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Electronic and structural properties of MgH_2

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The electronic and structural properties of MgH_2 are calculated using an *ab initio* pseudopotential method. The calculated quantities are the equilibrium structural parameters, the cohesive energy, a few selected elastic constants, the bulk modulus, the phonon frequency of a zone-center optical mode involving hydrogen vibration, the energy-band structure, the density of states, and the electronic charge distribution. The structural parameters and the cohesive energy are in good agreement with experiments. No comparisons are made for the other calculated properties because of the lack of experimental values. The bonding nature of MgH_2 is interpreted in terms of the band structure and the charge distribution. Covalent bonding was not found, in contrast to previous suggestions that it exists in MgH_2. Based on our band-structure and charge-density results, we suggest that MgH_2 doped with a monovalent element could be a superconductor.

I. INTRODUCTION

There has been a great interest in metal hydride systems[1,2] stimulated by both the fundamental interests and various applications. Metal hydrides exhibit a number of interesting effects, among these is superconductivity,[1] for example. Potential applications include using metal hydrides as storage media for hydrogen. Electronic structure studies of metal hydrides have been concentrated on the transition-metal hydrides and rare-earth hydrides.[3] On the other hand, first-principles calculations of simple-metal hydrides are rare. Magnesium hydride[4] is considered to be one of the most important candidates for the reversible storage of hydrogen because of its high weight percentage of hydrogen. However, its usefulness is impeded by the slow rate of reaction and dissociation.[4] In order to improve on its performance, an understanding of the electronic and structural properties of magnesium hydride is essential.

A number of investigations on magnesium hydride using perturbative or other approximate methods have been reported. Stander and Pacey[5] have performed a Born-Mayer type of calculation of the lattice energy of MgH_2 assuming that MgH_2 is purely ionic. Their theoretical value was greater in magnitude than the experimental value by a sizeable amount. This difference was interpreted by them as evidence of an appreciable covalent contribution to the bonding in the crystal. Lindner and Berggren[6] investigated the structural properties using a nearly free-electron model. They predicted the stable structure correctly and their calculated lattice parameters were in reasonable agreement with experiment. Another calculation was done by Krasko,[7] which employed an iteration-perturbation approach of covalent bonding. The equilibrium cell volume and the charge density were investigated. His calculated binding energy implied that MgH_2 cannot be formed from Mg metal and H_2 gas in contrast to experiments. Empirical pseudopotentials were employed in both studies. More recently, Felsteiner *et al.*[8] used the orthogonalized-plane-wave (OPW) method and the linear combination of atomic orbitals (LCAO) method to study magnesium hydride but they concentrated on the Compton profile. The details of the electronic band structure and other properties of MgH_2 have not been fully investigated.

In view of the above situation, we have performed a comprehensive study on the electronic and structural properties of magnesium hydride. The *ab initio* pseudopotential approach[9,10] within the density functional formalism[11] is used. We have determined the structural parameters, the cohesive energy, a few selected elastic constants, the bulk modulus, the phonon frequency of a zone-center hydrogen-vibrational mode (Γ_1^+), the electronic band structure, the electronic density of states, and the valence charge distributions. The calculated structural parameters and the cohesive energy are in better agreement with experiments than those of the previous calculations. We did not find experimental values for the other calculated quantities. We also investigated the bonding nature of MgH_2. Although the electrons are found to be localized around the H sites in general, the hydrogen ion is not H^-. There is about 19% of charge in the interstitial region. We found that there is no covalent bond charge between the nearest-neighbor H and Mg sites. Our results indicate that the Mg potentials have little effect on the structure of the valence band, but are important for the determination of the indirect energy gap. Based on our calculated band structure and charge density, we suggest that magnesium hydride doped with a monovalent element could be a superconductor. The remainder of the paper is arranged as follows. In Sec. II the calculational procedure is described in detail. The structural properties and phonon frequency are given in Sec. III. The calculated electronic properties are presented and discussed in Sec. IV. Comparison with experimental results is made wherever they are available. The possibility of superconductivity in doped MgH_2 is discussed in Sec. V. A brief summary is given in Sec. VI.

II. CALCULATIONAL DETAILS

The calculation is based on the pseudopotential method[9] within the density-functional formalism.[11] The core electrons of the atoms are assumed to be atomiclike and do not respond to the chemical environment. The interaction of the valence electrons and the core is simulated by pseudopotentials. Exchange and correlation are taken into account in the local-density approximation (LDA). The Wigner interpolation formula[12] is used for the exchange and correlation functional in the present work. We have also used other expressions for the exchange and correlation potential,[13,14] the results are comparable.

The *ab initio* pseudopotentials are generated using the method of Hamann, Schlüter, and Chiang.[10] These potentials are nonlocal, i.e., angular momentum dependent. In this study the Mg potential is generated from the atomic configuration Mg $3s^1 3p^1$. In order to ensure that the potential accurately simulates the core-valence interaction, the results for several ionic configurations were compared with those of the all electron calculations. For hydrogen, only the s potential is generated. Since there are no core electrons for hydrogen, the potential that the valence electron experiences should be strictly that of the proton. However, the pseudopotential and the protonic potential produce almost the same eigenenergy since the potentials are appreciably different only near the nucleus. The difference between the total energies of the pseudoatom calculation and the all-electron calculation for H atom is less than 10^{-4} Ry with various forms of exchange and correlation, spin polarized and non-spin-polarized. The most convenient scheme for crystal band-structure calculation is to expand the wave functions in terms of plane waves.[15] This approach has proved to be very successful in the study of a wide variety of materials.[16–21] Due to the localized nature of the hydrogen 1s orbital, a large number of plane waves are required for the satisfactory convergence of the total energy. Diagonalization is carried out using the residual minimization method of Bendt and Zunger.[22] The kinetic energy cutoff is 30 Ry for the calculation of all the properties. This corresponds to about 1200 plane waves for the equilibrium lattice parameters. Extrapolation to infinite cutoff energy yielded a decrease in total energy by 0.9 eV per unit cell. A six-special-**k**-point scheme[23] is employed for the Brillouin-zone (BZ) integration of the charge density and the band energy. The difference between the total energies calculated with the six-special-**k**-point scheme and with 50 **k** points over the $\frac{1}{16}$th irreducible part of the Brillouin zone is less than 1 mRy. The calculation is done self-consistently. The solution is iterated until an accuracy of 10^{-4} Ry in the self-consistent potential is achieved. The corresponding tolerance of the total energy is less than 10^{-5} Ry.

Under ambient conditions, MgH_2 crystallizes in the tetragonal phase of the rutile type,[24,25] which has the space group $P4_2/mnm$. Figure 1 shows the Mg and H atoms in the unit cell. The primitive cell contains two Mg atoms and four H atoms. The Mg atoms are located at the corner and the center of the cell. A parameter x describes the position of the four H atoms. Each Mg atom is octahedrally coordinated to six H atoms, and each H atom is coordinated to three Mg atoms in the same plane. This structure has three independent structural and lattice parameters, they are x, c/a, and a. The tetragonal structure is assumed in our calculations. The total energy is calculated for different values of x, c/a, and a. A quadratic fit for the total energy is then used to determine the equilibrium values of the three parameters.

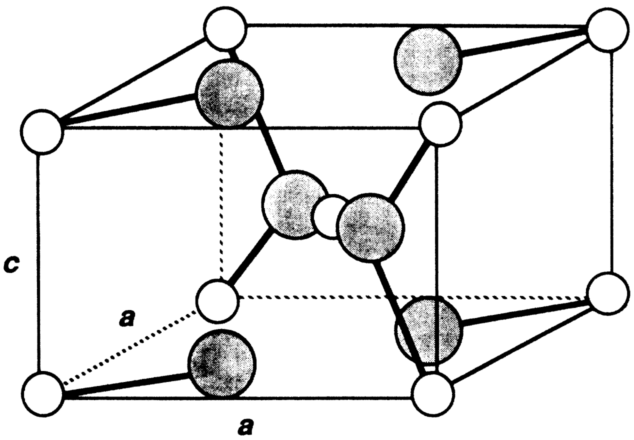

FIG. 1. Arrangement of H and Mg atoms in the tetragonal cell of the rutile type. The open circles are Mg atoms, and the shaded circles represent H atoms. The thick lines between the atoms are used for visual purposes. Two Mg atoms are located at (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and four H atoms are located at $(x,x,0)$, $(1-x,1-x,0)$, $(\frac{1}{2}+x,\frac{1}{2}-x,\frac{1}{2})$ and $(\frac{1}{2}-x,\frac{1}{2}+x,\frac{1}{2})$ in units of lattice constants $a=4.517$ Å and $c=3.021$ Å. Experimental value of x is 0.306.

III. STRUCTURAL PROPERTIES

A. Lattice parameters

In this work the minimum energy is found at the following lattice and structural parameters, $a/a_B=8.604$, $c/a_B=5.747$, and $x=0.304$. We have calculated the total energy at 27 points in the neighborhood of the above values. The parabolic fit is accurate to 5×10^{-5} Ry. Same results are obtained whether c or c/a is treated as an independent variable in the parabolic fitting. These calculated values are compared with the experimental values in Table I. The differences with the experimental values are given in parentheses. Lindner and Berggren[6] have computed the equilibrium lattice parameters for alkaline-earth hydrides using empirical pseudopotentials and a nearly free-electron approach. More recently, Krasko[7] used empirical pseudopotentials and an iteration-perturbation approach of covalent bonding to determine the equilibrium volume by fixing the parameters c/a and x to the experimental values. The results of these two calculations are also given in Table I. Our calculated structural and lattice parameters are in better agreement with experiment.[25] The maximum difference is 2.2% between our calculated and the experimental unit cell volume.

TABLE I. Calculated and experimental structural properties and cohesive energy of MgH_2. Differences are given in parentheses. Length is in units of Bohr radius and cohesive energy in eV per unit cell. The bulk modulus and elastic constants are in units of 10^{12} dyn/cm^2. The phonon frequency is in units of 10^{13} Hz. See text for elastic constants and quantities below them.

	Experiment	Calculations		
		Present work	Lindner and Berggren (Ref. 6)	Krasko (Ref. 7)
x	0.306[a]	0.304(+0.002)	0.306(0.0)	
$a(a_B)$	8.536	8.604(+0.068)	8.62(+0.084)	8.746(+0.21)
$c(a_B)$	5.709	5.747(+0.038)	6.18(+0.471)	
c/a	0.669	0.668(−0.001)	0.717(+0.048)	
Cell volume (a_B^3)	416.0	425.5(+9.5)	459.2(+43.2)	447.5(+31.5)
Cohesive energy [eV/(unit cell)]	13.4[b]	11.2–13.5[c] −(2.2–+0.1)		6.4(−7.0)
$C_{11}+C_{12}$ (10^{12} dyn/cm^2)		1.1		
C_{13} (10^{12} dyn/cm^2)		0.3		
C_{33} (10^{12} dyn/cm^2)		1.0		
Bulk modulus B_0 (10^{12} dyn/cm^2)		0.50		
B_0'		4.9		
Γ_1^+ optical mode (10^{13} Hz)		3.81		

[a] Reference 25.
[b] See text.
[c] See text.

For crystals with the rutile structure, each cation is surrounded by six anions forming an octahedron. This octahedron is irregular, and the distances between the cation and the anions take two values. If we demand these two separations to be equal, the parameter x is then related to c/a ratio by $x=\frac{1}{8}[2+(c/a)^2]$. This is true to within about 1.5% for most crystals for which the x value is known (Table IV,3 of Ref. 24, except FeF_2). For MgH_2, the value of x calculated from the experimental c/a using the above expression is 0.306, which is the same as the experimental result. One could argue on the basis of a pair-potential model that these equal distances are favored by the total energy of the crystal. The experimental values of the c/a ratio of most crystals falls within the range of about 0.65 to 0.7. To correlate this with an approximate theoretical prediction, we can examine the variation of the Madelung energy with respect to c/a. Since the Madelung energy alone does not give a stable structure, we need to constraint the other parameters. From the above discussion, it seems reasonable to let the six nearest-neighbor Mg-H distances equal. Another reasonable constraint is to fix the unit cell volume. With these two conditions, we obtain an energy minimum at $c/a \simeq 0.67$. If we keep the nearest-neighbor Mg-H distances constant instead of the cell volume, the Madelung energy then minimizes at $c/a \simeq 0.71$. Thus the crude consideration of the Madelung energy seems to give the c/a ratio which coincides with the range of the experimental values. However, one should not conclude from the above results that these crystals are fully ionic.

B. Cohesive energy

The cohesive energy is taken to be the difference between the total energy of the crystal and that of the atoms. We performed a spin-polarized calculation for the H atom with the Ceperly-Alder expression[14] for the exchange and correlation functional. The calculated total energy of the H atom is -0.958 Ry. The total energy of the pseudo-Mg atom is -1.688 Ry. The crystal energy calculated with the cutoff energy of 30 Ry is -8.209 Ry per unit cell. Hence the cohesive energy is 13.6 eV per unit cell. Taking into account the 0.9-eV decrease of the total energy of MgH_2 as the cutoff energy is extrapolated to infinity, the calculated cohesive energy becomes 14.5 eV per unit cell. This result does not include the vibrational energy of the solid. Since the Debye temperature for MgH_2 is fairly high, the zero-point energy may not be neglected. At the present, there is no experimental value available for the complete phonon spectrum or the Debye temperature. Following Stander and Pacey,[5] we use as the Debye frequency the maximum frequency at which the infrared absorption peak occurs, which is 3.48×10^{13} sec^{-1}. This corresponds to a Debye temperature θ_D of 1670 K. The zero-point energy is approximated by $\frac{9}{8}k_B\theta_D$ per atom using the Debye model.[26] The corrected cohesive energy is 13.5 eV per unit cell. One may argue that one should use the exact total energy of the H atom, that is, -1.0 Ry. The cohesive energy will then be 11.2 eV per unit cell. If the Gunnarsson-Lundqvist-Wilkins expression[27] for the spin-polarized exchange and correlation potential is used, the total energy of the H atom is -0.984 Ry and the cohesive energy of MgH_2 is 12.1 eV per unit cell. We consider that the theoretical value for the cohesive energy ranges from 11.2 to 13.5 eV. We evaluated the experimental cohesive energy from the heat of formation of magnesium hydride (0.70 eV/molecule), the cohesive energy of Mg solid (1.52 eV/atom), and the bonding energy of H_2 molecule (4.48 eV/molecule).[28] The experimental cohesive energy is 13.4 eV per unit cell. The difference between our theoretical value and the experimental value ranges from ~0.0 to 0.37 eV/atom. This difference is on the same order of magnitude as that obtained in other local-density calculations for metals.[16,17] We also calculated the total crystal energy at the above equilibrium parameters using different forms of exchange and correlation potential. The Hedin-Lundqvist expression[13] gives a cohesive energy greater than the result with Wigner interpolation formula[12] by 0.14 eV/atom. The Ceperly-Alder form for the exchange and correlation[14] gives almost the same cohesive energy as the Wigner interpolation formula.

C. Elastic constants and bulk modulus

From the quadratic fit of the total energy with respect to the parameters a, c, and x described above (Sec. III A), the elastic constants can be obtained. There are six elastic constants for a tetragonal crystal. Four of these C_{11}, C_{12}, C_{13}, and C_{33}, are related to the variation of the parameters a and c. Since the strain e_1 is always equal to e_2 in our calculation, C_{11} is coupled to C_{12}, and they cannot be determined individually. The expression for the potential energy density is

$$U=\tfrac{1}{2}[2(C_{11}+C_{12})e_1e_1+4C_{13}e_1e_3+C_{33}e_3e_3] .$$

Comparing this expression with the quadratic fit, we obtained the following values for the elastic constants:

$$C_{11}+C_{12}=1.1\times10^{12}\ \text{dyn/cm}^2 ,$$

$$C_{13}=0.3\times10^{12}\ \text{dyn/cm}^2 ,$$

and

$$C_{33}=1.0\times10^{12}\ \text{dyn/cm}^2 .$$

No experimental results are available to our knowledge. These elastic constants can be used to determine the bulk modulus. Assuming the c/a ratio is unchanged with volume, the strains e_1, e_2, and e_3 are equal. It is readily shown that the bulk modulus is then given by

$$B_0=\tfrac{1}{9}[2(C_{11}+C_{12})+4C_{13}+C_{33}] .$$

Substitution of the elastic constants gives $B_0=4.9\times10^{11}$ dyn/cm^2.

To make a more accurate determination of the bulk modulus and the pressure derivative of the bulk modulus, we have calculated the total energy for large volume variations. In principle, the parameter x and c/a should be allowed to vary for each given volume. However, due to the complexity of the calculation, we have fixed these two parameters at their respective equilibrium values. The volume is allowed to vary within 10% of the equilibrium value. The calculated energy versus volume curve is plotted in Fig. 2. The squares are the calculated values, and the solid line represents a fit to the Murnaghan equation of state.[29] The root-mean-square difference between the fit and the calculated values is 2.5×10^{-5} Ry. From the fit, we obtain a bulk modulus B_0 of 5.0×10^{11} dyn/cm^2. The pressure derivative of the bulk modulus B_0' is found to be 4.9. These are also listed in Table I. This bulk modulus differs only by 2% from what we derived above from the elastic constants. The experimental value for the bulk modulus is not available for comparison. We note that our calculated bulk modulus is greater than that of the Mg metal (3.54×10^{11} dyn/cm^2). The addition of the H atom thus increases the stiffness of the material.

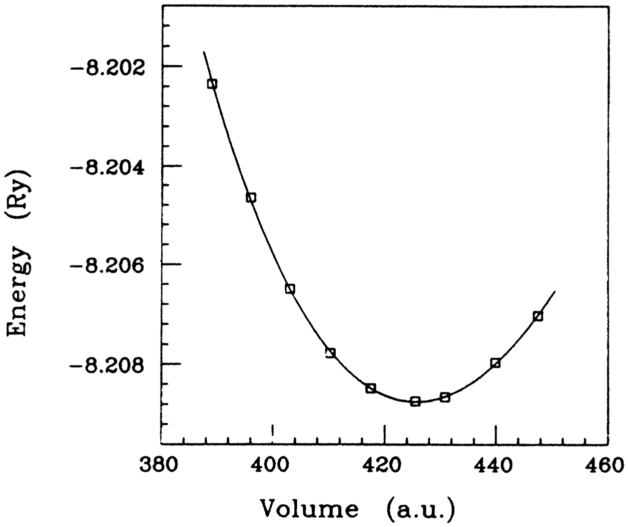

FIG. 2. The total energy of MgH_2 at different unit cell volumes. The parameters c/a and x are fixed at their equilibrium values, respectively. The squares are the calculated total energy, and the curve is a fit to the Murnaghan equation of state.

We have not taken into account the effect of changing c/a and x in the above calculations of the bulk modulus. The inclusion of the variation of these two parameters would result in a smaller bulk modulus. The change in the result can be estimated again from the quadratic fit of the crystal energy to the structural parameters. Relaxing all the structural parameters, we determine the unit cell volume which corresponds to the minimum energy at a given hydrostatic pressure. The bulk modulus obtained is 4.8×10^{11} dyn/cm^2. Thus the bulk modulus decreases by only 4% if the variations of the parameters c/a and x are taken into account.

D. Zone-center phonon

Since there are six atoms in the primitive cell, there are 15 optical phonon modes. Most of these oscillations do not preserve the symmetry of the crystal. However, there is one optical mode at the center of the Brillouin zone which is consistent with the symmetry of the crystal. The phonon frequency of this optical mode Γ_1^+ at the center of the Brillouin zone is calculated with the frozen-phonon method. This oscillation involves the motion of the four hydrogen atoms in such a way that it corresponds to the oscillation of a single parameter x. The unit cell and the crystal symmetry are unchanged. By displacing the four hydrogen ions up to 0.1 Å, the total energy is calculated as before. In the adiabatic approximation, the variation of the total energy is the potential energy for this mode of oscillation. The calculated phonon frequency is 3.81×10^{13} Hz by a quadratic leastsquares fit. The experimental value is not available at present. This Raman-active frequency is slightly higher than the highest infrared-active mode as reported in Ref. 8. This is not true in the case of MgF_2 which also assumes the rutile structure.[30] Our calculated frequency is comparable to the corresponding frequency in MgF_2, 12.7×10^{12} Hz (taken from Fig. 2 of Ref. 30), assuming the two frequencies are inversely proportional to the square root of the mass of the H and F atoms, respectively.

It is interesting to note that the Γ_1^+ mode is very harmonic. The quadratic fit for the phonon frequency is good to a few parts in 10^3 even when the displacement of H atoms is increased to 0.6 Å. The fitted phonon frequency changes by 2% from the value that we obtained above. If this harmonic behavior is true throughout the entire phonon spectrum, the crystalline MgH_2 should have a high thermal conductivity.

IV. ELECTRONIC PROPERTIES

A. Band structure and density of states

The Brillouin zone of the tetragonal cell of MgH_2 is shown in Fig. 3(a). The symmetry points and symmetry axes are indicated. The calculated band structure along several high-symmetry directions is shown in Fig. 3(b). We have adopted the notations of Ref. 31 for the group representations. The calculated density of states is shown in Fig. 4. To calculate the density of states, the eigenenergies are computed at 50 **k** points within the $\frac{1}{16}$th irreducible part of the Brillouin zone, and the analytical linear tetrahedron method is used. Only two conduction bands are included in the density-of-states calculation. The energy reference for the band structure and density of states is arbitrary. Since the unit cell contains eight valence electrons, the four valence bands are completely filled and the conduction bands are empty. Thus magnesium hydride is an insulator. An indirect gap is found for the present system. The minimum of the conduction band is along S at about 20% of the way from A_1 toward Z_1. The maximum of the valence band is not well distinguished. There are several maximum energies close to each other within the range of 0.1 eV along different symmetry axes. We find that the maximum energy is half way between Γ_4^+ and X_1 along Δ. These close maximum energies of the valence band result in high density of states and a sharp cutoff of the density of states at the valence-band edge. The calculated energy gap is 3.06 eV. The calculated width of the valence band is 6.75 eV. The density-of-states curve exhibits two main peaks in the valence band. These two peaks come from the states near A and R from the first two degenerate bands and the degenerate third and fourth bands, respectively. The experimental result of a UV-absorption study[32] gives an absorption edge of 5.16 eV. Thus our calculated band gap differs from the experimental value by 2.1 eV. This underestimation of the band gap by about 40% is typical of the calculations for semiconductors and insulators using the local-density theory.

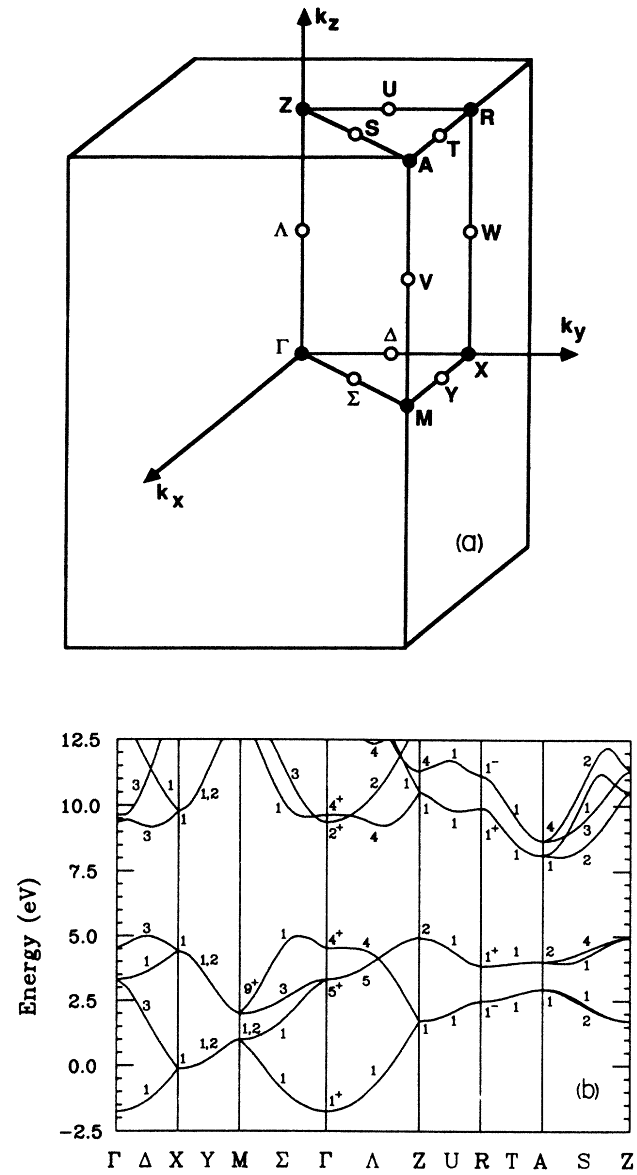

FIG. 3. (a) Brillouin zone of the tetragonal structure of the rutile type (space group $P4_2/mnm$) and its symmetry points and axes. (b) Electronic energy-band structure plotted along several high-symmetry directions. Symmetry labeling of Ref. 31 is used.

How does the band structure depend on the Mg and H potentials? To answer this question, we have looked at the character of a hypothetical system in which the H atoms are situated as in MgH_2 but the Mg atoms are removed. The energy-band structure is obtained from the self-consistent calculation and is shown in Fig. 5. We see that the four lowest bands resemble very much those of MgH_2. This indicates that the Mg atoms are not very influential on the valence bands of MgH_2. The bottom four bands span an energy range of 5.78 eV, which is slightly smaller than the width of the valence band of MgH_2 (6.75 eV). This difference could be due to the contribution of the Mg potentials to the energy-overlap integrals in part and also the larger electron-electron Coulomb repulsion in MgH_2 because there are twice as

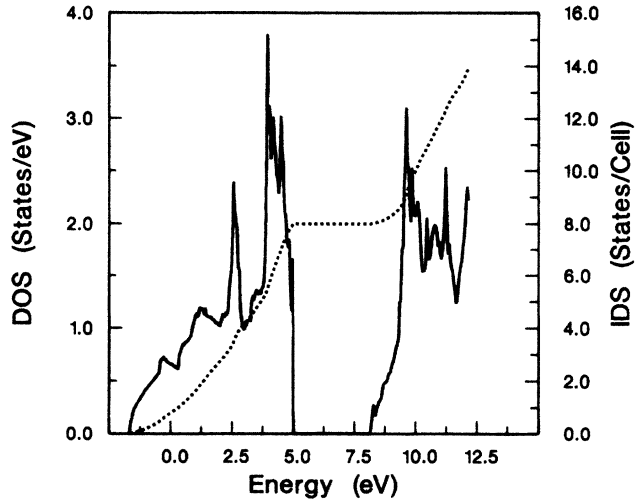

FIG. 4. Electronic density of states per unit cell (solid line) and the integrated density of states (dashed line) of MgH_2.

many electrons in MgH_2 than in this hypothetical H crystal. The most significant difference between this hypothetical system and MgH_2 is in the fifth band where the state Γ and the states near A becomes almost equal in energy. The "energy gap" increases to 5.0 eV compared to 3.06 eV calculated for MgH_2. The Mg potentials are thus important for determining the energy gap of MgH_2. This is consistent with our wave-function analysis that the state at the conduction-band edge near the symmetry point A has a large probability distribution around the Mg atoms.

From the variation of the valence bands with $\mathbf{k}$ vector, we could separate the valence bands into two different regimes. Figure 4 shows that the bottom of the valence bands is free-electron-like. In fact, by fitting the eigenenergies to a quadratic expression of the three components of wave vector, we obtain a fairly isotropic effective mass at Γ which is about 1.1 times the free-electron mass. This effective mass can be understood from the $\mathbf{k}\cdot\mathbf{p}$ method. The inverse effective mass tensor is given by the summation of the inverse free-electron mass and a term coming from the momentum matrices between the first and higher states at Γ (see Appendix E of Ref. 33). The nondiagonal elements of the mass tensor vanish identically due to the symmetry of the crystal; there is a mirror symmetry which takes $k_z \rightarrow -k_z$ and there is a 90° rotation which takes $k_x \rightarrow k_y$ and $k_y \rightarrow -k_x$. To calculate the diagonal inverse mass elements, we may consider just the valence bands because the contribution of the conduction bands should be small due to the large energy denominators. According to the angular momentum decomposition, all the valence states at Γ are symmetric with respect to the reflection about the xy plane. Thus $(m^{-1})_{33}$ is simply $1/m_e$ neglecting the conduction bands. The other two elements $(m^{-1})_{11}$ and $(m^{-1})_{22}$ are also not very different from $1/m_e$. The reason is that the wave functions of all the valence states are mostly localized on the H atoms and are mostly s-like, there is no $\mathbf{k}\cdot\mathbf{p}$ matrix element between states with the same angular momentum. By inverting the effective mass tensor, we should obtain effective mass tensor with the diagonal terms close to the free-electron mass.

The upper part of the valence bands is very narrow. Examination of the wave function shows that the states are fairly localized on the H atoms. One would thus expect to use a simple tight-binding model to describe the bands. We have attempted this by including only the s-like orbitals on the H sites and five overlap integrals. Although the general features of most part of the bands are reproduced, there are some basic differences. Felsteiner *et al.*[8] fitted the Compton profile with a LCAO calculation. They found that the calculated Compton profile did not converge until the overlaps of 162 ions were considered.

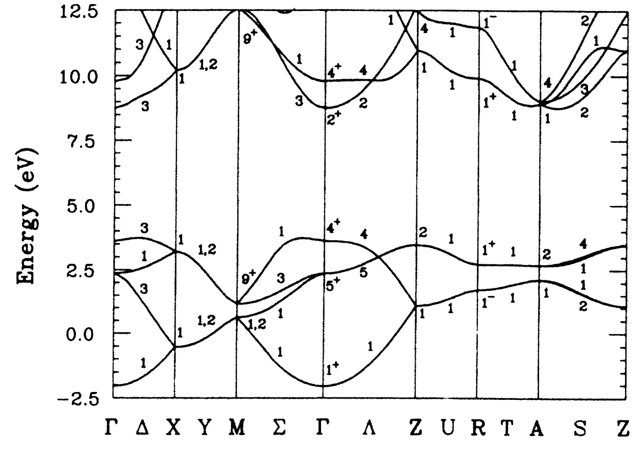

FIG. 5. Energy-band structure of the hypothetical tetragonal crystal without the Mg atoms, but otherwise is the same as MgH_2.

B. Charge distribution and bonding

The valence charge density is obtained directly from the self-consistent calculation. Two contour plots of the valence charge distributions in the (001) plane (perpendicular to the c axis) and in the (110) plane (parallel to the c axis), are shown in Fig. 6. Both planes include the nearest-neighbor Mg-H bonds, with slightly different bond distances. The contour lines are in intervals of 5.0 electrons per unit cell volume. The average charge density is 8 electrons per unit cell volume. The charge-density plots show the ionic character of the crystal, the charges are localized around the hydrogen sites in both projections. The highest charge density is 95.0 electrons per unit cell volume at the hydrogen sites. Following the common practice with ionic crystals, we can assign ionic radii to Mg and H ions assuming the nearest-neighbor ions are in contact with each other. In our case, the ionic radius of H is determined by the nearest-neighbor H-H distance and the radius of Mg is determined by the nearest-neighbor Mg-H distance. We then obtain a radius of 1.26 Å for the H ions and 0.69 Å for the Mg ions. To estimate how ionic the crystal is, we calculated the valence charges within the spheres of ionic radii. We find 0.05 electrons around the Mg ions and 1.6 electrons

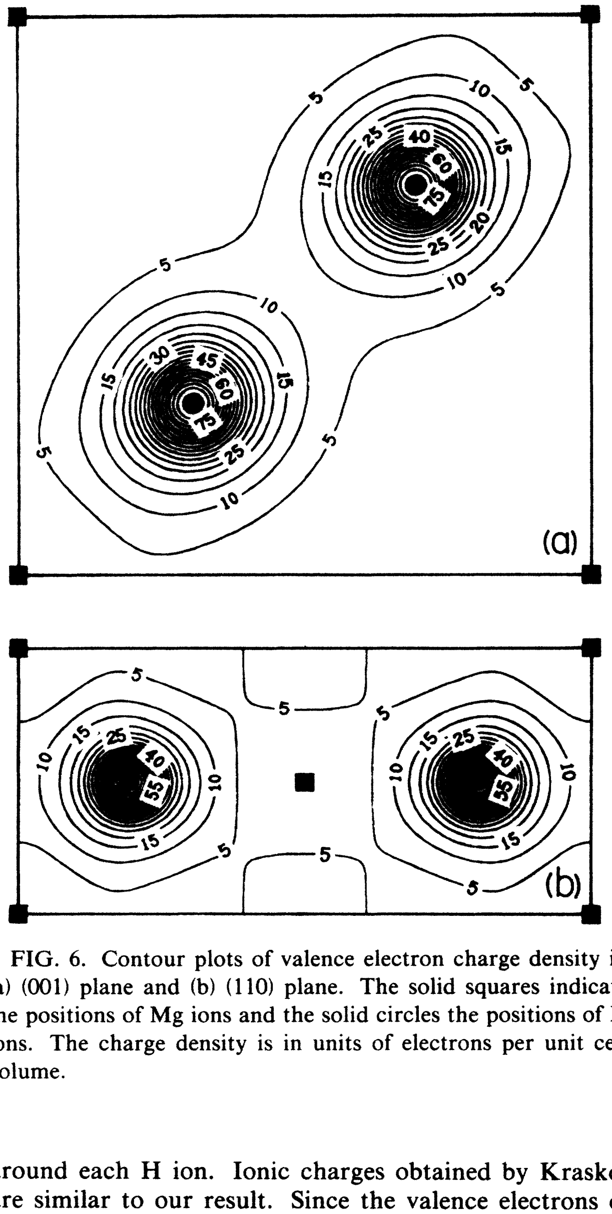

FIG. 6. Contour plots of valence electron charge density in (a) (001) plane and (b) (110) plane. The solid squares indicate the positions of Mg ions and the solid circles the positions of H ions. The charge density is in units of electrons per unit cell volume.

around each H ion. Ionic charges obtained by Krasko[6] are similar to our result. Since the valence electrons of Mg decreased to 0.05 from the atomic value of 2.0, Mg can be considered to be in the form of Mg^{2+}. However, the H ions do not acquire ionic charge close to -1 and there are about 1.5 electrons per unit cell (19% of the total number of valence electrons) in the interstitial region. The crystal as a whole should not be taken as purely ionic. A covalent bond is normally reflected by some closed contour between the atoms. We have made contour plots with smaller increment (1.0). No closed contour lines between the nearest-neighbor H and Mg sites were observed. The covalent bonding that was presumed to exist[2,5] is thus nonexistent or negligible in this crystal.

The ionic radius of H ion we obtained above is 1.26 Å, which is different from 2.08 Å, the value given by Pauling[34] for H^- while the radius of Mg^{2+} (0.69 Å) is consistent with Pauling's value (0.65 Å). The difference between Pauling's radius for H^- and the smaller value of the H ion in the present system is compatible with the charge of the H ions. The hydrogens in this crystal are not H^- but approximately $H^{-0.6}$. This leaves a portion of the electrons in the interstitial region. The small H-H distance also results in the fairly large overlap of the orbitals of the nearest-neighbor H-H ions. These could result in the complexity of the bands and might explain the difference between the results of our simple tight-binding model and the true band structure.

V. SUPERCONDUCTIVITY

Based on our calculations of the band structure and the charge density, we suggest that magnesium hydride substitutionally doped with a monovalent element could become a superconductor. This conclusion is drawn from the following observations.

(1) The valence band of magnesium hydride is determined predominantly by the hydrogen-hydrogen interaction, the cation has very little influence on the valence-band structure [see Figs. 3(b) and 5]. To the first order of approximation, the rigid-band model is valid. Hence, magnesium hydride can be made metallic if it is doped substitutionally with a monovalent element. The carriers will be of the hole type.

(2) The density of states will be very high for this doped magnesium hydride. (See Fig. 4.)

(3) The orbitals of the carrier will be mainly of the character of hydrogen orbital. That is, the carrier will interact strongly with the hydrogen potential. Regardless of the type of pairing mechanism involved, a strong electron-ion interaction is necessary (but not sufficient) for a strong effective electron-electron coupling.

There exist metal-hydride systems which are superconductors, a noted example is PdH_x ($x \simeq 0.8$) with $T_c \simeq 9$ K.[1] In this case, the superconductivity is believed to arise from the electron-phonon coupling with the hydrogen optical mode. Superconductivity also correlates with the amount of hydrogen states at the Fermi level. One of the reasons that T_c is only 9 K for PdH_x could be that the electronic structure of PdH_x is dominated by the Pd *d* states, and the hydrogen exerts only a small effect on the band structure. The electronic structure of magnesium hydride, on the other hand, is dominated by hydrogen. One may think of magnesium hydride as a metallic-hydrogen system which is stabilized by magnesium. However, magnesium hydride is not metallic. By doping it with a monovalent element, we are compromising between metallic behavior and stability.

What should we dope MgH_2 with? Lithium seems to be a good candidate because Li^+ has a size similar to Mg^{2+}. It is not certain that magnesium hydride can be doped sufficiently for superconductivity and yet remains structurally stable in the rutile structure. We have performed some calculations on $LiMgH_4$, replacing one Mg in the unit cell by Li and keeping the H ions in the calculated equilibrium positions of MgH_2. The result indicates that the crystal energy of $LiMgH_4$ is only slightly above that of MgH_2 (by about 0.2 eV/atom). It is reasonable to expect that magnesium hydride doped with 10–20% of Li will be stable. Furthermore, hydrides of $Mg_{0.8}Li_{0.1}X_{0.1}$ ($X =$Ni,Zn,Sn,Si,Cu) alloys have been reported in connection with a hydrogen storage study.[35] No conductivity measurements nor structural analyses were reported for these alloys. How much lithium is needed? It is difficult to predict the optimal dopant level. If we draw a comparison with the oxide superconductors, we would estimate a dopant level of 10 to 20%. Since MgH_2 is an ionic system, charge compensation implies that there will be hydrogen vacancies. It may be necessary to anneal the sample under hydrogen atmosphere.

The view of metallic hydrogen in the form of metal hydride has also been put forth by Overhauser.[36] He analyzed the structure of $LiBeH_3$ and $LiBeH_4$ and suggested that if these compounds are metallic then they could be high-temperature superconductors for the same reasons that metallic hydrogen could be a high-temperature superconductor.

VI. SUMMARY

We have investigated the structural, dynamical, and the electronic properties of MgH_2 with the pseudopotential formalism. Good agreement with the available experimental results were obtained. The crystal is found to be ionic but with fair amount of charge in the interstitial region. No covalent bonding was found. The structure of the valence bands are weakly dependent on the Mg potentials. However, the band gap is strongly influenced by the Mg potentials. Based on the electronic calculations, the possibility of superconductivity in doped MgH_2 is suggested. Future experimental results on the structural, dynamical, and electronic properties are necessary in order to confirm our calculations.

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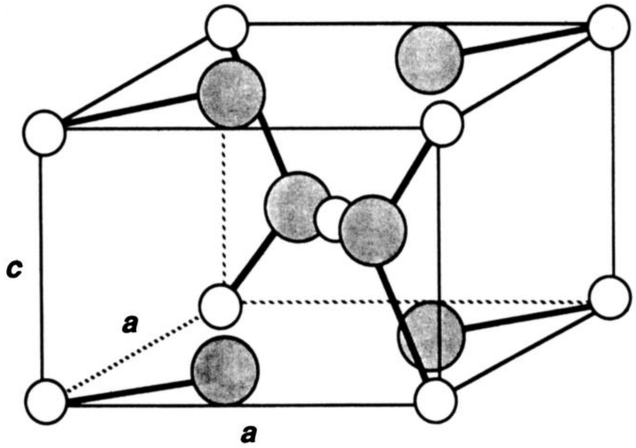

FIG. 1. Arrangement of H and Mg atoms in the tetragonal cell of the rutile type. The open circles are Mg atoms, and the shaded circles represent H atoms. The thick lines between the atoms are used for visual purposes. Two Mg atoms are located at (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and four H atoms are located at $(x,x,0)$, $(1-x,1-x,0)$, $(\frac{1}{2}+x,\frac{1}{2}-x,\frac{1}{2})$ and $(\frac{1}{2}-x,\frac{1}{2}+x,\frac{1}{2})$ in units of lattice constants $a=4.517$ Å and $c=3.021$ Å. Experimental value of x is 0.306.