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Electronic structure of $BaReH_9$

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Abstract

$BaReH_9$ and hydrides such as A'_2TH_9 (A'=Na, K, T=Tc, Re) present an unusual high hydrogen coordination around the transition metal. This feature makes these hydrides interesting due to the hydrogen to metal ratio, the largest encountered among the known ternary hydrides. With the aim of improving the understanding of the chemical bonding in this class of compounds, we have investigated the electronic structure of the new hydride $BaReH_9$ by calculating ab initio the energy bands, density of states and the partial wave and symmetry analysis of the density of states at each atomic site. We found that this hydride is an insulator with a large energy gap as experiment indicates. The partial wave and symmetry analysis of the density of states show that the electronic properties of this compound are strongly dominated by the Re–H bonding interactions in the ReH_9 cluster. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: $BaReH_9$; Electronic structure

1. Introduction

In recent years the chemistry of complex transition metal hydrides belonging to the VII family (Mn, Tc and Re) has been developed. New compounds have been synthesized such as the magnetic hydrides A_3MnH_5 (A= K, Rb, Cs) [1,2] containing MnH_4 tetrahedric units. Up to now, only one Tc-based hydride is known, K_2TcH_9 [3], which is isostructural to A'_2ReH_9 (A'=Na,K) [4–7]. These Tc and Re hydrides have an unusual coordination of the transition metal [TH_9] (T=Tc,Re). In recent years new rhenium hydrides have been synthesized such as Mg_3ReH_7 which contains octahedral ReH_6 units [8]. Stetson and coworkers have revisited the synthesis and crystal chemistry of such Re-based compounds obtaining a new phase $BaReH_9$ [9].

Both K_2ReH_9 and $BaReH_9$ show a high hydrogen to metal ratio. In the case of K_2ReH_9 this ratio is 3:1 giving a hydrogen density 1.5 times that of liquid hydrogen. $BaReH_9$ yields a 4.5:1 hydrogen to metal ratio and a H density twice that of liquid hydrogen. In both cases, these values are the highest encountered amongst the numerous ternary metal hydrides investigated up to now. The interest of understanding the properties of such kind of compounds is obvious if we are looking for new materials for hydrogen storage.

$BaReH_9$ crystal is transparent. Stetson et al. [9] indexed their X-ray powder diffraction data in the $P6_3/mmc$ hexagonal space group (Fig. 1), in which the [ReH_9] units show trigonal prismatic D_{3h} point symmetry. In this compound the Re–H distances are short (d(Re–H)=1.69 Å) while the Re–Re distances are large (d(Re–Re)=5.29 Å). Besides the high coordination of rhenium and the relatively short Re–H, the most remarkable feature of this hydride is the short H–H distances. The inter-unit H(2)–H(2) distance is 1.85 Å while the intra-unit H(1)–H(2) shortest distance is 1.97 Å. Both H–H distances are lower than the minimum value usually found in metal–hydrogen systems 2.1 Å [10–12]. Neutron diffraction data confirmed that $BaReH_9$ belongs to the indicated space group, however, the H atomic position were not refined owing to intrinsic experimental difficulties associated to the neutron diffraction studies on non-deuterated samples. In this paper we will present our results on the electronic structure investigation of $BaReH_9$ hydride by means of the augmented plane wave (APW) method.

2. Methodology

We used the APW method [13] to calculate ab initio the energy bands of $BaReH_9$ at 30 $\vec{k}$-points of the irreducible wedge of the hexagonal Brillouin zone. The crystal potential was modelled in the muffin-tin approximation introducing the exchange term in the local density approximation (LDA). The form of the LDA used was the Slater X_α which has been proved to be adequate to study these

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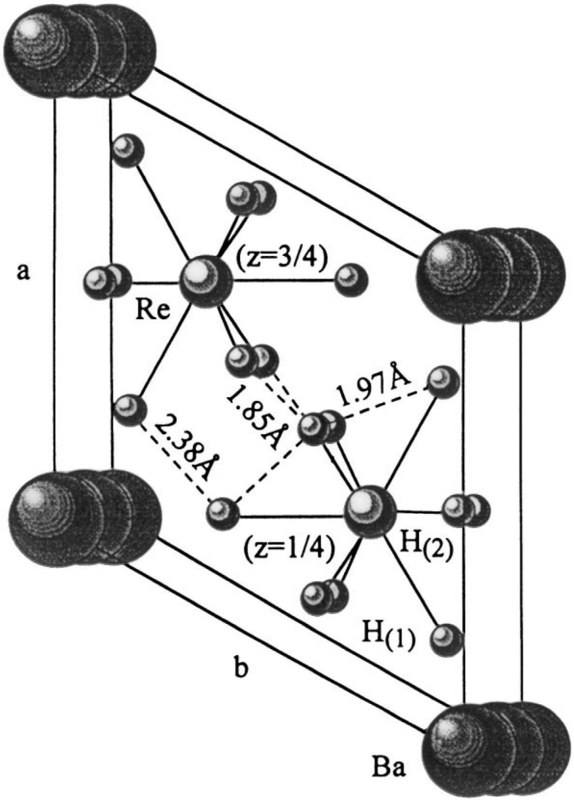

Fig. 1. Representative cell of the BaReH$_9$ hydride.

kind of materials [14–17], the effect of self-consistency and relativistic corrections not included in the present work, are not expected to modify the main features of the chemical bonding investigated here. The energy cut-off was fixed in order to insure a 1 mRy convergence in the energy eigenvalues. The total density of states (DOS) as well the partial wave symmetry analysis of the density of states at each atomic site was calculated by means of the linear energy tetrahedron integration scheme [18].

3. Results and discussion

In Figs. 2–4 we plot the energy bands along some high symmetry directions of the irreducible hexagonal Brillouin zone, the total density of states per formula, and the partial wave analysis of the density of states at each atomic site, respectively. In Table 1 we list the symmetry analysis of the wave function coefficients at the centre of the Brillouin zone, Γ, for the 18 occupied states and the first unoccupied state. In Fig. 2 we observe 18 narrow filled bands containing 36 valence electrons (for the two BaReH$_9$) in the unit cell. The total density of occupied states (Fig. 3) can be divided essentially into four structures corresponding to different transition metal–hydrogen and H–H interactions. The first structure, due to the first two bands at the bottom of the energy scale, has a band width of 0.94 eV. From the analysis outlined in Table 1, this structure is the result of the interactions between the transition metal and hydrogen s orbitals. As it can be seen in the partial DOS (Fig. 4), the Re-d$_{z^2}$ and Ba-p states contribute appreciably to the DOS in this energy range. At higher energies, the second narrow structure of a total width of 0.98 eV is composed by 10 filled bands. They are the result of the Re-d$_{xz}$-d$_{yz}$/H(2)-s, Re-d$_{xy}$-d$_{x^2-y^2}$/H(1)-s and Re-d$_{z^2}$/H(1)-s orbital interactions, each one belonging to different symmetries. In this structure the high peaks observed in the partial DOS (Fig. 4) are due to the Re-d/H-s orbitals which are dominant in the energy range, however, it is interesting to note the existence of non-negligible Ba-p and Ba-s contributions. The third structure, of width 1.55 eV, is composed by two filled bands containing four electrons. due to H(2)-s/Re-p$_z$/Ba-p$_x$-p$_y$ interactions. The fourth structure, of width 1.39 eV, is

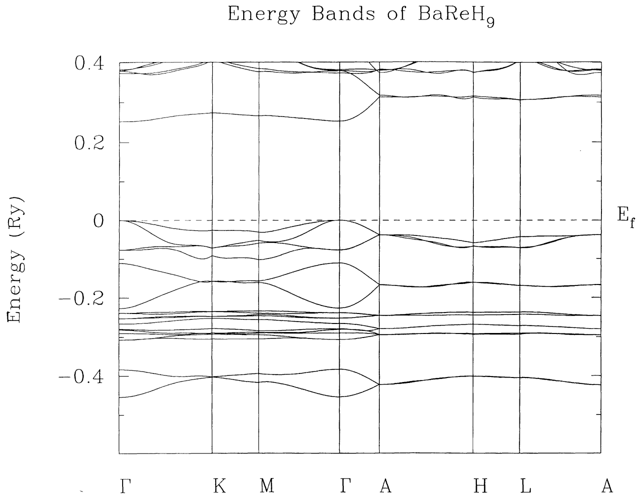

Fig. 2. Energy bands of the BaReH$_9$ hydride (in Ry) plotted along some high symmetry directions of the hexagonal Brillouin zone.

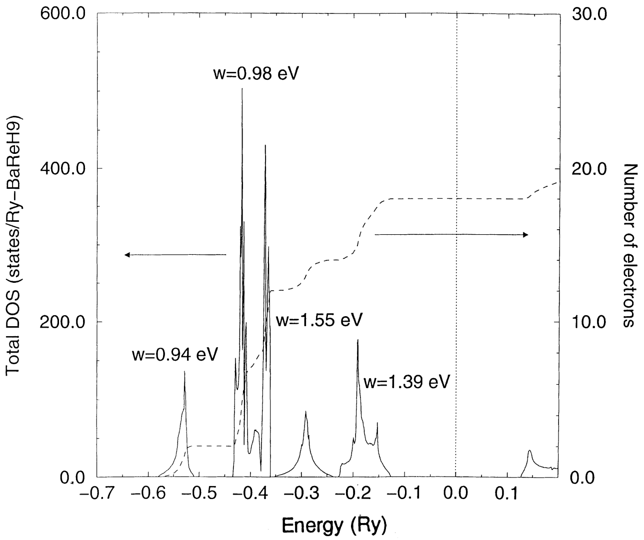

Fig. 3. Total DOS (full line curve, in states/Ry-BaReH$_9$) and number of electrons (dotted line curve) of the BaReH$_9$ hydride.

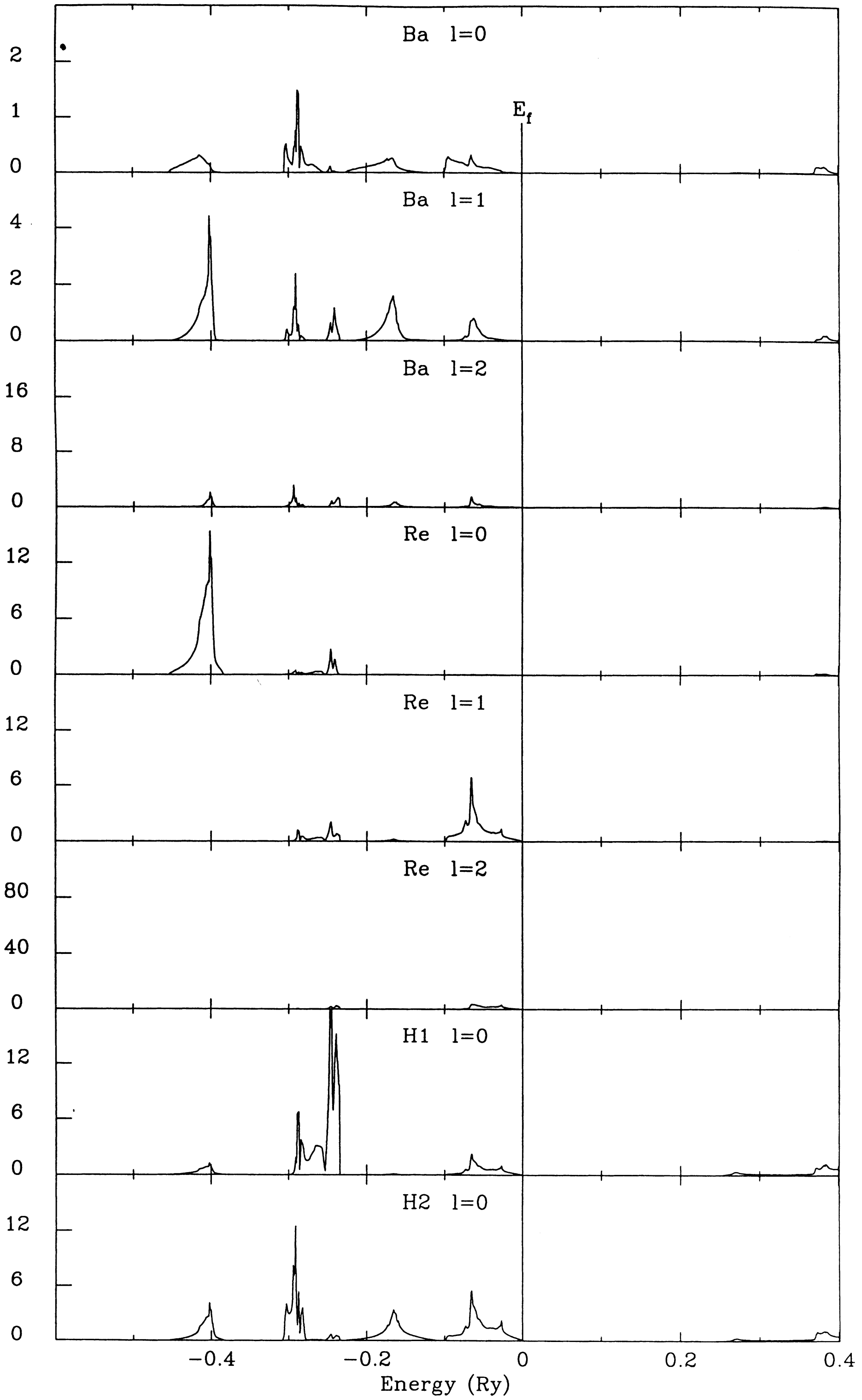

Fig. 4. Partial DOS of Ba, Re and H atoms in $BaReH_9$ hydride (in states/Ry-atom).

formed by four bands filled with eight electrons. These bands result from the complex H(2)-s/Re-p_x-p_y, Ba-p and Re-d_{xy}-$d_{x^2-y^2}$ orbital interactions.

An energy gap of 3.44 eV is present between the occupied and the first unoccupied bands. Abrahams and coworkers [6] found an optical energy gap of 5.71 eV in K_2ReH_9, a compound which has the same hydrogen coordination. This discrepancy between the experimental and calculated value of the energy gap is not surprising. It is well known that the absolute values of energy gaps

Table 1
Symmetry analysis of the wave function coefficients at the Brillouin zone centre Γ for $BaReH_9$ hydride. The energies (Ry) are referred to the top of the valence band

Energy	Symmetry	
−0.454	a_1'	H(2)-s/Re-s,- d_{z^2}/H(1)-s/Ba-s
−0.384	a_1'	H(2)-s/Re-s,- d_{z^2}/Ba-p_z/H(1)-s
−0.308	e''	Re-d_{xz}-d_{yz}/H(2)-s
−0.293	a_1'	Re-d_{z^2}/H(1)-s
−0.280	e''	Re-d_{xz}-d_{yz}/H(2)-s
−0.266	a_1'	Re-d_{z^2}/Ba-p_z/H(1)-s
−0.253	e'	Re-d_{xy}-$d_{x^2-y^2}$/H(1)-s/Ba-p_x-p_y
−0.240	e'	Re-d_{xy}-$d_{x^2-y^2}$/H(1)-s/Ba-p_x-p_y
−0.229	a_2''	H(2)-s/Re-p_z/Ba-s
−0.112	a_2''	H(2)-s/Re-p_z
−0.076	e'	H(2)-s/Re-p_x-p_y/Re-d_{xy}-$d_{x^2-y^2}$/Ba-d_{xy}-$d_{x^2-y^2}$
0.000	e'	H(2)-s/Re-p_x-p_y/Re-d_{xy}
0.253	(a_1')*	Re-d_{z^2}/Ba-d_{z^2}/H(2)-s/H(1)-s

obtained within the local density approach are not reliable. This energy gap is direct and appears at the centre of the Brillouin zone (Γ). The first unoccupied state at Γ is the result of Re-d_{z^2}/Ba-d_{z^2}/H(2)-s/H(1)-s interactions. However, the partial wave analysis of the DOS (Fig. 4) shows that the most important contribution to the conduction band arises from the Ba-d_{xy}-$d_{x^2-y^2}$/Re-d_{xy}-$d_{x^2-y^2}$ states.

The molecular orbital (MO) energy diagram of the ReH_9^{-2} anion sketched in Fig. 5, can be compared to the energy states at Γ of the solid outlined in Table 1. It can be observed that the first energy state (bottom of the energy scale) belongs to the a_1' symmetry. This is followed by a complex manifold concerning the e'', a_1' and e' states in the solid. The third structure in the solid corresponds to the a_2'' states at Γ as well as in the MO energy diagram. The last occupied state in both cases is doubly degenerate belonging to the e' symmetry and the first unoccupied (antibonding) state to a_1'.

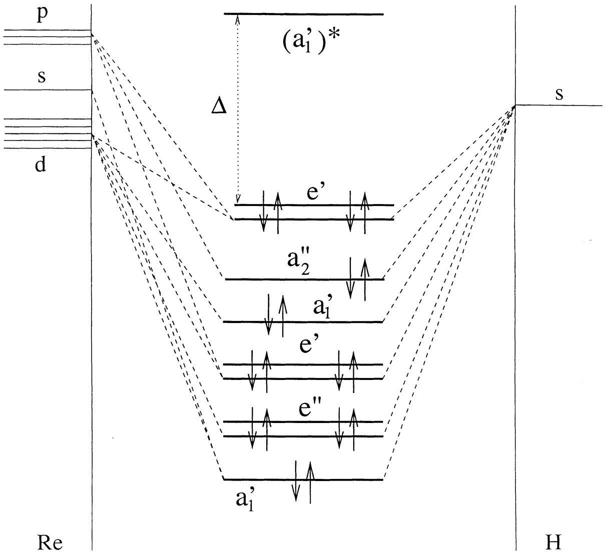

Fig. 5. Schematic σ-bonding molecular orbital diagram of a nine-fold coordinated D_{3h} complex.

Manganese hydrides with hydrogen coordinations higher than four have not been observed. It is possible to estimate the minimum value of the transition metal radii (r_T) needed to have a coordination of nine. By simple geometrical arguments, the non-overlap condition between hydrogen atomic spheres is expressed by the inequality; $d(H(1)–H(2)) \geq 2\ r_H$, where $d(H(1)–H(2))$ and r_H are the H(1) to H(2) distance and the hydrogen atomic radii, respectively. The transition metal to hydrogen distances are essentially the same for both types of hydrogen in those hydrides. So, $d(T–H(1)) \approx d(T–H(2)) = r_T + r_H$. This yields the estimate $r_T \geq d(T–H1) - 0.5 \times d(H(1)–H(2))$. With the experimental values for $BaReH_9$; $d(T–H(1)) = 1.68$ Å and $d(H(1)–H(2)) = 1.97$ Å, we obtain $r_T \geq 0.69$ Å. The standard crystal mean-radii for coordination 6 and oxidation state VII for Mn, Tc and Re are 0.60, 0.70 and 0.67 Å respectively [19]. It is clear that this condition is only fulfilled by Tc and Re, the Mn radii being 15% smaller.

4. Conclusions

$BaReH_9$ is remarkable due to the exceptional coordination which yields the maximum hydrogen to metal ratio encountered among the complex hydrides up to now discovered. Transition metal–hydrogen distances are short and the H–H distances do not respect the Westlake criterion [10–12]. The energy bands, total density of states and the symmetry analysis of the partial density of states at each atom, show that this solid is an insulator with direct energy gap of 3.44 eV, strongly dominated by the Re–H bonding interactions. However, the relatively strong contributions of the Ba-p orbitals below the Fermi energy, and the Ba-d interactions in the conduction band should be noted. This hydride is another example of an *18-electrons* *rule* compound, which is dominated by the strong transition metal–hydrogen interactions.

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