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Possibility of Li-Mg and Al-Mg hydrides being metallic

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Within the framework of the local-density approximation and the *ab initio* pseudopotential theory, it is shown that alloying of MgH_2 with Li or Al may be described in terms of the rigid-band model. Metallization of insulating MgH_2 upon doping with Li or Al should therefore be possible. Doping with Li appears to be more favorable both from a thermodynamic point of view as well as from the objective of obtaining a high density of states at the Fermi level.

Simple metal hydrides have attracted considerable interest because of the following two reasons.

(i) They may be promising materials for H storage because of their high weight percentage of H.[1,2]

(ii) If they are metallic, they may be candidates for high-T_C superconductivity.[3–6]

It is well known that Mg forms a stable hydride.[1] Unfortunately, the high thermodynamic stability is unfavorable for the desorption procedure and therefore is an obstacle for the application of MgH_2 for hydrogen storage. Furthermore, the system is electrically insulating and so no superconductivity is expected.

It was shown by Yu and Lam[4] using an *ab initio* pseudopotential method that the bonding in MgH_2 is ionic with electrons localized mainly at the hydrogen sites. There is an energy gap of about 3 eV between the top of the valence band, where the density of states (localized at the H atoms) is very large, and the bottom of the conduction band. Yu and Lam found indications that the cation has very little influence on the valence-band structure, and that therefore alloying effects can possibly be described within the rigid-band model. As a result, one should be able to make the hydride metallic by doping with monovalent elements, creating holes at the top of the valence band, where the density of electronic states is very high.

It may be speculated that for such a metallic hydride the energy gain upon hydrogenation is smaller than for MgH_2 because the H atoms can bind less electrons on the average; i.e., that the metallic hydride is less stable.[2] Furthermore, because the electronic states at the top of the valence band are localized at the H atoms, there should be strong interaction with the hydrogen vibrations. The combination of a high density of electronic states at the Fermi level and strong electron-phonon coupling may produce high-T_C superconductivity in such solids.[3–6]

Fischer, Köstler, and Schlapbach[2] tried to prepare hydrides of magnesium-rich Li-Mg alloys. At elevated temperatures they observed a decomposition with MgH_2 formation rather than metallization of the Li-Mg alloy. However, because the kinetics of hydride formation is sometimes rather complicated, this does not in principle exclude the formation of Li-Mg hydrides at appropriate experimental conditions. Nachman and Rohy[7] investigated the thermodynamic properties of $Mg_{0.8}Li_{0.1}X_{0.1}$ hydrides, where X = Ni, Cu, Zn, or Sn, but they determined neither the structure nor the conductivity. It is self-suggesting to try to metallize MgH_2 by alloying with the trivalent Al, hoping that the rigid-band model remains valid and that conduction-band states are occupied upon alloying. Experimentally, it turns out that AlH_3 is unstable[1] and that the product of hydriding Mg_2Al_3 or $Mg_{17}Al_{12}$ is a decomposition[8] into MgH_2 and Al. Again, this does not of course exclude the formation of Al-Mg hydrides at appropriate experimental conditions.

There are three main objectives of the present paper. First, we want to show by *ab initio* calculations within the framework of the local-density approximation (LDA) that the basic assumption underlying the above discussion, i.e., the rigid-band model to describe alloying of MgH_2 with monovalent or trivalent simple metal atoms, is very likely valid. The validity of the rigid-band model was anticipated by Yu and Lam,[4] and the present paper will underpin this by explicit calculations.

In order to do this, we perform calculations for hypothetical $LiMgH_4$ and $AlMgH_4$ (obtained by replacing one Mg atom in the unit cell of MgH_2 by Li or Al) and for $LiMgH_3$. The reason for investigating the latter type of system is that the chemically similar compound $LiBeH_3$ can indeed be produced experimentally. Analyzing x-ray powder diffraction data of Bell and Coates,[9] Overhauser[3] suggested a modified perovskite structure for $LiBeH_3$. In contrast, *ab initio* calculations by Martins[6] and Yu and Lam[5] pointed toward a simple perovskite structure for $LiBeH_3$. Most recently,[10] a $LiBeH_3$ compound with "essentially" ilmenite structure (which is quite similar to a perovskite structure) was identified by x-ray diffraction. We adopted the perovskite structure for our own calculations on $LiMgH_3$. The second objective is to find out whether Li or Al is more appropriate to obtain a high density of states at the Fermi level (Yu and Lam[4] suggested Li but did not consider Al). The third objective is to obtain a feeling for how much doping is needed to obtain a good metal. This question was also raised by Yu and Lam,[4] and they estimated a dopant level of 10–20% just by comparison with the oxide superconductors.

Due to the lack of experimental data about the forma-

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tion of the above-mentioned systems, we have calculated the free enthalpy of formation, ΔG_0, per Mg atom under standard conditions ($T_0 = 298.15$ K, $p_0 = 1$ atm). These quantities are mainly determined by the cohesive energies of the participants (which we obtain from experiments for Mg, Li and Al, and within the LDA for the hydrides) and by the entropy contribution $T_0 S_0$ of the H_2 gas (which is given experimentally[11]). All other finite-temperature contributions to ΔG_0 turn out to be rather small. Because the cohesive energies are poorly described in the LDA, these calculations yield at best a realistic estimate of ΔG_0. The results are given in Table I. It is found that $AlMgH_4$ and $LiMgH_4$ are unstable. $LiMgH_3$ appears to be thermodynamically stable. However, its formation is less favorable than the formation of LiH and MgH_2 when exposing Li and Mg to a hydrogen gas. Altogether, the calculations indicate that the production of Li-Mg hydrides or even more of Al-Mg hydrides of any conceivable structure requires special measures which favor the corresponding formation kinetics.

The calculation were performed within the framework of the LDA based on the exchange-correlation functional of Hedin and Lundqvist,[12] and within the *ab initio* pseudopotential theory. For Mg, Li, and Al the norm-conserving *s*, *p*, and *d* pseudopotentials were constructed according to Vanderbilt,[13] including the partial-core correction.[14] For H a local *s* pseudopotential according to a modified Kerker prescription[15,16] was used. The energy cutoff E_c for the plane-wave basis set and the number n_{irr} of *k* points in the irreducible part of the Brillouin zone were chosen in such a way that the structural data and the bulk modulus were very close to convergence. This was achieved by $E_c = 35$ Ry and $n_{\text{irr}} = 40$ (MgH_2), 64 ($LiMgH_4$, $AlMgH_4$), and 56 ($LiMgH_3$). When the energy cutoff is further increased, the curve of the total energy E_0 vs the volume of the unit cell was shifted more or less rigidly to lower energies for each volume, roughly according to $E_0(E_c) = E_0(\infty) + \alpha / E_c$, with $\alpha = \text{const}$. Extrapolating our data for $E_c \leq 35$ Ry according to this prescription, we obtained $E_0(\infty)$. The structural parameters, i.e., the lattice parameters a and c as well as those coordinates of the atoms which are not fixed by the symmetry of the space group, were determined by minimization of the total energy. MgH_2 crystallizes in rutile structure with space group D_{4h}^{14} with crystallographically equivalent Mg atoms at the corner points (Mg_2) and the center (Mg_1) of a tetragonal cell (lattice parameters a and c). The H atoms are located at (in units of a and c) $H_1 = (\frac{1}{2}+x, \frac{1}{2}-x, \frac{1}{2})$, $H_2 = (\frac{1}{2}-x, \frac{1}{2}+x, \frac{1}{2})$, $H_3 = (1-x, 1-x, 0)$, and $H_4 = (x, x, 0)$, the value of x not being fixed by the symmetry of the space group. For $LiMgH_4$ and $AlMgH_4$ we replace the central Mg atom in MgH_2 by Li or Al, generating an orthorhombic structure with space group D_{2h}^{19}, containing only the symmorphic symmetry operations of D_{4h}^{14}. The H positions $H_1 = (\frac{1}{2}+x_2, \frac{1}{2}-x_2, \frac{1}{2})$, $H_2 = (\frac{1}{2}-x_2, \frac{1}{2}+x_2, \frac{1}{2})$ are no longer crystallographically equivalent to the H positions $H_3 = (1-x_1, 1-x_1, 0)$, $H_4 = (x_1, x_1, 0)$. However, we kept a unit cell of tetragonal type. For $LiMgH_3$ we use the simple perovskite structure with space group O_h^1, with Li atoms at the corner points and the Mg atoms at the center of a cube, and with H atoms at the face centers. In this case, the only structural parameter is the edge length of the cube. We also performed calculations for the inverse perovskite structure generated by exchanging the Li and Mg atoms. It turned out that the cohesive energy of the simple perovskite structure was about 3% lower than that of the inverse perovskite structure.

TABLE I. The free enthalpies of formation under standard conditions, ΔG_0, per Mg atom, for various reactions.

Reaction	ΔG_0/Mg atom
$Li + Mg + \frac{3}{2}H_2 \rightarrow MgH_2 + LiH$	-1.70 eV
$Li + Mg + \frac{3}{2}H_2 \rightarrow LiMgH_3$	-1.07 eV
$Li + Mg + 2H_2 \rightarrow LiMgH_4$	$+0.54$ eV
$Al + Mg + H_2 \rightarrow MgH_2 + Al$	-0.99 eV
$Al + Mg + 2H_2 \rightarrow AlMgH_4$	$+8.66$ eV

The results for some structural and cohesive properties (volume V of the unit cell, c/a ratio, parameter x, bulk modulus B_0) are given in Table II, in comparison with the theoretical data of Yu and Lam[4] and with the experimental data.[17] For MgH_2 our values of c/a and $x_1 = x_2 = x$ are close to the ones of Yu and Lam and to the experimental data. Our value of V_0 is smaller than the experimental value (by 5.7%), as expected for LDA calculations. Yu and Lam obtained an equilibrium volume which is larger than our value (and larger than the experimental value), and, accordingly, a smaller bulk modulus B_0. Possible reasons for these differences are the use of different exchange-correlation functionals (Yu and Lam worked with the interpolation formula of Wigner[18]), different pseudopotentials (Yu and Lam worked with the pseudopotentials of Hamann, Schlüter,

TABLE II. The structural parameters and the bulk modulus B_0 of MgH_2, $LiMgH_4$, $AlMgH_4$, and $LiMgH_3$.

	MgH_2	$LiMgH_4$	$AlMgH_4$	$LiMgH_3$
V_0 [(a.u.)^3]	392.1	359.7	373.55	340.0
Yu and Lam (Ref. 4)	425.5			
experiment (Ref. 17)	416.0			
$\frac{c}{a}$	0.670	0.724	0.716	1
Yu and Lam (Ref. 4)	0.668			
experiment (Ref. 17)	0.669			
x_1	0.304	0.316	0.322	
Yu and Lam (Ref. 4)	0.304			
experiment (Ref. 17)	0.306			
x_2	0.304	0.296	0.299	
Yu and Lam (Ref. 4)	0.304			
experiment (Ref. 17)	0.306			
B_0 (Mbar)	0.55	0.42	0.55	0.41
Yu and Lam (Ref. 4)	0.50			

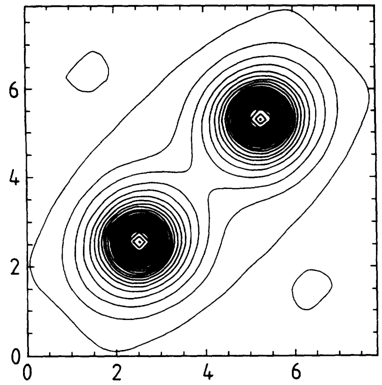

FIG. 1. The contour plot of the pseudovalence electron charge density in the basal plane of $AlMgH_4$. The outermost contour line represents an electron density of 0.01 electrons/(a.u.)^3, the separation of the lines is 0.01 electrons/(a.u.)^3. Only the outer contour lines are shown. The numbers on the two axes give the coordinates in the basal plane in atomic units (a.u.).

and Chiang[19]), different energy cutoffs (Yu and Lam had $E_c = 30$ Ry) and different Brillouin-zone samplings. For $LiMgH_3$ we obtained an equilibrium volume of 340 (a.u.)^3 which is much larger than the one of Yu and Lam[5] for $LiBeH_3$ [$V = 219.3$ (a.u.)^3, reflecting the fact that Mg has a much larger ionic radius (1.23 a.u.) than Be (0.59 a.u.)].

A contour plot of the pseudovalence electron charge density in the (001) plane of $AlMgH_4$ is given in Fig. 1. The contour plots for MgH_2 look very much like that of $AlMgH_4$. For $AlMgH_4$ the near-spherical symmetry of the contour lines around the H atoms as observed for MgH_2 or $LiMgH_4$ is slightly disturbed, and the charge distribution is a bit deformed in the direction of the Al atoms. In agreement with the results of Yu and Lam,[4] the charge distribution shows the ionic character of the crystal, with charges localized around the H atoms. As in the paper by Yu and Lam[4] in the following we assign ionic radii to the atoms in two steps: First, we demand that the spheres around the neighboring H atoms touch. Second, we adjust the spheres of the metal atoms in such a way that they touch the spheres of the neighboring H atoms. All space outside the spheres is denoted as interstitial area. Table III shows the obtained ionic radii and the total charge in the ionic sphere and the interstitial area. Whereas the cation carries about one (Li), two (Mg), or three (Al) positive charges, the H anions do not attract a whole electron in their spheres, so that an appreciable amount of electron charge density is distributed in the interstitial area. This is consistent with Compton-

TABLE III. Ionic radii r_i and total charge q (electrons plus nucleus) in the corresponding ionic spheres and in the interstitial area (I).

		r_i (a.u.)	q (elementary charge)
MgH_2	Mg	1.28	+1.97
	H	2.32	−0.48
	I		−2.03
$LiMgH_4$	Mg	1.38	+1.95
	Li	1.03	+0.98
	H_1, H_2	2.29	−0.38
	H_3, H_4	2.06	−0.13
	I		−1.92
$AlMgH_4$	Mg	1.39	+1.96
	Al	1.12	+2.95
	H_1, H_2	2.29	−0.57
	H_3, H_4	2.03	−0.35
	I		−3.06

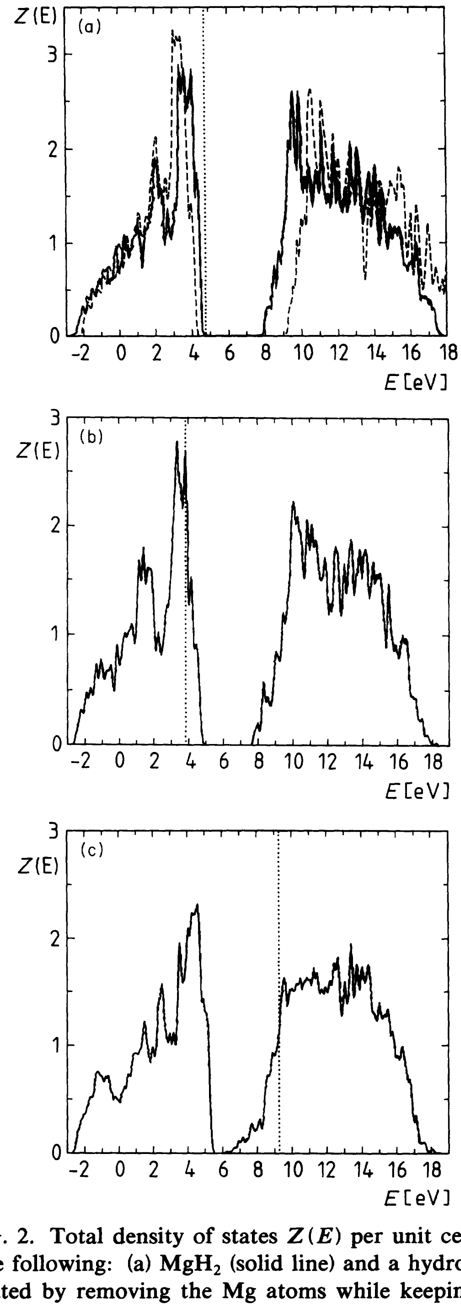

FIG. 2. Total density of states $Z(E)$ per unit cell in (eV)$^{-1}$ for the following: (a) MgH_2 (solid line) and a hydrogen crystal generated by removing the Mg atoms while keeping the positions of the H atoms fixed (dashed line). The elementary unit cell of MgH_2 contains two Mg and four H atoms. (b) $LiMgH_4$. (c) $AlMgH_4$. The dotted vertical lines denote the position of the Fermi level.

scattering experiments by Felsteiner *et al.*[20] for MgH_2. Yu and Lam[4] obtained for MgH_2 a slightly smaller charge in the interstitial area (-1.5 elementary charges), most probably because of their larger equilibrium volume which favors localization of the electrons around atoms. For $AlMgH_4$ the additional electron of Al as compared to Mg is totally distributed in the interstitial area.

To demonstrate the approximate validity of the rigid-band model, Fig. 2(a) represents the total density of states per unit cell for MgH_2 and for a hydrogen crystal generated[4] by removing the Mg atoms while keeping the positions of the hydrogen atoms fixed. Figure 2(b) and 2(c) show the corresponding quantity for $LiMgH_4$ and $AlMgH_4$. The k points used for the calculations of the density of states were generated according to Monkhorst and Pack[21] (126, 392, and 576 k points in the irreducible part of the Brillouin zone for MgH_2, $LiMgH_4$, and $AlMgH_4$, respectively). Gaussian smearing of the discrete energy levels with a smearing parameter of $\Delta=0.1$ eV was applied. In agreement with experiments, MgH_2 turns out to be an insulator. The LDA band gap of 3.4 eV is slightly larger than the one obtained by Yu and Lam,[4] probably because we used a slightly larger energy cutoff, which results in the lowering of the valence band, whereas the lower band edge of the conduction band remains nearly unaffected. When going from MgH_2 to the hydrogen crystal, the band gap increases to 4.8 eV without an appreciable change of the shape of the density of state curve. Because of the smaller number of electrons (compared to MgH_2) the Fermi level now is located in the former valence band and the system is metallic. For $LiMgH_4$ and $AlMgH_4$ the band gap is reduced to 3.0 and 1.4 eV, respectively, again without an appreciable change in the shape of the density-of-states curve, especially for the valence bands. However, the Fermi level now is again located in the former valence band ($LiMgH_4$) or in the conduction band ($AlMgH_4$), i.e., the systems are indeed metallic.

Figure 3 shows the local density of states within the above-defined ionic sphere of a H atom or a Mg atom in MgH_2. When comparing Figs. 2(a) and 3, one should take into account that the unit cell of MgH_2 contains two Mg atoms and four H atoms. From such a comparison it becomes obvious that the states are not localized at the Mg atoms but mainly at the H atoms and in the interstitial area, the interstitial area being more important for the more delocalized conduction states than for the valence states. The angular-resolved density of states at the H atom (Fig. 4) reveals a nearly exclusive s character of the occupied valence states, and a dominant p character of the conduction states. The same features are observed for $LiMgH_4$ and $AlMgH_4$.

Altogether, it can be concluded that MgH_2 may be conceived as an insulating hydrogen crystal stabilized by Mg atoms rather than as a Mg metal with H atoms. When replacing one Mg atom per unit cell by Li and Al, the bands are more or less rigidly shifted (reducing the band gap) and the Fermi level appears in the former valence band with s-type states strongly localized at the H atoms ($LiMgH_4$), or it appears in the conduction band ($AlMgH_4$) with more delocalized p-type states. Of course, these results do not mean that any hydride based on Li-Mg or Al-Mg is metallic in any structure. We have

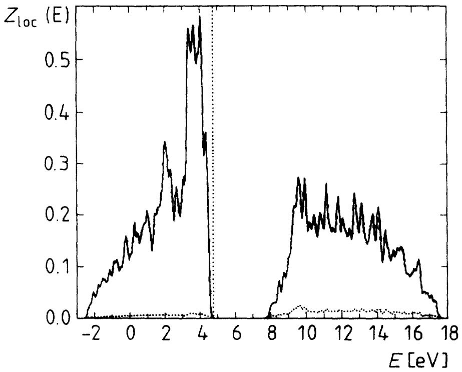

FIG. 3. The local density of states $Z_{loc}(E)$ per ionic sphere in $(eV)^{-1}$ per atom for the H site (solid line) and the Mg site (dotted line) in MgH_2. The vertical line denotes the position of the Fermi level.

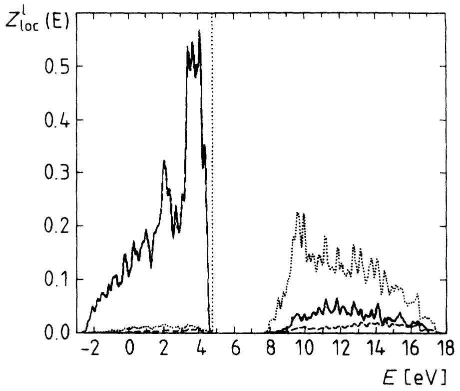

FIG. 4. The angular-resolved density of states $Z^l_{loc}(E)$ in $(eV)^{-1}$ per atom for the ionic sphere at the H site in MgH_2. Full line: $l=0$; dotted line: $l=1$; dashed line: $l=2$.

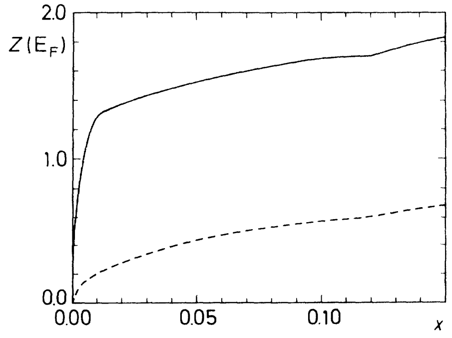

FIG. 5. The total density of states $Z(E_F)$ per unit cell in $(eV)^{-1}$ per atom at the Fermi level E_F for $LiMgH_4$ (solid line) and $AlMgH_4$ (dashed line). Because for the Gaussian smearing the quantity $Z(E_F)$ depends sensitively on the smearing parameter Δ and on the number of k points, we evaluated $Z(E)$ of MgH_2 for this figure with the tetrahedron method [75 k points according to Monkhorst and Pack (Ref. 21)].

just demonstrated the validity of the rigid-band model for alloying of MgH_2 with Li and Al while keeping the structure of MgH_2. Indeed, in our calculations $LiMgH_3$ appears to be insulating both in the simple and in the inverse perovskite structure.

So far we do not know whether stiochiometric Li-Mg or Al-Mg hydrides of the above-discussed type may be produced in reality (see above). The natural question arises whether it is possible in principle (in spite of the unsuccessful attempt of Ref. 2) to prepare Mg hydrides slightly doped with Li or Al. In the following we consider alloy hydrides of the type $Li_xMg_{1-x}H_2$ and $Al_xMg_{1-x}H_2$ with $0 \leq x \leq 0.5$. Based on our experience with MgH_2, $LiMgH_4$ and $AlMgH_4$ (see Fig. 2) we adopt the rigid-band model, i.e., we consider the calculated shape of the density of states curve for MgH_2, independent of x, and determine the total density of states $Z(E_F)$ at the Fermi level E_F as a function of x (Fig. 5). Because the slope of the density-of-states curve at the upper band edge of the valence band of MgH_2 is very large [see Fig. 2(a)], we expect a high density of states upon slight doping with Li. It becomes obvious from Fig. 5 that indeed doping with Li is much more effective than doping with Al to obtain a high $Z(E_F)$.

To conclude, we have provided strong indications that insulating MgH_2 may be made metallic by alloying with Li or Al. Thereby doping with Li appears to be more favorable both from a thermodynamic point of view (see above) as well as from the objective of obtaining a high density of states at the Fermi level. Furthermore, because $Z(E_F)$ decreases strongly upon slight doping with Li atoms but flattens out for higher doping levels, it appears that good metallic behavior is already obtained at $x \geq 0.01$, a value which is much smaller than the one estimated by Yu and Lam.[4]

The authors are indebted to L. Schlapbach for bringing this interesting problem to their attention.

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