ELECTRONIC STRUCTURE OF $KMgH_3$, $KMgH_2F$, $KMgF_3$ WITH THE PEROVSKITE STRUCTURE

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(Received May 16, 1995; revised version June 30, 1995)

*Dedicated to Professors Krzysztof Pigoń, Józef W. Rohleder and Zdzisław Ruziewicz on the occasion of their 70th birthdays**

The electronic structures of fluoroperovskite $KMgF_3$, hydridoperovskite $KMgH_3$ and the dihydrido-fluoro derivated $KMgH_2F$ have been investigated. The energy bands, density of electronic states and partial wave analysis of the density of electronic states have been determined by means of the non-self-consistent augmented plane wave method with the von Barth–Hedin parametrization for the exchange-correlation term. Our results indicate that all three compounds are ionic insulators. Replacing the hydrogen atom by fluorine atom leads to increasing in the energy gap.

PACS numbers: 71.25.Pi, 71.20.Cf

1. Introduction

Unlike hydrides of transition and rare earth elements, saline hydrides have not been widely investigated from a theoretical point of view. However, recently ternary hydrides of alkali and alkaline earth elements of perovskite and antiperovskite derived structures have received some attention from theorists [1–3]. The interest in systems such as $LiBeH_3$ and Li_2BeH_4 [1–2] increased after the suggestion made by Overhauser [4] that these compounds, if metallic, could be superconductors.

Hydrides and fluorides of alkali and alkaline earth metals present structural analogies due to the closeness in the ionic radii of the anions H^- and F^- and similar properties [5–7]. $KMgH_3$ and $KMgF_3$ have a cubic perovskite structure

*Submitted on invitation of the Institute of Physical and Theoretical Chemistry, Technical University of Wrocław, Wrocław, Poland.

with Goldschmidts's tolerance factors equal to 0.96 and 0.95, respectively [7]. The analogy between hydrides and fluorides suggested the synthesis of hydrido-fluorides such as $KMgH_2F$ and $KMgHF_2$ [7–9], X-ray diffraction data appear to support a random distribution on the anions sites.

In the present work we have investigated the electronic structure of $KMgH_3$, $KMgF_3$ and $KMgH_2F$. The lattice parameters used in the present work are listed in Table I. The assumed ordered crystal structure of $KMgH_2F$ is shown in Fig. 1.

TABLE I

Structural parameters (in a.u., X = H or F) [8, 9].

Distances	$KMgF_3$	$KMgH_2F$	$KMgH_3$
Lattice period a	7.5349	7.5722	7.6043
Mg–X	3.7674	3.7861	3.8022
X–X, K–X	5.3280	5.3544	5.3771
Mg–K	6.5254	6.5577	6.5856

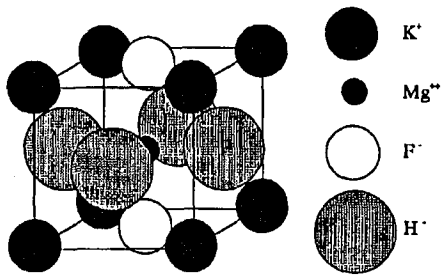

Fig. 1. The perovskite structure of $KMgH_2F$. Relative dimensions of ions correspond to the Pauling ionic radii.

2. Methodology

The electronic structure of the three compounds has been calculated using the augmented plane wave (APW) method suggested by Slater [10] and extended by Saffren and Slater [11]. Calculations have been carried out using the muffin-tin (MT) approximation to the crystal potential which is assumed to be spherically symmetric inside the spheres centered at each atomic site and constant outside these spheres. This potential has been derived from self-consistent Hartree–Fock–Slater calculations for each atom. The MT potential has been calculated by spherically averaging the superposed atomic potentials, using essentially the procedure described by Mattheiss et al. [12]. Calculations were performed with the von Barth–Hedin [13] parametrization of the local spin density (LSD) approximation instead of the X_α-Slater method for the exchange term of the potential [14]. The MT radii of the non-overlapping spheres were chosen to minimize the

discontinuities of the MT potentials at the sphere boundaries while maximizing the total volume inside the MT spheres. The departure from a constant value of the potential outside the MT spheres, the so-called "warped muffin-tin" corrections are included in the present calculation.

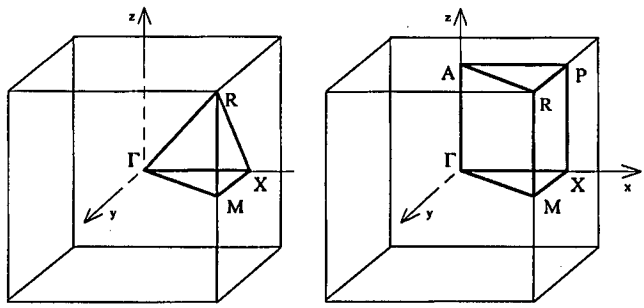

Fig. 2. The Brillouin zone and its irreducible wedge for the cubic and tetragonal structure.

The energy eigenvalues and wave functions have been calculated *ab initio* at 56 points in the irreducible wedge of the Brillouin zone (IBZ) of the cubic structure for $KMgH_3$, $KMgF_3$, and at 75 points in the IBZ of the tetragonal structure for $KMgH_2F$. The irreducible wedges of the BZs are shown in Fig. 2. The base expansion of the APWs has been selected for each system in order to guarantee the convergence of the eigenvalues within 1 mRy or less. The *ab initio* energy bands were expanded into a set of symmetrized plane waves: 39 for $KMgH_3$ and $KMgF_3$ or 57 for $KMgH_2F$. The density of states (DOS) has been calculated by the linear energy tetrahedron method [15].

3. Results

3.1. $KMgH_3$

The energy bands are plotted along the high symmetry directions of the cubic BZ in Fig. 3a. The valence bands contain electrons (Mg-$3s^2$, K-$4s^1$, 3H-$1s^1$) corresponding to the three filled bands. The total DOS is shown in Fig. 3b. In increasing order of energy at the BZ centre Γ point, the following states are observed (Fig. 3a): (i) the Γ_1 state corresponding to bonding interaction between the Mg-s, K-s and H-s states, (ii) the doubly degenerate $\Gamma_{12'}$ state resulting from the antibonding interaction between H-s/H-s. At the point R, the triply degenerate H-s state shows some hybridization with the Mg-p and K-d states. The valence structure of total width 4.90 eV is separated by an indirect energy gap $\Delta_g = 3.48$ eV between Γ and R from the conduction bands.

The partial wave DOS analysis inside the MT spheres plotted in Fig. 3c shows that the three lowest bands are essentially dominated by the H-s states. The lowest energy band is hybridized with the Mg-s and K-p states while in the next two valence bands the H states interact with Mg-p and K-p states. At the bottom of the conduction bands, the Mg-s and p states are dominant, they are

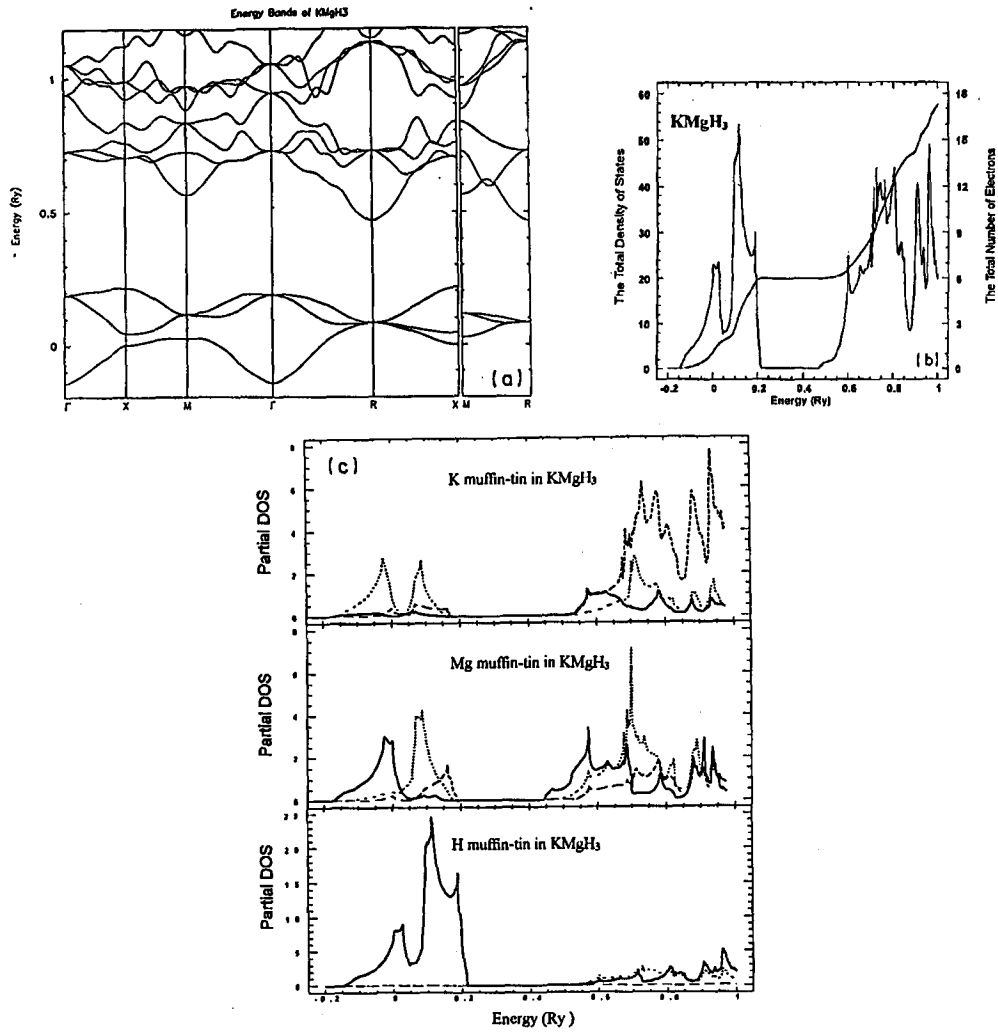

Fig. 3. (a) The energy bands (in Ry) of $KMgH_3$ along some high symmetry directions of the cubic IBZ; (b) Total DOS (states of both spins/Ry-unit cell) of $KMgH_3$; (c) Partial wave analysis of the DOS inside the MT spheres (states of both spins/Ry-atoms of the same type in a unit cell) of $KMgH_3$. (____) s contribution, (.....) p contribution and (- - - -) d contribution.

hybridized with K-s and p states. At higher energies the K-d states represent the major contribution to the total DOS.

The present results are in essential agreement with previous APW calculations performed using the X_α-Slater approximation with $\alpha = 1$ for the exchange potential [2]. The indirect energy gap previously found is almost the same $\Delta_g = 3.47$ eV, the valence band was slightly narrower (4.75 eV) [12].

3.2. $KMgF_3$

Figure 4a shows the band structure of the fluoride plotted along the high symmetry directions of the cubic BZ as for $KMgH_3$. There are nine valence states filled

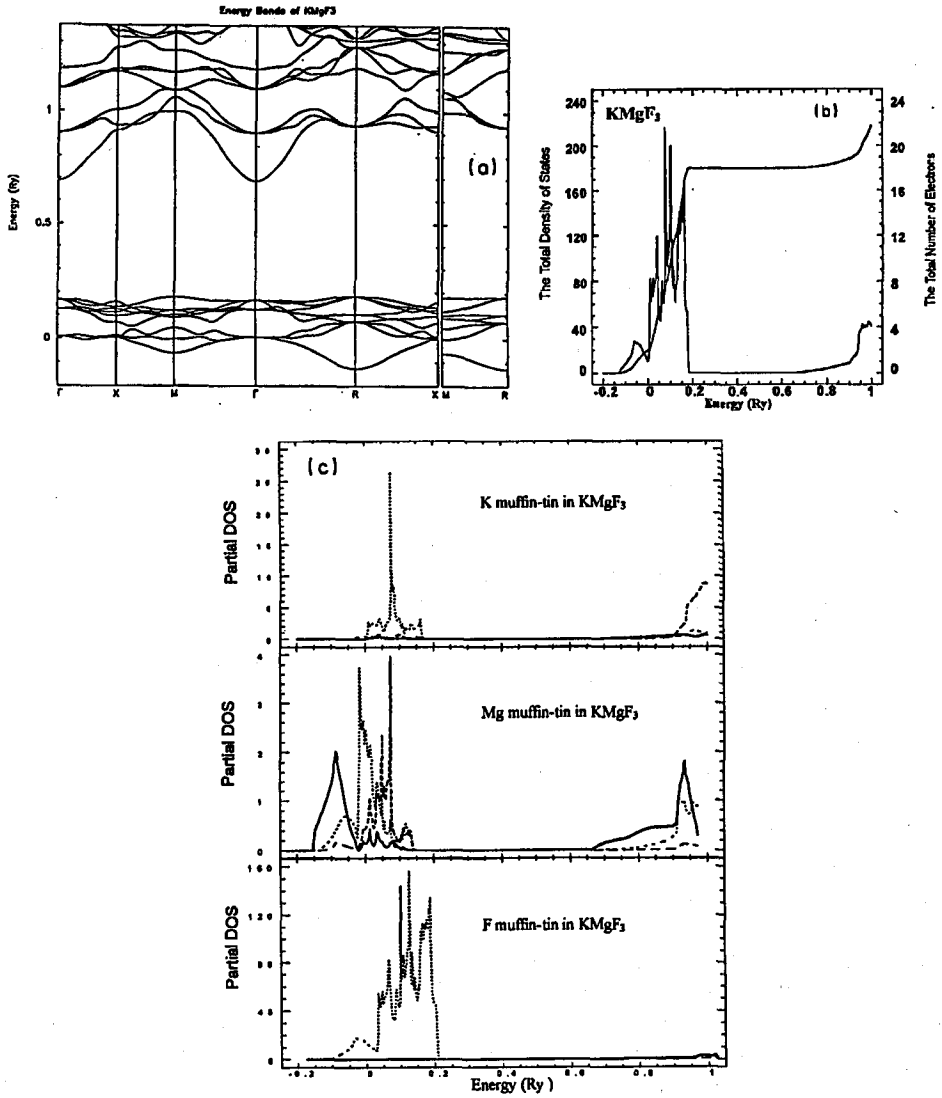

Fig. 4. (a) The energy bands (in Ry) of $KMgF_3$ along some high symmetry directions of the cubic IBZ; (b) Total DOS (states of both spins/Ry-unit cell) of $KMgF_3$; (c) Partial wave analysis of the DOS inside the MT spheres (states of both spins/Ry-atoms of the same type in a unit cell) of $KMgF_3$. (——) *s* contribution, (.....) *p* contribution and (- - - -) *d* contribution.

by 18 electrons (Mg-$3s^2$, K-$4s^1$, 3F-$2p^5$). They result from the fluorine–flourine and fluorine–metal interactions. At the point Γ there are three triply degenerate states. The first corresponds to bonding F-p states hybridized with Mg-p states. The second is a triply degenerate F-p state. The third triplet is due to an antibonding interaction between F-p states with weak K-p and Mg-p contributions. At the R point, the first three bands result from a bonding interaction between F-p and metal states. With the increase in energy, triply and doubly degenerate F-p states appear. The width of valence band is 4.22 eV between the low energy bonding state F-p/Mg-s and the ninth band at the point R. The bottom of the conduction band at Γ results from interactions between s states of each atom. The value of the indirect gap (6.8 eV) between R and Γ is nearly equal to the value of the direct gap at Γ (7.1 eV).

The analysis of the DOS into its partial wave contributions at the different sites plotted in Fig. 4b indicates clearly that the nine valence bands are dominated by F-p states. The lowest valence band is hybridized with Mg-s states while the next eight valence bands result from an interaction of F-p states with K-p and Mg-p and d states. At the bottom of the conduction bands, as in $KMgH_3$, we first observe the Mg-s and p states, the K-d states become dominant at higher energies.

3.3. $KMgH_2F$

The electronic structure of the fluorohydride is displayed in Fig. 5a. The energy bands are plotted along the high symmetry directions of the tetragonal BZ. The valence bands contain 10 electrons (Mg-$3s^2$, K-$4s^1$, 2H-$1s^1$, F-$2p^5$) corresponding to five filled bands. The first Γ_1 state corresponds to a bonding interaction of s states of each atom. The next states result from F-p/F-p interactions with a smaller Mg-p and K-p contribution. The filled non bonding orbitals p_x and p_y of fluorines lead to the doubly degenerate state. The top of valence band at Γ is due to the antibonding interaction of hydrogen s states.

The partial wave analysis of the DOS, at the different atomic sites plotted in Fig. 5b, shows that the low lying part of the valence band which corresponds to the first three bands is mainly composed of F-p states hybridized with K-p, H-s and Mg-s and p states. The top of the valence band corresponds to the next two bands which are dominated by the H-s states, hybridized with F-p and to a lesser extent with K-p, Mg-s and p states. The predominance of F-p derived states at the bottom of the valence band and of H-s states at the top is reminiscent of the relative position of the respective atomic levels.

The width of the valence band is equal to 4.20 eV between the bonding state corresponding to F-s and Mg-s interaction at the point P and the antibonding state at A corresponding to a H–H interaction. The top of the valence band at A is separated by an indirect energy gap (Δ_g = 4.15 eV) from the point M at the bottom of the conduction bands which is due to the interaction of Mg-s/F-s states.

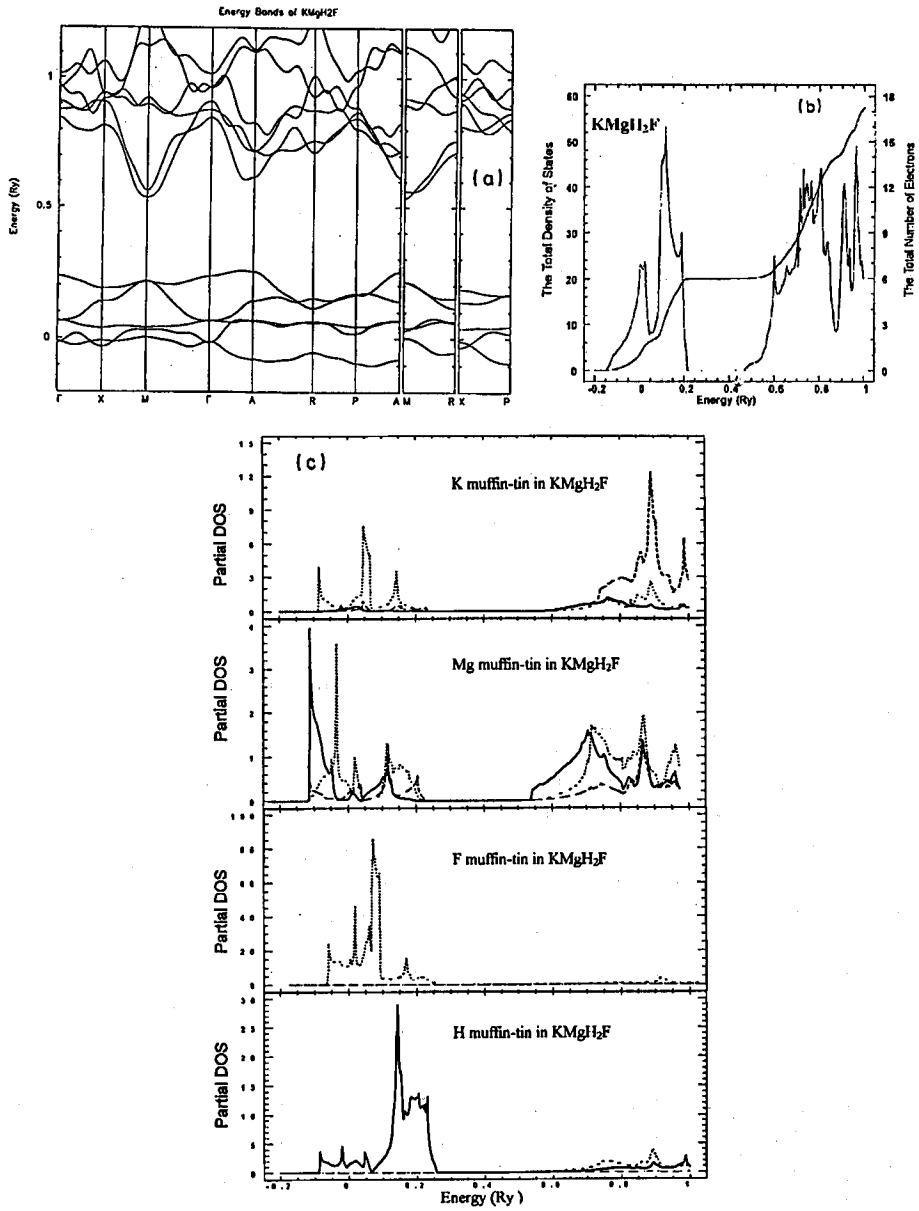

Fig. 5. (a) The energy bands (in Ry) of $KMgH_2F$ along some high symmetry directions of the tetragonal IBZ; (b) Total DOS (states of both spins/Ry-unit cell) of $KMgH_2F$; (c) Partial wave analysis of the DOS inside the MT spheres (states of both spins/Ry-atoms of the same type in a unit cell) of $KMgH_2F$. (——) *s* contribution, (.....) *p* contribution and (- - - -) *d* contribution.

4. Discussion

The three compounds under study were all found to be ionic insulators, with a decrease in the band width and an increase in the energy gap upon substitution of the hydride ions by fluoride ions. The change in the energy gap is substantial (see Table II); from 3.48 eV for the hydride to 6.87 eV for the fluoride. The valence band in the hydride and in the fluoride is dominated by the contribution of the filled orbitals of the anions: H-*s* and F-*p* respectively. In $KMgH_2F$ the upper edge of the valence band corresponds to almost pure H-*s* while the DOS at the bottom of the valence band is dominated by the F-*p* orbitals. The bottom of the conduction band in all three compounds contains a major contribution from Mg-*s* orbitals. The potassium orbitals play only a minor role at the bottom of the conduction bands, however the K-*d* states are dominant at higher energies.

TABLE II

Valence band width (ω) and the energy gap between the valence and conduction band (Δ_g) (in eV).

	$KMgH_3$	$KMgH_2F$	$KMgF_3$
ω	4.90 (4.75*)	4.71	4.20
Δ_g	3.48 (3.47*)	4.15	6.87

*from Ref. [2].

The analysis performed in the present work provides an interesting hint towards the possible variation of the properties of the material by chemical substitution. The new hardness formula, introduced by Parr and Yang [16] may be effectively explored in such prediction. Hardness of an ion is measured directly by the I–A difference (ionization energy–electron affinity). Replacing soft hydride H^- by hard fluoride F^- leads to an increase in the energy gap. It is then expected that substituting hard magnesium ion Mg^{+2} by some softer cation of the same charge and size may lead to a substantial decrease in the gap, hence to semiconducting or metallic state of the corresponding hydride. This conclusion is only valid for a series of isostructural compounds of the perovskite type.

Acknowledgments

The calculations presented in this report were performed at IDRIS computing center (CNRS-France). We are indebted to the staff for helpful technical assistance during this research. One of the authors (RB) thanks for hospitality in Orsay during his stay supported by a scholarship from the program TEMPUS (JEP-4407).

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