконечными. Это означает, что электроны в этих зонах неподвижны и $MgH_2$:Ti остается изолятором. Энергия, отсчитанная от потолка валентной зоны (или дна зоны проводимости) до уровня Ферми ≥2,8 эВ. Так как ширина запрещенной зоны $MgH_2$ составляет ~5,6 эВ, можно сказать, что энергия между дном зоны проводимости и уровнем Ферми также ~2,8 эВ. Таким образом, несмотря на наличие промежуточной зоны $MgH_2$ остается прозрачным в видимой части солнечного спектра, слегка отражающим и поглощающим инфракрасный свет. Это свойство может быть важно для смартовых солнечных коллекторов.

## *1. Introduction*

The idea of usage of intermediate bands in a wide band gap semiconductor is found to be useful to enhance efficiency of photovoltaic devices. They are suggested to facilitate absorption of photons with energy lower than the band gap and thus increase photocurrent without reducing the photovoltage [1, 2]. This expectation has been confirmed experimentally in dilute compound-semiconductor alloys [3] and quantum dots [4]. Deep-level impurities have been also considered as candidates for forming the intermediate bands [5] for absorbing low energy photons, which are commonly

active in non-radiative processes reducing carrier lifetime and device efficiency. The parasitic effect was suggested [5] to be avoided if the electrons associated with the deep-level impurities were delocalized, for example, via Mott metal-insulator transition. Here we study a role of the intermediate bands in metal hydride films, which are commonly used in the fields such as hydrogen storage/economy [6, 7], rechargeable batteries [7], smart windows [8–11], and are suggested to be used in solar cells [12, 13]. Ti-doped $MgH_2$ has been used as an example. $MgH_2$ is a transparent and color neutral insulator with wide band gap of 5.6 eV [14] with the possibility of H upload and release processes taking place at high temperatures (>300°C). Upon doping by Ti, the processes of H upload and release into/from $MgH_2$ are found to take place at much lower temperatures. Furthermore, as a result of variations of the H content, Mg–Ti alloy was shown [15] to exhibit an optical transition between a highly reflective, a black and a transparent states. The ability of the films to switch between the reflective and absorbing black states was suggested [16] to be useful for smart solar collectors, which absorbed light in normal operation condition and switched to a reflective state to avoid overheating. The other feature of switching between transparent and reflective states was shown to be useful for switchable mirror applications [16]. Here the interesting point is that despite doping by Ti, $MgH_2$ remains to be transparent to visible part of the solar spectra. In the present article we investigate this point by the study of electronic structure and optical properties of Ti-doped $MgH_2$ by using the *ab initio* softwares. We found that Ti impurity substituting Mg ($Ti_{Mg}$) formed an intermediate band in the band gap of $MgH_2$, which was partially filled with electrons, slightly increased reflectivity in the infrared part of the sunlight, and kept transparency to the visible part of the solar spectra.

## 2. Computational details

The computational work has been performed using MINDLAB package [17], which uses the full potential linear muffin-tin orbital (FP LMTO) method. For the core charge density, the frozen-core approximation is used. The calculations are based on GGA with the exchange-correlation potential parametrized according to Gunnarsson-Lundquist [18]. The base geometry in this computational method consists of a muffin-tin part and an interstitial part. The basis set is comprised of linear muffin-tin orbitals. Inside the muffin-tin spheres, the basis functions, charge density, and potential are expanded in symmetry-adapted spherical harmonic functions together with a radial function and Fourier series in the interstitial. For unit cells the self-consistent calculations were performed using a 4×4×4 mesh of special $k$-points and plane-wave cut-off energy of 300 eV. Convergence was achieved when the total energy difference between two consecutive iterations were $<10^{-6}$ eV.

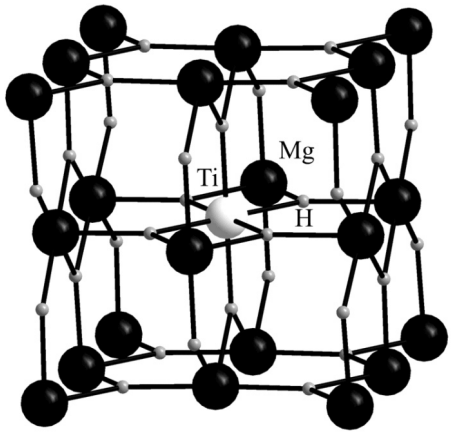


Fig. 1. Schematic presentation of $Mg_{Ti}$-doped $MgH_2$.

The imaginary part of the dielectric function was calculated from interband transitions. The real part of the dielectric function is then calculated using Kramers-Kronig transformation. These two spectra were then used to calculate all other optical spectra. Then, the calculated reflectivity $R(\omega)$, absorption coefficient $\alpha(\omega)$, the refractive index $n(\omega)$, the extinction coefficient $(\omega)$ and electron energy loss spectra (EELS) are defined. Optical spectra are calculated for the energy range 0–12 eV.

Ti impurity substituting Mg in the matrix of $MgH_2$ is schematically presented in Fig. 1. The supercell we considered corresponds to $Mg_{0.9375}Ti_{0.0625}H_2$. Such a high concentration of Mg is reasonable. Mg and Ti can alloyed $Mg_yTi_{1-y}$ by using physical vapor deposition, mechanical alloying, or $e$-beam deposition. In hydrogenated films the formation of $MgH_2$-like rutile phase is observed [16] for low Ti contents $y = 0.90$, whereas in $Mg_yTi_{1-y}$ with $y = 0.80$ and $y = 0.70$, a fluorite-like Mg–Ti–H phase is formed.

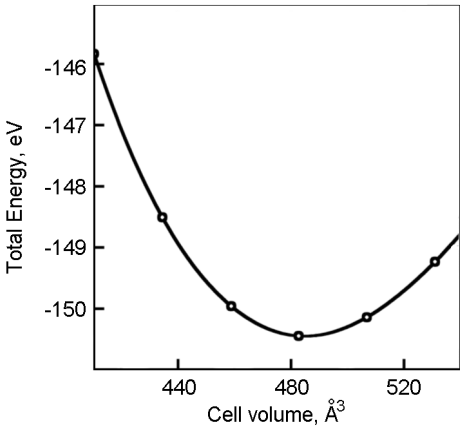


Fig. 2. Total energy vs volume ($V$) for $Ti_{Mg}$-doped $MgH_2$.

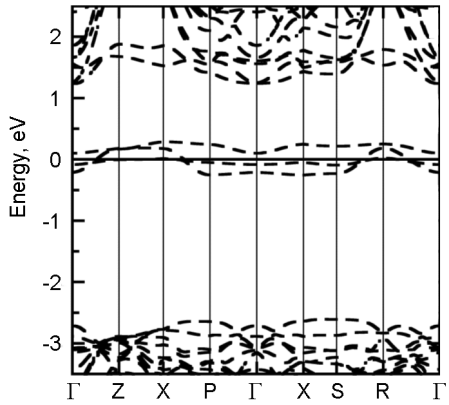


Fig. 3. Band structure and density of states of $MgH_2$. Fermi level is set to zero.

## 3. Results

Parameters of the optimized supercells of $MgH_2$ with Ti impurity substituting Mg has been used as input and dependence of the total energy has been studied as a function of the volume of the supercell (Fig. 2). The lattice parameters corresponding to the minimum of the dependence has been accepted as the equilibrium lattice parameters of the lattice and has been used for electronic structure studies.

Fig. 3 shows band structure of $Ti_{Mg}$-doped $MgH_2$. Analysis shows that $Ti_{Mg}$ forms an intermediate band in the band gap of $MgH_2$. Fermi level is located at ~2.8 eV from the top of the valence band. The calculated energy difference between the conduction band minimum and Fermi level is ~1.2 eV. However, commonly, the *ab initio* software systematically underestimates the band gap. The experimentally established band gap of $MgH_2$ is ~5.6 eV, so in reality the energy between the conduction band minimum and Fermi level is expected to be ~2.8 eV, which means that

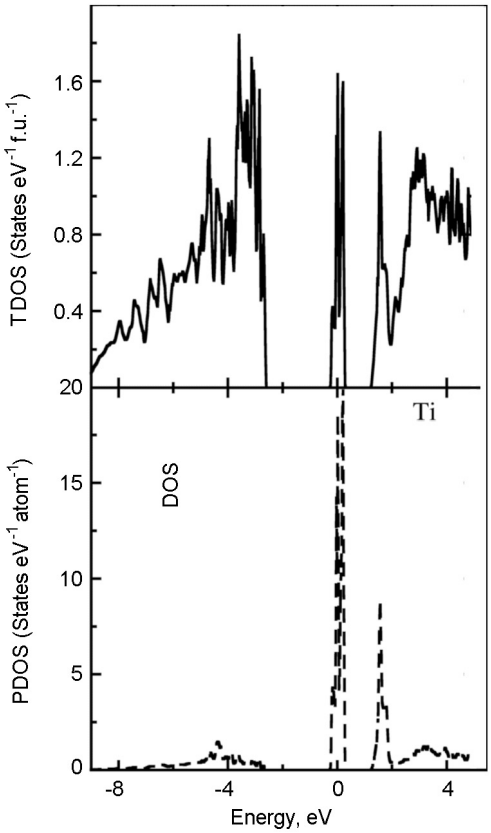


Fig. 4. PDOS for $Ti_{Mg}$-doped $MgH_2$. Fermi level is set to zero.

despite the intermediate band, $MgH_2$ should remain to be transparent to the visible part and absorbing the ultraviolet part of the solar spectra. This feature is very important in the smart solar collector applications of the material [16], which is transparent when hydrogenated and is black color when hydrogen is uptaken from the material. Also, it becomes clear why Ti-doped $MgH_2$ used in switchable mirrors is color neutral [15].

The intermediate band is almost dispersionless, which means that the second derivative from the energy over **k**-vector is zero. Consequently, effective masses of free electrons in the band are infinite. If so, then the carrier mobility through this band is expected to be almost zero. Therefore, electrical current cannot be transported through the intermediate band. Such a band can be useful for down-conversion of incident photons.

Analysis shows that the intermediate band consists of three lines. Since spin-orbit coupling is excluded from the computations, two electrons can be hosted by each of these three bands. Fermi level is crossing only two of the bands. Once Fermi-level crosses

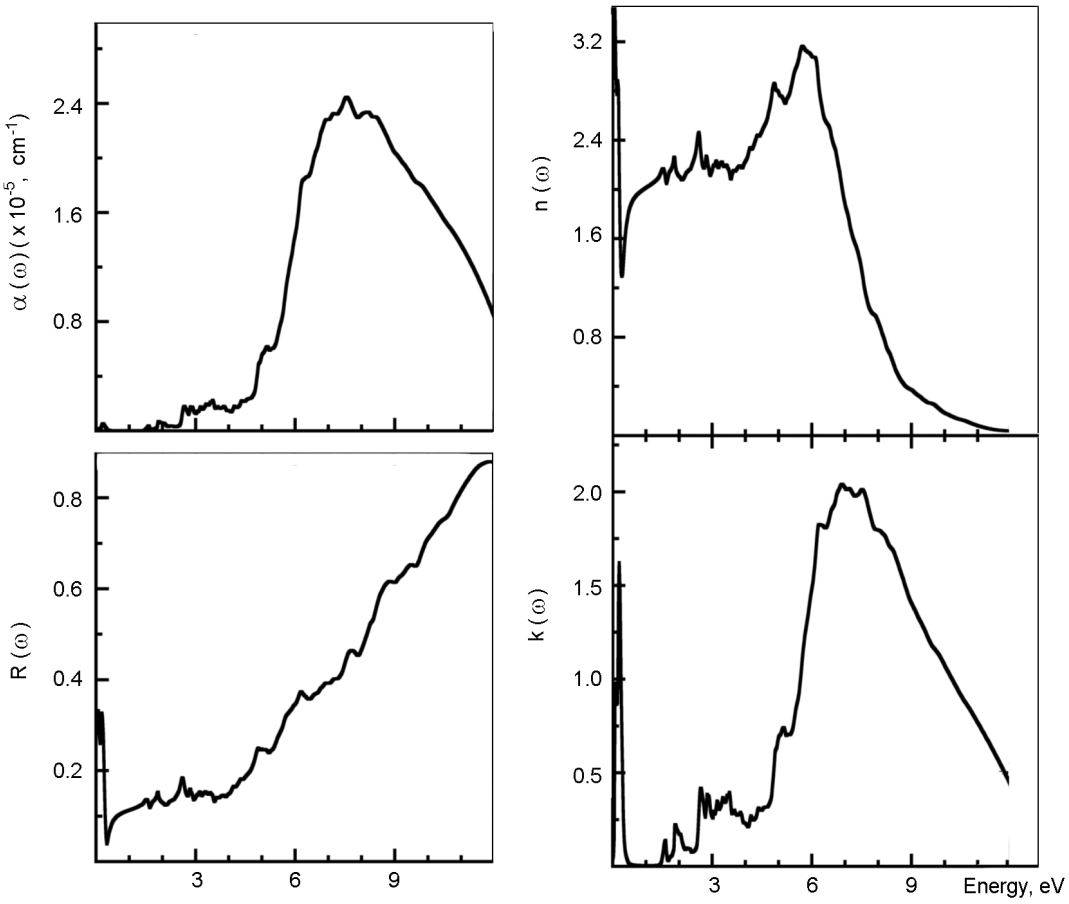


Fig. 5. Optical spectra of $T_{Mg}$-doped $MgH_2$.

the intermediate band, it indicates that some of the bands are not occupied by electrons. This creates the possibility for two-step photoexcitation. One is photoinduced electron transfer from the valence band into the conduction band, and the other one is electron transfer from the intermediate band into the conduction band. Also, in the theoretical studies, electronic structure $Ti_{Mg}$-doped $MgH_2$ can look like a metal because Fermi level is crossing the intermediate band. However, in reality the material can be insulator, because, as noted above, the intermediate band is flat and carrier mobility through it can be too small.

Analysis shows that location of Fermi level is sensitive on concentration of Ti in $MgH_2$. At smaller concentrations of Ti, the Fermi level can be located below the Ti-derived intermediate band. In such case two step photoexcitation can still exist, just the light-induced transition from the intermediate band into the conduction band cannot be well-enhanced. The reason is that because illumination by sunlight cannot create too many electrons in the intermediate band.

Once the bands are almost flat in $k$-space electrons in the intermediate bands are delocalized in $k$-space and are localized in real space, so the electrons are localized at an atom in the lattice. To know whether this localization is around $Ti_{Mg}$ or to know the origin of this intermediate band orbital and site projected, density of states has been studied, which is presented in Fig. 4. Analysis shows that the density of states corresponding to the intermediate band belongs to Ti-dopants. Consequently, the intermediate bands are well localized around and belong to Ti impurity.

The calculated reflectivity $R(\omega)$, absorption coefficient $\alpha(\omega)$, refractive index $n(\omega)$, and extinction coefficient $k(\omega)$ are displayed in Fig. 5. The analysis shows that absorption of the photons with energies in the range of 0–4 eV is negligible. However, this feature corresponds to well hydrogenated state of Mg–Ti alloy. As it is shown in [16], upon withdrawal of H from the material, it

might become a black colour metal with high absorption coefficient of the sunlight in the visible part of solar spectra. Reflectivity of the material is <0.3 in the infrared part and is <0.2 in the rest part of the solar spectra. However, the values of refractive index and the extinction coefficient in the infrared region are quite big. It shows that these two optical parameters can be modulated by Ti-doping.

### *4. Conclusion*

In summary, by the first-principles calculations we show that upon doping of $MgH_2$ by $Ti_{Mg}$ an intermediate band is formed, which is almost flat and is partially filled with electrons. Fermi level is crossing the band. However, despite metal-like band structure with $Ti_{Mg}$-derived partially filled intermediate band, $MgH_2$:Ti remains to be an insulator, because the intermediate band is almost flat, which means that the charge carriers possess very small mobility and are almost immobile. The electrons are shown to be localized around Ti impurities. Studies of optical properties of the material showed that because of the doping the material becomes slightly reflective. However, it remains to be transparent to visible part of the solar spectra.

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## Дослідження електронної структури $MgH_2$:Ti


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Досліджено електронну структуру $MgH_2$, легованого Ti за допомогою розрахунків з перших принципів. Показано, що домішки Ti, що заміщають Mg($Ti_{Mg}$), утворять частково заповнені електронами проміжні зони в забороненій зоні $MgH_2$. Ці зони локалізовані навколо домішки Ti. Відповідно, ефективні маси електронів у цих проміжних зонах можуть стати нескінченними. Це означає, що електрони в цих зонах нерухомі, і $MgH_2$:Ti залишається ізолятором. Енергія, відлічена від стелі валентної зони (або дна зони провідності) до рівня Фермі ≥2,8 еВ. Тому що ширина забороненої зони $MgH_2$ становить ~5,6 еВ, можна сказати, що енергія між дном зони провідності і рівнем Фермі також ~2,8 еВ. Таким чином, незважаючи на наявність проміжної зони, $MgH_2$ залишається прозорим у видимій частині сонячного спектра, що злегка відбиває і поглинає інфрачервоне світло. Ця властивість може бути важлива для смартових сонячних колекторів.