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Electronic structure of the new manganese ternary hydride Mg_3MnH_7

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Abstract

We have investigated the electronic structure of the new manganese hydride Mg_3MnH_7 by calculating ab initio the energy bands, density of states and the partial wave analysis of the density of states at each atomic site. We found that this hydride is an insulator with a large indirect energy gap of 2.56 eV. Partial wave analysis of the density of states shows that the electronic properties of this compound are strongly dominated by the bonding features of the MnH_6 and Mg_2H units.

Keywords: Electronic structure; Manganese ternary hydride

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1. Introduction

Recently, Bortz et al. [1] synthesized a new manganese-based ternary hydride, Mg_3MnH_7, which is isostructural to Mg_3ReH_7 [2]. Few Mn hydrides are known. In recent years, Bronger et al. [3] were successful in elaborating the first Mn-based hydrides A_3MnH_5 (A=K, Rb, Cs) which show tetrahedral MnH_4 units. These hydrides are isostructural to the zinc-based hydrides A_3ZnH_5 (A=K, Rb, Cs) [4] and to the halogenides Cs_3MnX_5 (X=Cl, Br) [5,6].

The A_3MnH_5 (A=K, Rb, Cs) compounds show magnetic properties, particularly at low temperatures, where a magnetic ordering transition occurs, while Mg_3MnH_7 samples have a paramagnetic moment consistent only with the presence of Mn^{2+} impurities [1]. It is interesting to recall that this new compound has an excellent hydrogen storage capacity of 5.2 wt% or 118.5 g H_2/l [1].

From neutron powder diffraction studies, the crystal structure of the deuteride Mg_3MnD_7 has been described in the $P6_3/mmc$ space group with two chemical formulas per hexagonal unit cell [1]. The manganese atoms occupy the 2*a* Wyckoff sites of this structure while the atoms occupying the 2*b*, 4*f*, 12*k* and 2*c* Wyckoff sites will be referred to hereafter as Mg(1), Mg(2), H(1) and H(2), respectively.

We can distinguish two subunits in Mg_3MnH_7; the first concerns octahedrally coordinated MnH_6 clusters which are stacked along the *c*-axis and separated by a Mg(1) atom. The second subunit consists of Mg(2)–H(2)–Mg(2) chain fragments along the *c*-axis. These dimerized chains are intercalated between MnH_6–Mg(1)–MnH_6 subunits. This arrangement is characterized by short (1.63 Å) transition metal to H(1) distances, but large (3.73 Å) Mn–H(2) distances. Owing to the Mg(1)–MnH_6–Mg(1) stacking, the Mn–Mn distances are large (4.7 Å). The Mg(1)–H(1) and Mg(1)–H(2) distances are 2.08 and 2.71 Å, respectively, while the Mg(2)–H(1) and Mg(2)–H(2) distances are 2.16 and 1.87 Å, respectively. So, the hydrogen atoms in this compound have very different environments; H(1) has one Mn atom at 1.63 Å while H(2) has two Mg(2) atoms at 1.87 Å. These positions and distances are shown in Fig. 1.

In this paper we present the results of our electronic structure investigation of Mg_3MnH_7 using the ab initio augmented plane wave (APW) method. The purpose of this work was to determine the properties at the Fermi energy, in particular whether the compound is metallic or insulating, and to study the nature of the bonds between hydrogen, the transition element Mn and the alkaline-earth Mg by means of a partial wave analysis of the wavefunctions and densities of states around the different atomic sites. This is an extension of our previous investigation of the new ternary VIIB transition metal hydrides [7].

2. Results and discussion

We calculated the energy bands and the total density of states (DOS) and partial wave analysis of the density of states (PDOS) of hexagonal Mg_3MnH_7 by means of the

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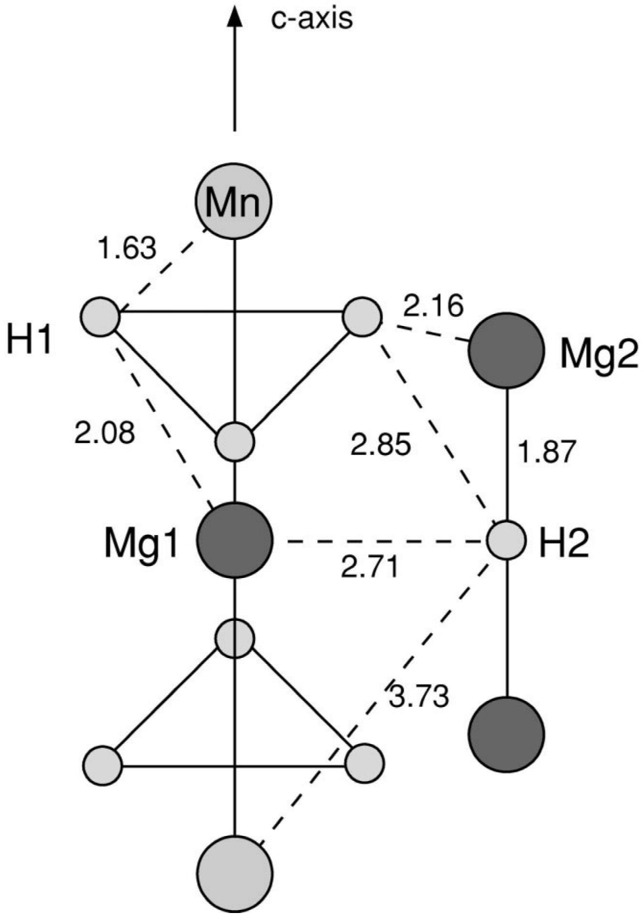

Fig. 1. Atomic positions and interatomic distances (Å) of $P6_3/mmc$ Mg_3MnH_7 hydride.

APW method [8]. We sampled the hexagonal irreducible Brillouin zone (IBZ) with 60 ***k***-points and calculated ab initio the energy eigenvalues and eigenvectors. The total and partial DOS were calculated by the linear energy interpolation-integration scheme [9]. The crystal potentials employed were obtained by overlap of atomic charge densities within the muffin-tin approximation, in which the exchange term was described in the von Barth–Hedin local approximation [10]. The unit cell contains two formula units; owing to the computational effort that such calculations present, we only tested self-consistency by using a reduced special ***k***-points integration scheme. We found that our results, the energy eigenvalues, band widths, gap energy and charge analysis, were not significantly modified. This effect has already been observed [11].

Fig. 2 shows plots of the energy bands along some high symmetry directions of the hexagonal IBZ together with the total DOS for two Mg_3MnH_7 in the unit cell. Fig. 3 shows the PDOS at each atomic site.

Analysis of the wave function coefficients at the center of the Brillouin zone, Γ, gives an indication of the bonding features in the crystal. The coefficients are listed in Table 1 for the Γ points for the occupied and first unoccupied energy states.

We obtain, at the bottom of the energy scale, two energy states corresponding to the Mn s/Mg(2) s/Mg(1) s/H(1) s and the Mn s/Mg(1) s/Mg(2) s/H(1) s bonding orbital interactions respectively. At Γ, these states are separated by 0.083 Ry from the following states. The third state is formed by the Mg(1) s/Mn p/Mg(2) p/H(1) s/H(2) s interactions.

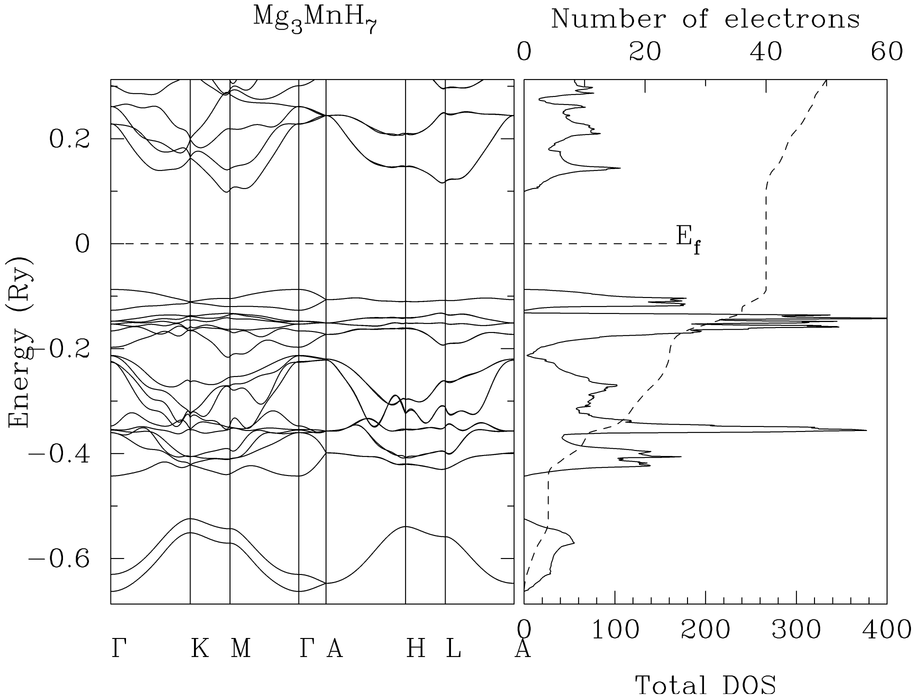

Fig. 2. Energy bands (in Ry) along some high symmetry directions of the hexagonal IBZ and total density of states (in states of both spins per Ry and unit cell) of Mg_3MnH_7.

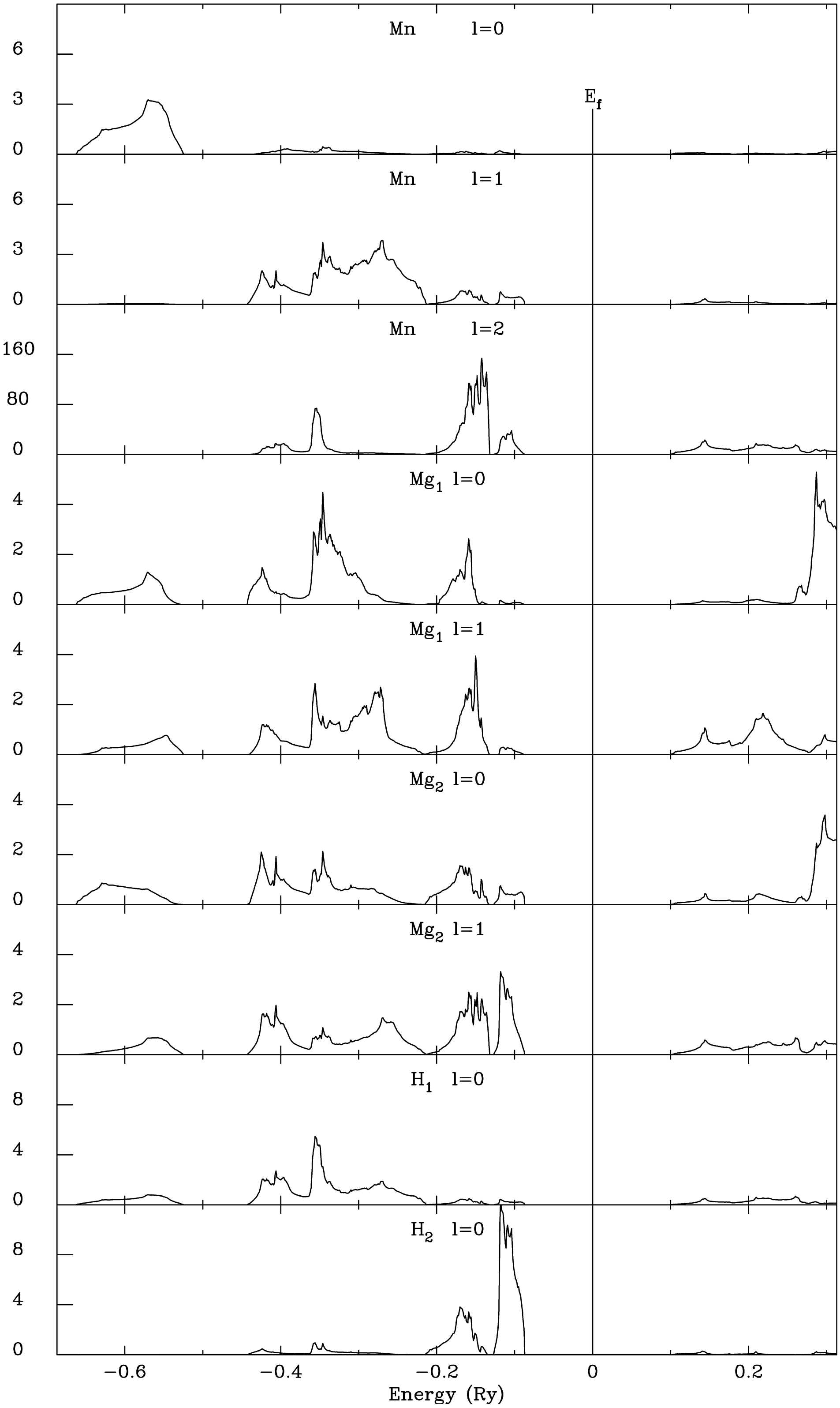

Fig. 3. Partial wave analysis of the density of states at each atomic site (in states of both spins per Ry and atom) of Mg_3MnH_7.

Table 1
Wave function coefficient analysis at the Brillouin zone center Γ for Mg_3MnH_7 hydride. The energies are in Rydbergs and the wave function coefficients are given per atom and have been multiplied by 100. The first 20 bands are occupied

Band	Energy	Mn s	Mn p	Mn d	Mg(1) s	Mg(1) p	Mg(2) s	Mg(2) p	H(1) s	H(2) s
1	−0.663	4.8	0.0	0.0	2.8	0.0	3.3	0.1	1.3	0.2
2	−0.630	5.3	0.0	0.0	0.0	1.9	3.4	0.3	1.4	0.0
3	−0.443	0.0	2.1	0.0	6.3	0.0	0.8	1.2	1.2	1.2
4–5	−0.361	0.0	0.0	22.3	0.0	0.7	0.0	0.2	1.5	0.0
6–7	−0.354	0.0	0.0	22.8	0.0	0.0	0.0	0.2	1.5	0.0
8	−0.349	0.0	3.2	0.0	0.0	4.5	0.4	0.8	1.9	0.0
9–10	−0.226	0.0	4.1	0.0	0.0	1.5	0.0	0.7	2.2	0.0
11–12	−0.213	0.0	4.3	0.0	0.0	0.0	0.0	0.7	2.2	0.0
13	−0.198	0.1	0.0	24.7	4.1	0.0	0.2	1.4	0.0	1.8
14	−0.167	0.1	0.0	36.0	0.0	3.2	0.5	0.3	0.0	0.0
15–16	−0.154	0.0	0.0	36.2	0.0	0.3	0.0	1.3	0.0	0.0
17–18	−0.148	0.1	0.0	36.7	0.0	0.0	0.0	1.2	0.0	0.0
19	−0.127	0.0	0.0	8.8	0.0	0.0	1.1	1.6	0.1	8.3
20	−0.087	0.0	1.1	0.0	0.0	0.0	1.8	0.7	0.6	9.9
21–22	0.228	0.0	0.0	22.9	0.0	1.4	0.0	1.2	0.8	0.0
23–24	0.261	0.0	0.0	23.1	0.0	0.0	0.0	1.8	0.9	0.0

At higher energies, we find a number of energy states associated with the Mn d and H s orbital interactions. The fourth and fifth states are doubly degenerate which is the result of strong Mn d/H(1) s bonding interactions. States 6 and 7 are very close in energy and have the same nature as states 4 and 5.

Energy state 8 results from Mg(1) p/Mn p/H(1) s orbital interactions. This kind of orbital mixing is also observed in the doubly degenerate states 9 and 10 located at slightly higher energies. States 11 and 12 also appear doubly degenerate and are essentially due to Mn p and H(1) s orbital interactions.

It is interesting to note Mn d/Mg(1) s/H(2) s energy state 13, which in addition to state 3, can be interpreted as the bonding form of weak H(2)–Mg(2)–Mn interactions.

The following five states are essentially non-bonding Mn d with a very slight contribution from the alkaline earth. A single energy state, labeled 14, shows, besides the strong Mn d character, a small but significant Mg(1) p contribution. The next doubly degenerate states (numbers 15 and 16 and numbers 17 and 18) show, besides a dominant Mn d character, a small Mg(2) p contribution.

This hydride contains 40 valence electrons in the unit cell, so there are 20 occupied energy bands. The two last occupied states at Γ are a complex orbital mixing of the predominant H(2) s/Mn d and H(2) s/Mn p contributions. We can interpret these energy states as the (weak) antibonding counterparts of states 3 and 13. The last occupied state is separated, at Γ, from the first unoccupied state by 0.315 Ry.

The first two bands, at the bottom of the energy scale, produce a relatively wide structure in the dispersion curves and total DOS plots of Fig. 2. This structure is 0.137 Ry in width and concerns, as previously indicated, the orbital Mn s and H(1) s bonding interactions with a Mg s contribution. This is visible in the PDOS plot shown in Fig. 3, where there is no H(2) contribution in this energy range. The bands ranging from labels 3 to 12 are filled with 20 electrons and form a structure of width 0.229 Ry. Bands, labeled at Γ, 3–8 correspond to the strong Mn d/H(1) s interactions and show a small dispersion and a flat peak in the total DOS plot. Bands 9–12 are spread over a larger energy range and complete the first part of this structure. These bands, as pointed out previously, are the result of Mn p/Mg p/H(1) s interactions. The following filled bands (numbers 13–18) contain 12 electrons and form a narrow substructure 0.080 Ry in width. This is the result of an overlap of essentially non-bonding Mn d states and H(2) s/Mn d orbital interactions, as can be seen from the PDOS plot. It is important to note the non-negligible contribution from Mg p orbitals in all these bands. The last narrow filled structure concerns the dispersionless H(2) s/Mn d and Mg(2) s,p anti-bonding interactions. This structure is 0.038 Ry wide.

The first unoccupied state appears at the M ***k***-point, 0.188 Ry above the top of the valence band which occurs at the Brillouin zone center Γ. We conclude that this hydride is an insulator with a large indirect energy gap of 2.56 eV as suggested by the observed orange-red color.

3. Conclusions

The essential features of the electronic structure of Mg_3MnH_7 can be summarized briefly as follows. (i) The material is characterized by strong bonding interactions in the MnH_6 units between the Mn s,p,d, and the H(1) s states. This leads to the formation, per formula unit, of six wide, low energy bands extending from −0.67 to −0.22 Ry. In addition, an important mixing with the Mg s,p states is also observed. (ii) The Mg–H interactions in the Mg(2)–H(2)–Mg(2) subunits are much weaker and the corresponding energy states are found at higher energies between -0.22 and -0.09 Ry, particularly in the tenth energy band at the top of the valence states. These states are also mixed with the Mn d states which provide the major contribution to the high DOS peaks associated with three narrow Mn d bands observed in particular between -0.22 and -0.16 Ry.

The first 10 bands are filled by the 20 valence electrons and the hydride is found to be insulating with an indirect energy gap of 2.56 eV opening between the Γ and M points of the Brillouin zone. We hope that the present work will stimulate further experimental investigations into this recently synthesized material.

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