Structural stability and pressure-induced phase transitions in MgH$_2$

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The structural stability of MgH$_2$ has been studied up to 16 GPa using a high-pressure synchrotron x-ray diffraction technique. Several pressure-induced phase transitions have been identified in this pressure range. Owing to the close structural similarity between the $\alpha$ and $\gamma$ modifications the high-pressure $\gamma$ form can be stabilized as a metastable phase after pressure release. The experimentally observed structural transition sequence and the volume changes at the transition points as well as bulk modulii are found to be in good agreement with theoretically calculated data. The bonding nature of MgH$_2$ is analyzed with the help of charge-density, charge-transfer, electron-localization-function, and Mulliken-population analyses which clearly show that all polymorphs of MgH$_2$ are to be classified as ionic materials with Mg and H in nearly 2+1− states, respectively.

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I. INTRODUCTION

Hydrogen is considered to be one of the leading candidates for clean energy in the future. For safe and efficient hydrogen storage, developments of new alloys are currently being researched. Their hydrogen-storage capacity, reversibility, and desorption temperature and pressure are the most important parameters for a storage material of practical interest. The hydrides ought to have a high hydrogen-to-metal ratio and should not be too stable in order to achieve hydrogen release without excessive heating. Magnesium has as a light metal already for decades attracted large attention owing to its large mass-adsorption capacity for hydrogen, 7.6wt.%. On this basis, magnesium and its alloys are promising materials for hydrogen storage. However, the high thermodynamic stability of the magnesium hydrides prevents dehydrogenation under mild conditions. Furthermore, the slow cleavage of dihydrogen to atomic hydrogen and the low diffusion rate in MgH$_2$ have prevented pure Mg from being a real candidate material. In order to improve the hydrogen-storage properties of Mg-rich alloys, understanding of the structural stability and bonding nature of MgH$_2$ is considered as essential.

Several steps have been discussed in the literature as rate controlling for the hydrogen absorption and desorption processes. Improved kinetics has been found when Mg is mixed with several metallic additives (e.g., LaNi$_5$, Pd, V, FeTi) and ball milled. Therefore, recent attention has been paid to the investigation of new specific material properties of Mg alloys. In high-pressure syntheses of technologically important metal hydrides like Mg$_2$NiH$_4$, metastable $\gamma$-MgH$_2$ often occurs as a by-product. Hence, a complete study of MgH$_2$, including its stability at high pressures, is desirable. Preparation of the MgH$_2$, which is an electrical insulator, occurs essentially at high temperatures (>440 °C) and high hydrogen pressures (>30 atm). From the structural point of view MgH$_2$ is less stable (easily changing from one polymorph to another under the influence of pressure and temperature) than other dihydrides such as those of the rare earths and other saline hydrides like CaH$_2$, SrH$_2$ and BaH$_2$. Recently we have demonstrated by theoretical methods that the structural stability of MgH$_2$ highly depends on pressure, $\alpha$-MgH$_2$ transforming into four other modifications on application of pressure. The theoretical findings have motivated the here-reported high-pressure x-ray diffraction study. The positions of the hydrogen atoms in metal hydrides should really be determined by neutron diffraction since the scattering power of hydrogen is too weak for an accurate determination by x-ray diffraction. However, high-pressure neutron-diffraction experiments face other difficulties which we could not cope within this work. The aim of the present study has been to remedy this situation by examining the high-pressure forms of MgH$_2$ by synchrotron-radiation-based x-ray diffraction and with the knowledge of structure type, unit-cell dimensions, and the establish H positions by theoretical means. Furthermore, the chemical nature of the polymorphs is considered in some detail using first-principles density-functional theory (DFT) calculations.

II. EXPERIMENTAL AND COMPUTATION DETAILS

A. Synthesis

Magnesium powder was activated by heating at 450 °C under dynamical vacuum. After cooling to room temperature, hydrogen was introduced at a pressure of 5 bars and the temperature was then increased to 365 °C under this hydrogen pressure. At 365 °C the pressure was increased to 20 bars, and the sample was kept under these conditions for about 12 h. The 20-bar hydrogen pressure was maintained during the cooling of the sample to room temperature and then released.

B. High-pressure experiments and data analyses

Angle-dispersive powder x-ray diffraction (XRD) diagrams were collected at the ID9 beamline of the European Synchrotron Radiation Facility, Grenoble (\(\lambda=0.4176\) Å, x-ray beam size $30 \times 30$ μm$^2$, sample distance 365 mm), using image plate detection. Integrated intensities were ob-
TABLE I. Experimentally observed and theoretically calculated (in parentheses) structural parameters, bulk modulus ($B_0$), and pressure derivative of bulk modulus ($B'_0$) for MgH$_2$ in ambient and high-pressure phases.

<table>
<thead>
<tr>
<th>Modification, structure type</th>
<th>Unit cell (Å)</th>
<th>Positional parameters</th>
<th>$B_0$ (GPa)</th>
<th>$B'_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$, TiO$_2$-rutile ($P4_2/\text{mmm}$)</td>
<td>$a$</td>
<td>$b$</td>
<td>$c$</td>
<td>Mg ($2a$): 0, 0, 0</td>
</tr>
<tr>
<td>4.5176</td>
<td>4.5176</td>
<td>3.0206</td>
<td>H (4$f$): 0.304$^a$, 0.304$^a$, 0$^a$ (0.3043, 0.3043, 0)</td>
<td>(55)$^b$, (50)$^c$</td>
</tr>
<tr>
<td>4.5168$^a$</td>
<td>4.5168$^a$</td>
<td>3.0205$^a$</td>
<td>(4.4853)</td>
<td>(4.4853)</td>
</tr>
<tr>
<td>$\beta$, Modified CaF$_2$ ($Pa\bar{3}$)</td>
<td>4.6655</td>
<td>4.6655</td>
<td>4.6655</td>
<td>Mg (4a): 0, 0, 0</td>
</tr>
<tr>
<td>PdF$_2$-type</td>
<td>4.7902</td>
<td>4.7902</td>
<td>4.7902</td>
<td>H (8$c$): 0.3429, 0.3429, 0.3429</td>
</tr>
<tr>
<td>$\gamma$, $\alpha$-PbO$_2$ ($Pbcn$)</td>
<td>4.5246</td>
<td>5.4442</td>
<td>4.9285</td>
<td>Mg (4$c$): 0.0, 0.3314$^d$, 1/4</td>
</tr>
<tr>
<td>4.5051$^d$</td>
<td>5.4197$^d$</td>
<td>4.9168$^d$</td>
<td>H (8$d$): 0.2727$^e$, 0.1089$^e$, 0.0794$^e$</td>
<td>(48)</td>
</tr>
<tr>
<td>(4.4860)</td>
<td>(5.4024)</td>
<td>4.8985</td>
<td>(0.2717,0.1085,0.0801)</td>
<td></td>
</tr>
<tr>
<td>$\delta'$; AuSn$_2$ ($Pbca$)</td>
<td>8.8069</td>
<td>4.6838</td>
<td>4.3699</td>
<td>Mg (8$c$): 0.8823, 0.0271, 0.2790</td>
</tr>
<tr>
<td>(8.9476)</td>
<td>(4.6065)</td>
<td>4.5625</td>
<td>H1 (8$c$): 0.7970,0.3765,0.1651</td>
<td>(58)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H2 (8$c$): 0.9738,0.7433,0.5207</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Experimental value from Refs. 18 and 19.
$^b$Theoretical value from Refs. 21 and 20.
$^c$Theoretical value from Refs. 21 and 20.
$^d$Experimental value from Ref. 22.

C. Computational details

The *ab initio* generalized-gradient approximation (GGA) was used to obtain accurate exchange and correlation energies for a given structural arrangement. The structures are fully relaxed for all volumes considered using force as well as stress minimization. Experimentally established crystal-structure data were used as input when available. The projected-augmented-wave (PAW) implementation of the Vienna *ab initio* simulation package (VASP) was used for the total-energy calculations to establish phase stability and transition pressures. In order to avoid ambiguities regarding the free-energy results the same energy cutoff and a similar k-grid density for convergence were always used. In all calculations 500 k points in the whole Brillouin zone were used for $\alpha$-MgH$_2$ and a similar density of k points was used for all structural arrangements. A criterion of 0.01 meV atom$^{-1}$ was placed on the self-consistent convergence of the total energy, and all calculations used a plane-wave cutoff of 400 eV. The Mulliken-population analysis was made with the help of the CRYSTAL03 code in which we used 5-11G and 8-61G basis sets for H and Mg, respectively. To estimate the bond strength we have used crystal-orbital Hamiltonian-population (COHP) analyses, as is implemented in the TBLMTO-47 package.

III. RESULTS AND DISCUSSION

Experimentally observed and theoretically optimized structural parameters for $\alpha$, $\beta$, $\gamma$, and $\delta'$-MgH$_2$ are listed in Table I. Observed and calculated diffraction patterns for the different modifications of MgH$_2$ are displayed in Figs. 1 and 2. Figure 1 shows that the sample also contains a small amount of unreacted magnesium (hexagonal; $P6_3/mmc$; $a=3.2089$ Å, $c=5.2101$ Å). The experimental unit-cell dimensions for $\alpha$-MgH$_2$ are very good agreement with data reported in the literature (see Refs. 18 and 19 and Table I). The relative amount of unreacted Mg apparently diminishes during the exposure to high pressures, thus making the sample apparently phase pure above some 10 GPa. The theoretical calculations identified the tetragonal TiO$_2$-rutile-type phase as the ground state. At higher temperatures and pressures $\alpha$-MgH$_2$ transforms into the orthorhombic $\gamma$-MgH$_2$ form with $\alpha$-PbO$_2$-type structure (see the structural illustrations in Fig. 3). Recently Bortz et al. established the full structure of $\gamma$-MgH$_2$ from powder neutron-diffraction data collected at 2 GPa. However, it should be emphasized that a complete conversion of $\alpha$-MgH$_2$ into $\gamma$-MgH$_2$ was never achieved in the present study and the actual $\alpha$-to-$\gamma$-MgH$_2$ transition pressure could accordingly not be established.

Our recent theoretical structural stability study of MgH$_2$ predicted several pressure-induced structural transitions for MgH$_2$. In the calculated energy-difference plot with respect to $\alpha$-MgH$_2$ (Fig. 4) transitions are marked by the arrows. The
the same structural arrangement. This may be the reason why the calculated transition pressure for the \( \alpha \)-to-\( \gamma \)-MgH\(_2\) conversion is 0.387 GPa [Fig. 5(a)]. The total energies for the two modifications are nearly the same at the equilibrium volume (Fig. 4), which is natural since \( \alpha \)- and \( \gamma \)-MgH\(_2\) take nearly the same structural arrangement. This may be the reason why the two phases in practice coexist in a certain pressure range. A subsequent phase transition from \( \gamma \)- to \( \beta \)-MgH\(_2\) is calculated to occur at 3.84 GPa. In the pressure range from 6.7 to 10.2 GPa the structural arrangements of the \( \beta \), \( \delta \), and \( \delta' \) modifications lie within a narrow energy range of some 10 meV (Fig. 4; a further transformation to \( \epsilon \)-MgH\(_2\) is predicted at 10.26 GPa, but this is not verified experimentally). This closeness in energy suggests that the relative appearance of these modifications will be quite sensitive to, and easily affected by, external factors like temperature and remanent lattice stresses, as well as by kinetics. In this connection it should be recalled that the theoretical simulation relates to a defect-free pure phase at 0 K, whereas the high-pressure diffraction experiments were performed at room temperature on a sample burdened with likely defects and impurities.

The theoretically obtained and the experimentally measured pressure versus volume relations are displayed in Fig. 5. At ambient pressure (1 bar) and room temperature MgH\(_2\) stabilizes in the TiO\(_2\)-rutile-type structure with space group \( P4_2/mnm \). The primitive unit cell [Fig. 3(a)] contains two Mg and four H atoms. Each Mg atom is octahedrally coordinated to six H atoms, whereas each H atom is coordinated to three Mg atoms in the same plane. During compression \( \gamma \)-MgH\(_2\) starts to form at 5.5 GPa and coexists along with \( \alpha \)-MgH\(_2\) up to some 9.5 GPa. In a narrow pressure window between 9.35 and 10.36 GPa, the \( \beta \)-MgH\(_2\) polymorph exists in a three-phase mixture with the \( \alpha \) and \( \gamma \) modifications. The \( \gamma \)-phase Mg is octahedrally coordinated by six H atoms, and these octahedra are strongly distorted (Mg-H bond lengths in the range 1.920–2.011 Å, Mg-H bond angles between 88° and 102°) compared to the less distorted \( \alpha \)-MgH\(_2\) (Mg-H distances from 1.944 to 1.961 Å, ideal 90° H-Mg-H bond angles). With respect to the cubic \( \beta \) polymorph, the diffraction data alone were unable to distinguish between a more ideal CaF\(_2\)-type structure and variants thereof. The structure takes in any cases an fcc sublattice of Mg atoms. However, the theoretical investigation (Fig. 4) shows that the calculated total energy for the ideal CaF\(_2\)-type variant occurs at 1.5 eV higher energy than that for a modified CaF\(_2\)-type structure. Hence, we here simply postulate that the \( \beta \) polymorph takes a modified CaF\(_2\)-type structure. This sequence of experimentally established high-pressure polymorphs generally agrees with the theoretical predictions, although the observed transition pressures deviate somewhat from the calculated values. The latter findings may reflect that neither entropy nor temperature effects are taken into account in the theoretical simulation and, furthermore, that the experimental sample is not 100% pure. In addition, nucleation of new phases at a first-order transition may have slow kinetics. In comparison, for alkali-metal monohydrides the experimentally observed and the theoretically calculated transition pressures vary 3–7 GPa. In this perspective, the presently predicted and observed transition pressures may even be regarded as in good mutual agreement.

At pressure above 10 GPa the experimentally established \( \alpha \)-, \( \gamma \)-, and \( \beta \)-phase mixture transforms into an AuSn\(_2\)-type phase (this polymorph being hereafter denoted \( \delta' \)). This phase is structurally quite different from the theoretically predicted orthorhombic \( \delta \) phase (space group \( Pbca_2 \)). However, a closer look at Fig. 4 shows that the energy difference between these two modifications is indeed very small, less than 1 meV. Hence, the discrepancy between theory and experiment may be explained as metastability of the \( \delta' \) phase—e.g., invoked by the particular pressure sequence used experimentally. Similar to the other polymorphs, the structure
of the $\delta'$ modification contains Mg atoms in octahedral coordination by six H atoms and like in the $\gamma$ polymorph these octahedra are strongly distorted (Mg-H bond lengths between 1.796 and 1.899 Å and H-Mg-H bond angles between 83° and 108°). The $\delta'$ phase remained stable up to the highest pressures (16 GPa) reached in these experiments. It may be emphasized that the theoretical calculations suggest that an AlAu$_2$-type polymorph should be stabilized above 10.26 GPa.

Considerable hysteresis is observed in the phase changes upon pressure release. The $\delta'$ phase transforms into the $\beta$ polymorph at 9.85 GPa under decreasing pressure. This phase remains stable and constitutes the dominating phase at 6.23 GPa. The $\alpha$, $\gamma$ mixture finally converts into a single-phase product of $\gamma$-MgH$_2$ at 1.79 GPa. Hence, $\gamma$-MgH$_2$ remains as the final product after the completed decompression cycle. $\gamma$-MgH$_2$ is obviously metastable with respect to the stable $\alpha$ modification at ambient pressure. According to the theoretical calculations the involved energy difference between the $\alpha$ and $\gamma$ modifications is just 0.81 meV f.u.$^{-1}$. This closeness in energy can easily explain the occurrence of the $\gamma$ modification as a kinetically stabilized phase at ambient pressure. The observed volume difference between the $\alpha$ and $\gamma$ modifications at 298 K and 1 bar is small, $\gamma$-MgH$_2$ notably exhibiting the smaller volume [30.82 vs 30.65 (experiment), 30.64 vs 30.14 Å$^3$ f.u.$^{-1}$ (theory)]. The observed volume jump between the $\gamma$ and $\beta$ polymorphs upon compression (note two-phase mixture) is 1.16 Å$^3$ f.u.$^{-1}$, which is in good agreement with the theoretically obtained value of 1.45 Å$^3$ f.u.$^{-1}$. The initial impurity of Mg in the $\alpha$-MgH$_2$ sample appears to have disappeared on cycling of the sample through the $\delta'$ phase [compression to 15.36 GPa ($\delta'$ phase), decompression to 7.48 GPa ($\beta$ phase), decompression to ambient pressure (almost pure $\gamma$ phase)]. It should be noted that a phase change has been observed in carbonaceous MgB$_2$ above 9 GPa at 300 K after stress relaxation by laser heating. Continued research with such thermal annealing may bring out more insight into the kinetics of the $\alpha$-to-$\gamma$ phase transition.

All the experimentally verified MgH$_2$ polymorphs have distinct structural aspects in common. Closely related are $\alpha$- and $\gamma$-MgH$_2$, both comprising MgH$_6$ octahedra and three-coordinated hydrogen. Linear chains of edge-shared octahe-
dra run along the fourfold axis of the TiO$_2$-rutile-type structure of $\gamma$-MgH$_2$, whereas the octahedra are zigzag arranged in $\alpha$-MgH$_2$ with the $\alpha$-PbO$_2$-type structure. On turning to the $\beta$- and $\delta'$-MgH$_2$ modifications the chains no longer prevails. In $\beta$-MgH$_2$ the three-coordinated hydrogen atoms connect MgH$_6$ octahedra by corner sharing, whereas in the $\delta'$ polymorph edge sharing and increased effective coordination numbers (increased Mg-H distances; see Table II) for both H and Mg are observed. The MgH$_6$ octahedra become more severely distorted on increasing pressure. Furthermore, the H-H distance shrinks considerably, from around 2.5 Å in $\gamma$-MgH$_2$ to 2.3 Å in $\delta'$-MgH$_2$. The pressure induced $\alpha$-to-$\gamma$-to-$\beta$-to-$\delta'$ transition sequence involves reconstructive rearrangements (viz., some bonds are broken and others reestablished).

The bulk modulus ($B_0$) and its pressure derivative ($B'_0$) were extracted by fitting the experimentally observed pressure versus volume data to the third-order Birch-Murnaghan equation of state$^{27}$ (EOS) using the computer program EOS-FIT V5.2.$^{28}$ As inputs for $\alpha$-MgH$_2$ we used the equilibrium volume ($V_0=30.82$ Å$^3$ f.u.$^{-1}$) together with $B_0=50$ GPa and $B'_0=4$, the refined values of $B_0$ and $B'_0$ for the different polymorphs being included in Table I. In general, the theoretical $B_0$ values are slightly overestimated compared with those based on the experimental data. This is due to the underestimation of the equilibrium volume in the total energy calculations. The bulk moduli for the MgH$_2$ phases exceed that of Mg metal (35.4 GPa), implying that the introduction of hydrogen increases the stiffness. All MgH$_2$ polymorphs have rather similar $B_0$ values: according to the present data $\gamma$-MgH$_2$ has the lowest (44.03 GPa) and $\delta'$-MgH$_2$ the highest (49.84 GPa) $B_0$ value. Compared to, e.g., transition-metal dioxides, MgH$_2$ is a soft material, on the other hand, 3–4 times harder than alkali-metal aluminum hydrides.$^{29,30}$

**Bonding**

A number of investigations of magnesium hydrides using perturbative or other approximate methods are reported.
TABLE II. Interatomic distance (in Å) for the MgH$_2$ in the $\alpha$, $\beta$, $\gamma$, and $\delta'$ polymorphs (multiplicity in parentheses) derived using theoretically calculated positional parameters together with experimentally derived unit-cell dimensions.

<table>
<thead>
<tr>
<th>Distance</th>
<th>$\alpha$-MgH$_2$</th>
<th>$\gamma$-MgH$_2$</th>
<th>$\beta$-MgH$_2$</th>
<th>$\delta'$-MgH$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-H</td>
<td>1.944(2x)</td>
<td>1.920(2x)</td>
<td>1.906 (6x)</td>
<td>1.796(1x)</td>
</tr>
<tr>
<td></td>
<td>1.961(4x)</td>
<td>1.955(2x)</td>
<td>1.870(1x)</td>
<td>1.879(1x)</td>
</tr>
<tr>
<td></td>
<td>2.011(2x)</td>
<td></td>
<td>1.880(1x)</td>
<td>1.882(1x)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.899(1x)</td>
<td>2.085(1x)</td>
</tr>
<tr>
<td>Mg-Mg</td>
<td>3.021(2x)</td>
<td>3.073(2x)</td>
<td>3.299(12x)</td>
<td>2.849(1x)</td>
</tr>
<tr>
<td></td>
<td>3.534(8x)</td>
<td></td>
<td>3.023(2x)</td>
<td></td>
</tr>
<tr>
<td>H-H</td>
<td>2.501(1x)</td>
<td>2.507(1x)</td>
<td>2.489 (6x)</td>
<td>2.263(1x)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.249(1x)</td>
<td></td>
</tr>
</tbody>
</table>

Stander and Pacey$^{31}$ performed a Born-Mayer type of calculation of the lattice energy assuming that MgH$_2$ is purely ionic. Despite obvious significant overestimation, this theoretical value has been interpreted as evidence for appreciable covalent contributions to the bonding. The substantial difference in the electronegativities of Mg and H suggests strong ionic character with the Mg valence electrons transferred to the H sites under the formation of an insulator with stoichiometric MgH$_2$ composition. According to the present study the bonding characteristics are virtually the same in all MgH$_2$ polymorphs. The recent experimental study by Noritake et al.$^{32}$ mapped the charge-density distribution of $\alpha$-MgH$_2$, and owing to the mentioned similarity between the polymorphs, we display the only charge density, charge transfer, and ELF distribution for this polymorph in Figs. 6 and 7. The experimental (room temperature$^{32}$) and theoretically obtained (0 K) charge densities are indeed very similar, the distribution around Mg being almost spherical as expected for a nearly ideal ionic substance. The much lower charge density around the H sites is experimentally found to be slightly nonspherical with spreading in the direction toward neighboring Mg and H atoms. A closer look at the experimental electron distribution near the H sites shows that the deviation from spherical shape is higher than the corresponding feature in the theoretical distribution. This could be due to the effect of the different temperatures used in the two studies or an artifact produced by systematic discontinuities in the experimental data. However, both the experimental and theoretical charge-density maps clearly demonstrate the striking ionic character of $\alpha$-MgH$_2$ with small localized charges around the hydrogen sites. Following the common practice for ionic substances we assign ionic radii to the Mg and H ions on the assumption that the nearest-neighbor ions make touching contact. In this case an estimate of the radius for H isobtained from the shortest H-H distance and that for Mg from the shortest Mg-H distance (Table II). This gives a radius of 1.26 Å for H$^-$ and 0.69 Å for Mg$^{2+}$, which is quite different from the Pauling value of 2.08 Å for H$^-$, whereas the radius of Mg$^{2+}$ (0.69 Å) is consistent with the Pauling value (0.65 Å).

A qualitative perspective of the charge transfer in $\alpha$-MgH$_2$ is given in Fig. 7(a) which clearly shows a loss of charge from the Mg sites and a redistribution of this charge at the H sites, viz., another piece of evidence of strong ionic interaction between Mg and H. A different perspective of the bonding is provided by the ELF (an indicator of the electron-pair distribution, which takes values between 0 and 1; see Refs. 33–35). Figure 1(b) displays ELF contours similar to the charge densities in Fig. 6 and shows high ELF values, not only at the Mg sites, but also at the H sites. These characteristics nicely reveal the very distinct ionic nature of MgH$_2$. The ELF values between Mg and H is very low although a degree of polarization is visible, especially at the H$^-$ sites.

In order to further explore the bonding and estimate the amount of electrons on and between the participating atoms, we have performed Mulliken-population analysis. The calculated Mulliken effective charges (MECs) are listed in Table III for all MgH$_2$ polymorphs. MEC is +1.87$e$ for magnesium and −0.93$e$ for hydrogen in $\alpha$-MgH$_2$ whereas the overlap population between Mg$^{2+}$ and H$^-$ is almost zero. Similar MEC values and overlap populations are found for the other polymorphs, which leads to the conclusion that the bonding is virtually identical in all MgH$_2$ polymorphs. The bond strength between Mg and H in the various MgH$_2$ polymorphs, as expressed in terms of COHP, is displayed in Fig. 8. The valence band is in all cases seen to comprise mainly bonding orbitals (negative COHP), whereas antibonding or-

![FIG. 6. (a) Experimentally observed [at room temperature (Ref. 32)] and (b) calculated (at 0 K) charge-density distribution in the (001) plane of $\alpha$-MgH$_2$. The contour lines are drawn from 0.0 to 1.5 at 0.15$e$ Å$^{-3}$ intervals.](image-url)
bitalss are found above $E_F$. The integrated COHP’s (ICOHP’s) up to $E_F$ for the Mg-to-H bond gave values between $-1.61$ and $-1.71$ for the different polymorphs. This indicates that the different polymorphs are in nearly in the same bonding situation. Furthermore, it may be recorded that the value of the ICOHP for the Mg-H interactions takes almost half of that for the Al-H interaction in $\text{AAH}_4$ ($\text{A}=$alkali metal) series.\textsuperscript{36} A quantitative oriented partitioning scheme for assessment of energies associated with covalent and metallic bonds in solids has been proposed by Bester and Fähnle recently.\textsuperscript{37} However, the present focus has been on MgH\textsubscript{2} where ionic interactions dominate and for such problems COHP analysis still provides the best aid.

Let us finally recall that kinetic enhancement of hydrogen desorption from $\alpha$-MgH\textsubscript{2} (viz., destabilization of the $\alpha$-MgH\textsubscript{2} structure) has been achieved by the introduction of certain substitutional ingredients. On this background it seems logical to attempt such a substitution also in high-pressure form to see if this can stabilize or metastabilize some of the other modifications at ambient conditions as well as improving the desorption properties compared with $\alpha$-MgH\textsubscript{2}. Note that a previous density-functional study\textsuperscript{20} suggests that substitution of MgH\textsubscript{2} with monovalent or trivalent elements may introduce some metallic character in this salt. If this turns out to be of some relevance, it would certainly be interesting to explore the other polymorphs of MgH\textsubscript{2} along the same line.

TABLE III. Mulliken-population analysis for the MgH\textsubscript{2} polymorphs. The Mulliken effective charges (MEC) are given in terms of $e$.

<table>
<thead>
<tr>
<th>Polymorph</th>
<th>Atom</th>
<th>MEC</th>
<th>Overlap population</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>Mg</td>
<td>+1.87</td>
<td>$-0.040$ (Mg-H)</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>$-0.93$</td>
<td>$-0.124$ (H-H)</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Mg</td>
<td>+1.99</td>
<td>$-0.021$ (Mg-H)</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>$-0.99$</td>
<td>$-0.122$ (H-H)</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Mg</td>
<td>+1.98</td>
<td>$-0.024$ (Mg-H)</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>$-0.98$</td>
<td>$-0.115$ (H-H)</td>
</tr>
<tr>
<td>$\delta'$</td>
<td>Mg</td>
<td>+2.01</td>
<td>$-0.032$ (Mg-H)</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>$-1.01$</td>
<td>$-0.183$ (H-H)</td>
</tr>
</tbody>
</table>

FIG. 7. (Color online) (a) Calculated charge-transfer (see text) and (b) electron-localization-function maps for $\alpha$-MgH\textsubscript{2} in the (001) plane.

FIG. 8. Calculated crystal-orbital-Hamiltonian-population (COHP) profiles for the Mg-to-H bonds in different MgH\textsubscript{2} polymorphs. Integrated COHP value for $\alpha$, $\beta$, $\gamma$, and $\delta'$-MgH\textsubscript{2} is $-1.61$, $-1.65$, $-1.70$, and $-1.62$ eV, respectively.
IV. CONCLUSION

The present combined experimental and theoretical study has shown that $\alpha$-MgH$_2$ undergoes several pressure-induced structural transitions up to 17 GPa. Theoretical simulations have predicted that $\alpha$-MgH$_2$ transforms into $\gamma$, $\beta$, $\delta$, and $\epsilon$ modifications upon exposure to pressure, the $\gamma$ and $\beta$ forms being verified experimentally. Calculated and experimental unit-cell parameters are in excellent agreement wherever a comparison can be made. The high-pressure $\gamma$ modification is maintained as the metastable phase when the pressure is released at room temperature after a completed pressure loading-unloading cycle. A possible reason for this behavior is identified from the theoretical simulation. Instead of a theoretical $\delta$ modification with AuSn$_2$-type structure a $\beta'$ modification is established experimentally, whereas the existence of an $\epsilon$ modification could not be identified experimentally up to 17 GPa. The calculated and experimentally measured transition pressures and volume differences at the transition points are in good mutual agreement. The pressure-induced transitions in MgH$_2$ appear to be sensitive to the mode of the pressure and temperature changes. The charge-density, charge-transfer, electron-localization function and Mulliken-population analyses reveal that all polymorphs of MgH$_2$ have a dominant ionic character.

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