Effect of hydrogen on magnetic properties in MgO studied by first-principles calculations and experiments

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We investigated the effects of both intrinsic defects and hydrogen atom impurities on the magnetic properties of MgO samples. MgO in its pure defect-free state is known to be a nonmagnetic semiconductor. We employed density-functional theory and the Heyd–Scuseria–Ernzerhof (HSE) density functional. The calculated formation energy and total magnetic moment indicated that uncharged V0Mg and singly charged V−1Mg magnesium vacancies are more stable than oxygen vacancies (VO) under O-rich growth conditions and introduce a magnetic moment to MgO. The calculated density of states (DOS) results demonstrated that magnetic moments of VMg result from spin polarization of an unpaired electron of the partially occupied valence band, which is dominated by O 2p orbitals. Based on our calculations, VMg is the origin of magnetism and ferromagnetism in MgO. In contrast, the magnetic moment of the magnetic VMg-MgO crystal is suppressed by hydrogen (H) atoms, and unpaired electrons are donated to the unpaired electronic states of VMg when the defect complex H-VMg is formed. This suggests that H causes a reduction in magnetization of the ferromagnetic MgO. We then performed experimental studies to verify the DFT predictions by subjecting the MgO sample to a thermal treatment that creates Mg vacancies in the structure and intentionally doping the MgO sample with hydrogen atoms. We found good agreement between the DFT results and the experimental data. Our findings suggest that the ferromagnetism and diamagnetism of MgO can be controlled by heat treatment and hydrogen doping, which may find applications in magnetic sensing and switching under different environmental conditions.

Magnesium oxide (MgO) has shown attractive functionality in many applications, including as a material for refractory protective layers of AC plasma displays and a magnetic shielding/insulator layer in tunneling magnetoresistance (TMR) sensors for the hard disk drive (HDD) industry. MgO is a great insulator with a band gap of 7.8 eV. It can also be synthesized in many forms by several methods and has been intensively studied as a barrier layer for magnetic tunnel junctions. MgO is an important material for developing spintronic devices and has been widely utilized as a miniaturized magnetic sensor. However, there are still some features of MgO that are not understood. For example, MgO has been reported to exhibit ferromagnetism at room temperature, while it is known to be a diamagnetic material. This makes it unsuitable for spintronic applications since the barrier is supposed to be an electrical insulator that does not interfere with the spins of other layers.

The d0 magnetism is one of the phenomena that cause ferromagnetism in diamagnetic materials such as MgO, HfO2, ZnO, and CaO. The ferromagnetism arises from metal atom vacancies in the structure and the free electrons in oxygen atoms surrounding the vacancies couple together, resulting in the unbalanced magnetic
E \text{tot} matching the two values. The magnitude of this correction is \( \Delta V = <V_{\text{bulk}}>-<V_{\text{defect}}>/\). Where <V_{\text{bulk}}> and <V_{\text{defect}}> are the average self-consistent potentials calculated for the bulk and defect supercells, respectively. The alignment correction term (∆V) was approximately 0.1–0.4 eV for our calculations. The chemical potentials \( \mu_{\text{Mg}}, \mu_{\text{O}}, \) and \( \mu_{\text{H}} \) were limited by the energies of solid Mg, gaseous \( \text{O}_2 \), and \( \text{H}_2 \), which we referenced as zero energy. To grow MgO in thermal equilibrium, the chemical potential should satisfy \( \mu_{\text{Mg}} + \mu_{\text{O}} = \mu_{\text{MgO}} \). The calculated MgO chemical potential is \( \mu_{\text{MgO}} = -6.26 \text{eV} \), which is in agreement with the experimental enthalpy of formation value of \( -6.236 \text{eV} (601.7 \text{kJ/mol}) \). Therefore, in our calculations, we used \( \mu_{\text{Mg}} = -6.26 \text{eV} - \mu_{\text{O}}, \) where \( -6.26 \mu_{\text{O}} \leq 0 \) (defined that \( \mu_{\text{O}} = 0 \) was defined as half of the \( \text{O}_2 \) energy). In the presence of \( \text{O}, \) Mg forms MgO rather than solid Mg. Therefore, the upper limit of \( \mu_{\text{Mg}} \) is set by MgO precipitation limits, i.e., \( \mu_{\text{Mg}} = \mu_{\text{MgO}} - \mu_{\text{O}} \). For oxygen-rich conditions (\( \mu_{\text{O}} = 0 \)), \( \mu_{\text{Mg}} = -4.06 \text{eV} \).
Experimental procedure. The MgO samples used in this study contained defects such as Mg vacancies ($V_{Mg}$) and hydrogen atom impurities that were intentionally introduced into the samples. We note that all MgO samples were prepared from 96.0% MgO commercial powder (LOBA Chemie). $V_{Mg}$ was induced into the commercial MgO powder by heating it in a vacuum (pressure of $2 \times 10^{-2}$ Torr) at a temperature of 550 °C, and this was labeled “MgO vacuum heated”. After that, intentional hydrogen doping was carried out by flowing ultrahigh purity hydrogen gas (99.999%) at room temperature to the vacuum heated MgO sample for at least 5 h with different pressures, including 40 and 70 bars; these samples were labeled MgO vacuum heated with H$_2$ gas doping of 40 and 70 bars, respectively. Their magnetic behaviors were measured with a vibrating sample magnetometer (VSM) option in the VersaLab instrument (Quantum Design, USA) operated at applied magnetic fields between −5000 and 5000 Oe. The structures of all MgO samples were investigated with X-ray diffraction (XRD, Bruker D8 ADVANCE) using Cu-Kα radiation and operated at 40 kV and 40 mA. For Rietveld refinement analyses, high-quality X-ray diffraction patterns were collected in the 2-theta range 10°–120° with an interval step of 0.02° and a scan rate of 2 s/step. Rietveld refinement, using TOPAS software, was utilized to obtain crystallographic information. The FP peak type was utilized as the peak profile for fitting. Note that KCl was inserted into the XRD samples to act as an internal standard. The presence of the hydrogen dopant was characterized by Fourier transform infrared spectrometry (FT-IR, Bruker Tensor 27-Hyperion).

Results and discussion
Defect formation energy and electronic structures. As a first step toward understanding the magnetic properties and effects of hydrogen impurity atoms in MgO, we obtained the electronic structures and formation energies of intrinsic O and Mg vacancy defects as well as H impurity atoms. It was found in previous studies that when the aforementioned defects were present in MgO, they affected the magnetic properties of MgO.$^{17,24,41,42}$ Figure 1 shows relaxed atomic structural models for perfect bulk MgO (Fig. 1a) and the hydroxide salt Mg(OH)$_2$ (Fig. 1b), which was used as a reference and to study the hydrogen formed in MgO compounds in nature. The relaxed atomic structure of the point defect form (such as $V_{Mg}^0$, H$^+_1$, (H$^{-}_1$-$V_{Mg}$)$^{-1}$ and H$_2^{+1}$), which focuses on nearest neighbor atoms, is also shown in Fig. 1c–f, respectively. The perfect bulk MgO has a rock salt structure with a lattice constant of 4.199 Å, while the hydroxide form Mg(OH)$_2$ is hexagonal with lattice con-
The Mg-O bond lengths in MgO and Mg(OH)$_2$ are 2.099 Å and 2.115 Å, respectively. We found that the lowest energy atomic configuration of interstitial hydrogen in MgO (Fig. 1d) was quite similar to that of H formed in Mg(OH)$_2$. The interstitial H was bonded to an oxygen atom and bent off-axis from the Mg-O bond direction with an O–H bond length of 0.988 Å, which is comparable with the O–H bond length of 0.972 Å seen for Mg(OH)$_2$. For the VMg structure (Fig. 1b), the O anion moved away from the point defect; on the other hand, the Mg cation moved toward the point defect, causing the total volume of the cell around the point defect to decrease because Mg is larger than O. In the Hi case (Fig. 1d), the O nearest neighbor H atoms moved toward the H interstitial atom, whereas Mg moved outward from Hi because of the Coulomb repulsion between the cations, which increased the total volume of the cell. However, when the VMg and Hi form Hi-VMg complexes (Fig. 1e), the O anion still moves away from the VMg point defect, and Mg moves outward from Hi but less than in the previous single point defect cases because Coulombic repulsions were suppressed, resulting in a decrease in the total volume of the cell. Note that in calculations of defect cases, we found an approximate lattice constant by measuring the average Mg-to-Mg distance for atoms that surround the defect point (as shown in Fig. 1). The calculated lattice constants for VO$_{Mg}$, H$_{i}$, VMg, (Hi-VMg)$_0$ and (Hi-VMg)$_{-1}$ were 4.142, 4.422, 4.103, and 4.093 Å, respectively.

Figure 2 shows the formation energies calculated under O-rich conditions for the oxygen vacancy (VO) (solid black line), magnesium vacancy (VMg) (solid red line), hydrogen impurity (Hi) (solid green line), hydrogen impurity formed with a Mg vacancy (Hi-VMg) (solid purple line), and hydrogen impurity substituted on oxygen vacancy complex (HO) (solid yellow line) plotted as a function of Fermi energy. The zero Fermi energy is relative to the valence band maximum level, while the maximum Fermi energy represents the conduction band minimum. The slopes of the plots reflect changes in the charge states of the defect, and the kinks in the plots correspond to the energies at which transition from one charge state to another takes place, as discussed in the text. The binding energy levels of the (Hi-VMg) complex and HO are plotted as a function of Fermi energy with dashed lines.

For the formation energies of native vacancies (Fig. 2), VO is a donor defect with the lowest formation energy at a Fermi energy below 3.5 eV (p-type growth condition), which can be stable with +2 charges and form with a negative formation energy at Fermi energies below 2.5 eV. VMg is the lowest formation energy at a Fermi energy above 3.5 eV (n-type growth condition) and forms with a negative value at a Fermi energy above 5 eV. VMg is a shallow acceptor with a defect transition level change from the charge state q = 0 to the charge state q = −2 (eV/0−2) at a Fermi energy level of 4.7 eV. The relationship between the formation energy of a defect X of charge state q, $E_f(X^q)$, and its concentration $C(X^q)$ for a sample under thermal equilibrium is defined as $C(X^q) = \frac{N_{site}}{k_B T} \exp\left[-\frac{E_f(X^q)}{k_B T}\right]$, where $N_{site}$ is the number of equivalent possibilities with the same energies in which the defect can be incorporated (per unit volume), $k_B$ is Boltzmann’s constant, and $T$ is the temperature. Therefore, the defects with the lowest formation energies are stable and likely to form at high concentrations. These results suggest that VO and VMg can occur in the Fermi energy range of the sample under O-rich growth.

![Figure 2](https://doi.org/10.1038/s41598-022-13949-w)
conditions because both defects can be formed with highly negative formation energies. In addition, the defect concentration can be increased by increasing the temperature (T) of the sample. In general, the shift in Fermi energy due to doping is proportional to the temperature. If a MgO sample is heated at high temperature, the Fermi level will shift to a high energy. Therefore, under heat treatment conditions, \(V_{\text{Me}}^\text{−}\) is more likely to form than \(V_0\). When hydrogen (H) is doped into the MgO system, among several possible configurations studied for H, the interstitial structure shown in Fig. 1d turned out to have the lowest energy. The H impurity is likely to occupy interstitial sites close to an oxygen atom and act as a donor defect with +1 charge and formation energy lower than both \(V_0\) and \(V_{\text{Me}}\). As a charged defect, it can be compensated by a native defect with the opposite charge.

Potential compensating point acceptor defects include \(V_{\text{Me}}\). The formation energy of the H complex formed with \(V_{\text{Me}}\) (\(V_1\)) was calculated (the atomic structure is shown in Fig. 1c), and \(V_1\)− was stable for charge states 0 (\(H_1^{-}-V_{\text{Me}}^0\)) and -1 (\(H_1^{-}-V_{\text{Me}}^{-1}\)) (Fig. 2). \(H_1^{-}\) can donate an electron to the available states of \(V_{\text{Me}}\) charge state 0 (\(V_{\text{Me}}^0\)) and -2 (\(V_{\text{Me}}^{-2}\)), respectively. \(H_1^{-}-V_{\text{Me}}^0\) is a shallow acceptor exhibiting a defect transition level change from charge state \(q = 0\) to charge state \(q = -1\) at a Fermi energy level of 4.7 eV with a negative formation energy over the entire Fermi level range. This indicated that \(H_1^{-}-V_{\text{Me}}^0\) is quite stable and can form at high concentrations. Therefore, \(V_{\text{Me}}\) can be a compensating defect in H-doped MgO samples and form \(H_1^{-}-V_{\text{Me}}\). In the case of \(V_0\), hydrogen impurities cannot form defect complexes with \(V_0\) by substitution at vacancy sites surrounded by Mg cations (the atomic structure is shown in Fig. 1f). The \(H_1\) acts as a shallow donor, and it is stable only in charge state +1 (Fig. 2), meaning that the H acts as \(H_1^+\) to react with \(V_0\) in a stable charge state +2 (\(V_0^2^+\)). Therefore, the \(H_1\) behaves as a negative multicenter for defect structures, in agreement with Janotti et al. However, the formation energy of \(H_1\) is relatively high and positive throughout the Fermi level range for O-rich conditions. To determine the stabilities of such defect complexes (i.e., Fig. 2), we obtained the defect binding energy, which may be defined as \(E_{\text{bind}} = E(A-B) - E(A) - E(B)\), where \(E(A-B)\) is the formation energy of the A–B complex. The defect binding energy is more likely to form in Fig. 2, we observe the lowest binding energy of \(-2.45\) eV (purple dashed line) for \(H_1^{-}-V_{\text{Me}}\) and 1.97 eV (yellow dashed line) for the \(H_1\) complex. The binding energy of \(H_1^{-}-V_{\text{Me}}\) becomes negative at a high Fermi level (>4.5 eV) close to the conduction band edge. These results indicate that such complex defects are most stable and likely to form at a high concentration in that energy region. Therefore, \(H_1^{-}-V_{\text{Me}}\) is the dominant defect complex and has a lower binding energy than the \(H_1\) complex under O-rich growth conditions. This indicates that \(H_1\) can interact strongly with \(V_{\text{Me}}\) in MgO, which might cause suppression of the ferromagnetic properties of MgO, as reported in other experimental studies.

To understand the origin of defect-induced magnetization in MgO, we calculated the density of states (DOS) for perfect MgO and Mg(OH)\(_2\) (Fig. 3), as well as for various defect types (Fig. 4). The valence was defined by the state below the Fermi level. According to the orbital-resolved projected DOS, the valence bands of both perfect MgO (Fig. 3a) and Mg(OH)\(_2\) (Fig. 3b) were dominated by O 2 s (red) and O 2p (violet) orbitals, whereas almost all Mg 3 s (green) and 3p (blue) orbitals contributed to the conduction band. The valence band maximum was occupied only by O 2p electrons. In comparison, Mg 1 s orbitals (orange line in Fig. 3b) contributed to the upper (energy below −5 eV) and lower valence bands (energy below −20 eV for Mg(OH)\(_2\)). From the projection of the atomic orbitals, Mg 1 s orbitals formed covalent bonds with both O 2 s and O 2p orbitals. We found that the DOS for perfect MgO and Mg(OH)\(_2\) were symmetrical over the entire energy range for both spin-up (white area) and spin-down (gray area) states, indicating the sums of the magnetic moments or magnetizations of both MgO and Mg(OH)\(_2\) were zero, in good agreement with other published works. In other words, neither MgO nor Mg(OH)\(_2\) have any unpaired electron states. Therefore, a magnetic moment cannot occur in pure MgO or Mg(OH)\(_2\).

The total magnetic moments and specific magnetizations of various defect types are summarized in Table 1. The magnetic moment due only to the spin of an electron is 1 Bohr Magneton (\(\mu_B\)) = 9.27 × 10\(^{-22}\) emu. To convert this into magnetization, which is the magnetic moment per gram (or the magnetic moment per unit volume), we used the magnetic moment per cubic cell and divided this moment by the cell volume to obtain the magnetization in units of emu/cm\(^3\). The specific magnetization (emu/g) was obtained by dividing the above magnetization by the MgO density (3.47 g/cm\(^3\)). Our calculations showed that neutral \(V_{\text{Me}}^0\) and singly charged \(V_{\text{Me}}^0^+\) and \(V_{\text{Me}}^0^−\) were responsible for the magnetic moment of MgO, which originates from the partially occupied valence band. Other defects, i.e., \(V_{\text{Me}}^0\), \(V_{\text{Me}}^0^+\), and \(V_{\text{Me}}^0^−\), cannot induce magnetic moments in MgO. However, according to the formation energy, binding energy and magnetic moment results, oxygen vacancies can be ruled out under our conditions, as discussed above. In addition, there is \(V_{\text{Me}}^0^−\), which is responsible for the magnetic moment, but \(V_{\text{Me}}^0^−\) is not the charge defect with the lowest formation energy.

Figure 4a shows the total density of states for neutral \(V_{\text{Me}}^0\), which creates the hole state in MgO. Spin splitting exists in the valence band, and the spin-down states (gray area) are partially occupied, which is the cause for formation of the magnetic moment of ~2 \(\mu_B\). The projected atomic orbital DOS shows that the maximum valence is dominated by O 2p orbitals (solid violet line), which indicates that the magnetic moment is mainly induced by O 2p orbitals. In the same way, for \(V_{\text{Me}}^0\) (Fig. 4b), spin splitting also occurs in the valence band, and the spin-down states (gray area) are partially occupied, whereas \(V_{\text{Me}}^0\) also creates a magnetic moment (~1 \(\mu_B\)). In comparison, the spin-polarized electron orbitals of \(V_{\text{Me}}^0\) are symmetric. Therefore, \(V_{\text{Me}}^0\) cannot induce a magnetic moment (Fig. 4c). In other words, when removing Mg from MgO, the Mg-O bond is broken to form \(V_{\text{Me}}^0\) or \(V_{\text{Me}}^0\), which lose two and one donor electrons. This mechanism induced the hole state from O 2 p orbitals to compensate for the loss of electrons. However, \(V_{\text{Me}}^0\) has the lowest formation energy and can induce a magnetic moment. Therefore, under our experimental conditions, \(V_{\text{Me}}^0\) is the origin of the magnetism in MgO.

When we dope a donor H impurity into perfect MgO (\(H_1\)), the H defect creates unpaired states below the Fermi level and below the valence band (Fig. 4f) with H 1 s orbitals. This doping introduces a magnetic moment of 1 \(\mu_B\) (see Fig. 4f) because \(H_1\) contributes one s electron to the valence band (Fig. 4f). Hence, when the H impurity atom forms a defect complex with \(V_{\text{Me}}^0\), such as (\(H_1- V_{\text{Me}}^0\)), the H donates an electron to the O 2p hole state in the valence band of MgO, which is created by \(V_{\text{Me}}^0\) and fills the unpaired state, then the magnetic
moments remain 1 and 0 for \((H_1 - V_{Mg})^0\) and \((H_1 - V_{Mg})^{-1}\), respectively (see the DOS in Fig. 4d,e). Based on our calculation results, the origin of the magnetic moment in MgO is largely an unpaired electron from a Mg vacancy, in agreement with other works\textsuperscript{12,21–24}. Hydrogen impurities suppress the magnetic moment in magnetic MgO by donating electrons to unpaired electronic states. Therefore, hydrogen is the most significant cause of the reduced magnetic properties in ferromagnetic MgO, which might occur in aged MgO samples\textsuperscript{20,24}. For example, magnetic MgO samples are treated in air or under hydrogen gas. In this work, the \(V_{Mg}\) in MgO was induced by thermal heating in a vacuum environment because \(V_{Mg}\) is easy to form at low energy, whereas \(H_2\) gas injection into the MgO samples at different pressures was used to represent hydrogen doping. The structural and magnetic properties of MgO will be presented and discussed in the Experimental Section.

**Experimental results.** Figure 5 shows the XRD patterns for 96% MgO commercial powder (black line), vacuum heated (green line) MgO, and MgO vacuum heated with \(H_2\) gas doping at 40 bar (blue line) and 70 bar (red line). The diffraction peaks of the starting material were only indexed as the rock salt structure (Fm-3 m space group) of MgO, as indicated by ICDD No. 01-076-6597. The phase analyses for all samples mainly indicated MgO compositions. A small amount of CaCO\(_3\) is detected at 30° in the MgO commercial powder (black line), but this peak disappeared after heat treatment. Following the heat treatment, the data for the crystals were in agreement with ICDD No. 01-076-6597. We observed new small peaks present at approximately 35°, 50°, and 60° for the vacuum heated MgO sample (green line). Moreover, all of the new small peaks were significantly stronger after \(H_2\) gas doping at 40 and 70 bar (blue and red lines) and are possibly related to vacancy defects, \(H\) impurities, crystal direction, and lattice distortions in the MgO structure.

To further characterize the XRD results, Rietveld refinements of the data for the 96% MgO commercial sample and the vacuum heated MgO sample were utilized to obtain crystallographic information. Rietveld refinement is a useful method for investigating the full crystal structure details of synthesized materials, e.g., lattice parameters, atomic coordinates, and atomic occupancies. The approach is based on the least squares method, which can be described with the equation:

\[
S_y = \sum_i w_i \left[ y_i(\text{obs}) - y_i(\text{calc}) \right]^2,
\]

where \(w_i = 1/y_i\), \(y_i(\text{obs})\) is the observed intensity, \(y_i(\text{calc})\) is the calculated intensity and \(S_y\) is the weighted difference between these two values at step \(i\). The refinement procedure involves fitting of the observed XRD pattern to the calculated model structure or crystallographic information file to achieve the minimum \(S_y\). The fitting can be evaluated by the weight-profile R-value or \(R_{wp}\), where

\[
R_{wp} = \left\{ \sum_i w_i \left[ y_i(\text{obs}) - y_i(\text{calc}) \right]^2 / \sum_i w_i y_i(\text{obs})^2 \right\}^{1/2}.
\]

The site occupancy factor (SOF) is used to determine the fraction of a site occupied by a specific atom, which can be obtained with the structural factor.

**Figure 3.** Total density of states and projected density of states for (a) MgO and (b) Mg(OH)\(_2\), with projected orbitals (s, p, and d orbitals) from each atom. The Fermi energy is shifted to zero and is indicated by the gray dashed line. The white and gray shaded areas represent spin-up and spin-down electronic densities of states, respectively.
\[(F_{hkl}) \text{ equation: } F_{hkl} = \sum_{j=1}^{n} N_j f_j \exp \left[ 2\pi i (hx_j + ky_j + lz_j) \right] \]

where \(f_j\) is the scattering factor, \(N_j\) is the SOF, \((hkl)\) is the atomic plane and \((x, y, z)\) are fractional coordinates. If the SOF is equal to 1, every equivalent position \((x, y, z)\) is occupied. However, some of the sites are vacant if the SOF is less than 1.

**Figure 4.** Total density of states for various defects in MgO with (a) neutral \(V_0^{\text{Mg}}\), with projected atomic orbitals, (b) singly charged \(V_{\text{Mg}}^{-1}\), (c) doubly charged \(V_{\text{Mg}}^{2}\), (d) neutral \((H_1 - V_{\text{Mg}})^{-2}\) complex, (e) singly charge \((H_1 - V_{\text{Mg}})^{-1}\) and (f) singly charged \(H_1^{+1}\). The orange and gray shaded areas represent spin-up and spin-down electronic densities of states, respectively. The Fermi energy is shifted to zero and indicated by a black dash-dotted line.

**Table 1.** Total magnetic moments \((M)\) in Bohr magnetons \((\mu_B)\) and the specific magnetization in emu/g within corresponding defects.
Figure 5. XRD patterns for 96% commercial MgO (black line), MgO vacuum heated (green line), and MgO vacuum heated with H₂ gas doping at 40 bar (blue line) and 70 bar (red line). * is marked as CaCO₃ impurity.

Figure 6. Rietveld refinement plots of MgO and MgO-vacuum heated samples. MgO crystallized in the Fm-3 m (225) space group. KCl was used as an internal standard representing the CaCO₃ phase.

Figure 6 shows Rietveld refinement plots for the 96% MgO commercial sample and the MgO vacuum heated sample. In this work, the fits between the observed XRD patterns and the structural model showed convergence with good weight-profile R values (%Rwp) and goodness of fit (GOF), as shown in Table 2. The cell parameter a was decreased from 4.2202(2) Å to 4.2163(1) Å upon vacuum heating, which agreed with our DFT relaxed structure. The VMg results in a decrease in the lattice constant of the cell. The calculated and experimental lattice constants are summarized in Table 3. The results also revealed the phase compositions for both samples; the MgO sample contained 97.79(18) wt% of the MgO phase and 2.21(18) wt% of CaCO₃, while the MgO-vacuum heated sample included only the MgO phase. The crystallographic details obtained are shown in Tables 2 and 4. The site occupancy factor (SOF) was determined to be 1.0000(56) for Mg in the MgO sample, corresponding to the stoichiometric ratio in the starting material. However, the value was reduced to 0.9623(31) after vacuum heating, which indicated the formation of Mg vacancies. This result corresponded to the formation energy predicted by DFT, and Mg vacancies were induced by vacuum heating and are more stable than oxygen vacancies. Furthermore, equivalent isotropic thermal parameters (Beq.) of Mg and O atoms in MgO 96% commercial
powder and MgO-vacuum heated samples corresponded to the crystallographic information file (CIF file), as shown in Table 4. These values are useful for describing the motions of atoms in crystal structures, where lighter atoms vibrate stronger and exhibit higher values.

Figure 7 shows the magnetization-magnetic field hysteresis curves (M-H hysteresis curves) of commercial MgO powder (black dashed line), vacuum heated MgO (solid blue line), and MgO vacuum heated with H₂ gas at 40 bar (solid green line) and 70 bar (solid red line). Note that all presented data were analyzed with subtraction of the diamagnetic components. After subtraction, we found that the M-H hysteresis curves of all MgO samples showed ferromagnetic behavior with different magnetization values. The 96.0% MgO commercial powder produced an amplitude for the M-H curve with a small magnetization value of approximately 0.31 emu/g, which is close to zero. According to the DFT prediction, bulk MgO is diamagnetic, which should result in a magnetization value of 0 emu/g. In addition, the SOF values for 96.0% MgO commercial powder (Table 4) were equal to 1 for both Mg and O atoms. Therefore, the small magnetism of the commercial powder was from some magnetic element contaminant, and the specification data for commercial MgO powder included 0.0025% Fe and 0.0005% Pb. After heat treatment, the M-H hysteresis curve of the MgO vacuum heated sample increased to give the highest ferromagnetic magnetism of approximately 3.9 emu/g. We propose that the VMg induced by heat treatment caused the increase in the ferromagnetic magnetism of the MgO vacuum heated sample. Another possible mechanism for inducing magnetism may involve converting H impurities back to their original state (VMg) by using heat treatment [20,45]. Next, by doping with hydrogen, we found that the ferromagnetic magnetism of MgO vacuum heated with H₂ gas decreased to approximately 1.63 and 0.31 emu/g for gas pressures of 40 and 70 bars, respectively. Based on our theoretical DFT prediction, Table 1 shows that the neutral VMg, which was created by vacuum heating, has a total magnetic moment of 2.0478 µB or 9.75 emu/g, corresponding to a concentration of 3.06% for Mg vacancies (one Mg vacancy in a 64-atom supercell). If we dope hydrogen with the same concentration as VMg, hydrogen will form a (H – VMg)⁺ complex that gives a total magnetic moment of 1.0 µB or 4.83 emu/g. This prediction corresponds with experiment; when we treated the MgO vacuum heated sample with H₂ gas at 40 bar, the maximum ferromagnetic magnetism dropped from 3.9 to 1.63 emu/g, which was approximately 50% lower than the DFT prediction. Next, if we continued to treat the vacuum heated MgO with a hydrogen concentration greater than the VMg concentration, the situation might be described as (H – VMg)⁻¹ cases. The magnetization of (H – VMg)⁻¹ will be reduced to zero, consistent with DFT prediction, as shown in Table 1. This is because hydrogen donates an electron to (H – VMg)⁺, which completely fills the unpaired state of (H – VMg)⁻¹. This results in conversion of the magnetization for the vacuum heated MgO treated with H₂ gas at 70 bar back to the MgO initial value. We showed how introduction of magnesium vacancies VMg and hydrogen atom impurities can be used to control the magnetic properties of MgO.

Table 2. Crystallographic information obtained from Rietveld refinement of data for MgO and MgO vacuum heated samples (Mg-Vac).

| Sample            | Residual parameters | Lattice parameters |
|-------------------|---------------------|--------------------|
|                   | Rexp (%) | R_p (%) | Rwp (%) | GOF | a (Å) | V (Å³) |
| MgO               | 3.05     | 9.47    | 12.37   | 4.06 | 4.2202 (2) | 75.16 (1) |
| MgO-Vac           | 2.85     | 6.40    | 8.66    | 3.04 | 4.2163 (1) | 74.95 (1) |

Table 3. Experimental lattice constants for various experimental samples determined from XRD spectra (Fig. 5) and calculated lattice constants from predicted cases.

| Samples                      | Experimental lattice constant (Å) | Calculated lattice constant (Å) |
|------------------------------|----------------------------------|--------------------------------|
| MgO-commercial powder        | 4.22                             | 4.20                           |
| MgO-vacuum heated            | 4.21                             | 4.14                           |
| MgO vacuum heated with H₂ gas dopant at 40 bars | 4.21                             | 4.10                           |
| MgO vacuum heated with H₂ gas dopant at 70 bars | 4.21                             | 4.09                           |

Table 4. Atomic coordinates, site occupancy factors (SOF) and equivalent isotropic thermal parameters (Beq.) of MgO in MgO and MgO-vacuum heated samples.

| Atom   | Wyckoff Site | x    | y    | z    | SOF  | Beq   |
|--------|--------------|------|------|------|------|-------|
| MgO    | 4a           | 0    | 0    | 0    | 1.0000 (56) | 0.312 |
| MgO-Vac|              |      |      |      | 0.9623 (31) | 0.312 |
| Mg     | 4a           | 1/2  | 1/2  | 1/2  | 1    | 0.362 |
| O      | 4b           | 0    | 0    | 0    | 1    | 0.362 |
| Mg     | 4a           | 1/2  | 1/2  | 1/2  | 1    | 0.362 |
| O      | 4b           | 0    | 0    | 0    | 1    | 0.362 |
To confirm the presence of hydrogen in MgO, we measured FTIR spectra for the MgO commercial powder, vacuum heated MgO, MgO vacuum heated with H₂ gas doping at 40 bar and 70 bar, and the reheated vacuum heated MgO with H₂ gas at 70 bar. The FTIR spectra of all MgO samples recorded over the wavenumber range 0–4500 cm⁻¹ are shown in Fig. 8a, which shows two strong absorption peaks at 3700 cm⁻¹ and 1500 cm⁻¹. The absorption peak at 3700 cm⁻¹ corresponds to a –OH stretching vibration in MgO⁴⁶, whereas the absorption peak at 1500 cm⁻¹ is related to bending vibrational modes of physisorbed water⁴⁷. These observations may have resulted from reactions between all MgO samples and humidity in the ambient environment during sample preparation for FTIR measurements. The presence of the –OH vibration is consistent with our calculation and the VSM results, as discussed earlier. The MgO commercial powder (solid black line) showed an absorption peak at
3700 cm⁻¹, which was higher than that of the vacuum-heated MgO sample (solid green line), as shown in Fig. 8b. This indicated that the MgO commercial powder had already absorbed hydrogen, which might have come from humidity in the ambient environment during sample preparation, as indicated by a very intense physisorbed water peak at 1500 cm⁻¹. After heat treatment, we found that the vacuum heated MgO sample showed the weakest absorption peak at 1500 cm⁻¹ (see Fig. 8c), implying that the physisorbed water was removed and the structure was changed due to intrinsic defects such as VMg. After doping the vacuum heated MgO sample with H₂ gas, we observed that the absorption peaks at 3700 cm⁻¹ for MgO vacuum heated with H₂ gas at 40 bar and 70 bar (blue and red solid lines) were substantially increased, which was evidence of hydrogen absorption by the samples (see Fig. 8b). Hydrogen absorption was further confirmed by reheating the sample in a vacuum at 550 °C. The reheated MgO sample doped with H₂ gas at 70 bar (yellow dashed line) showed a decrease in the absorption peak at 3700 cm⁻¹ (see Fig. 8b), indicating that adsorbed hydrogen was eliminated by the heating process.

Conclusion
We used first-principles DFT calculations to investigate formation and the electronic and magnetic properties of MgO samples containing intrinsic vacancy defects and added hydrogen impurity atoms. We found that magnetic moments cannot exist in a perfect MgO crystal or the hydroxide Mg(OH)₂. Unpaired electrons dominate the formation of magnetic moments in MgO from VMg, which was confirmed by the formation energy and density of states. Moreover, a hydrogen impurity can be formed as an interstitial (Hᵢ) in MgO and is likely to form a Hᵢ − VMg complex. The magnetic moment of ferromagnetic VMg-MgO is suppressed by hydrogen in the Hᵢ − VMg form and donated to unpaired electronic states. Therefore, H causes the reduced and degraded magnetic properties in ferromagnetic MgO.

The XRD result showed that new small peaks seen at approximately 35°, 50°, and 60° after heat treatment and hydrogen doping correspond to vacancy defects and hydrogen impurities in the MgO structure. The VSM result confirms that the vacuum-heated MgO sample exhibits the highest ferromagnetic magnetization induced by VMg. The ferromagnetism of VMg-MgO can be suppressed by hydrogen doping, as ferromagnetic magnetism is decreased by increased doping with H₂ gas, which results from the formation of Hᵢ − VMg. The presence of doped hydrogen in MgO was confirmed by FTIR measurements. The FTIR result also shows that the hydrogen dopant in MgO can be eliminated by heating. Our findings demonstrate that the ferromagnetic and diamagnetic properties of MgO can be controlled by heat treatment and hydrogen doping, which is useful for applications in magnetic sensing and switching.

Data availability
Experimental and calculated data are available for access at https://1drv.ms/u/s!AvS-bfeefGHCjR36okvSinterneg?e=AXk4f26.

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Author contributions
I.F. and S.L. conceived the idea and designed the theoretical calculations. B.Y., W.J., T.T., and W.M. designed and carried out the experiments. I.F., W.J., and W.M. also contributed to writing and revising the manuscript. B.Y., W.M., W.J., and T.T. prepared all samples for the experiments. W.S. and N.T. performed the XRD and IR measurements and analyses. R.U. operated the system for preparing hydrogen-doped samples. N.C. and S.P. supported the VSM measurements and analyses. A.K. and P.T. provided data from previous experiments and discussions and contributed to the manuscript revision. W.M. provided research infrastructure and determined the project direction. All authors reviewed the manuscript and commented on various parts.

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Competing interests
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