

An Orbital Analysis of Hydrogen Pairing in Nonstoichiometric Transition-Metal Hydrides

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Hydrogen-hydrogen pairing is explored in the low hydrogen concentration metal hydride $\text{YH}_{0.2}$, using extended Hückel tight-binding calculations. A comparison with H_2 molecular complexes, where close H-H contacts occur, allows us to explain why through-space pairing must be ruled out in $\text{YH}_{0.2}$. An orbital explanation of the Switendick criterion is given. Compared to various possible occupation sites, the through-atom coupling observed in $\text{YH}_{0.2}$ might be favored because of Peierls distortion effects. This preference appears to be sensitive to the nature of the metallic host and the hydrogen concentration.

Introduction

Hydrogen pairing in metals such as Sc, Y, or any rare-earth metal is a very active field of experimental¹ and theoretical² research. It is now generally accepted that

when this pairing occurs, the two coupled hydrogen atoms are not in direct contact but rather are paired through a common metal atom to which they are both attached. In other words, the coupling may be thought of as being through-atom (which can be considered as a kind of a through-bond coupling) rather than of a through-space type in nature. This result is in full agreement with the so-called "Switendick criterion",³ which stipulates that the hydrogen-hydrogen spacing in metal hydrides cannot be lower than ~ 2.1 Å.

The first break-through in our understanding of these structures came from a diffuse neutron scattering experiment in which a particular linear ordering tendency in Lu was discovered.^{1b} All the experimental results in $\text{YD}_{0.19}$,^{1c} $\text{ScD}_{0.19}$, and $\text{ScD}_{0.33}$ ^{1a} show that the scattered intensity in reciprocal space cannot be explained by isolated pairs but that periodic arrangements of three or four pairs along the *c* axis should be taken into account. The neutron scattering data indicate the presence of chainlike interstitial hydrogen structures and evidence for interchain correlations.^{1c} Not long ago, Liu et al. presented a theoretical study of hydrogen pairing in yttrium based upon calculations of the electronic structure of small clusters.^{2a} The size of the clusters used by these authors is however much too small to represent the physical case of pairs of hydrogen in yttrium. Recent extended Hückel tight-binding calculations made by three of us have questioned the validity of Liu et al. results in regard to the YH_x system.^{2c} It was pointed out that, besides pairs along the *c* axis, there are many other pairs not investigated by Liu et al. The conclusion of that communication^{2c} was that, for a supercell of 14 atoms ($12\text{Y} + 2\text{H}$), the pairs along the *c* axis are not the most stable ones, in contradiction with the conclusions of Liu et al. Also it is not clear how Liu et al.

(1) See for example: (a) Daou, J. N.; Lucasson, A.; Lucasson, P. *Solid State Commun.* 1976, 19, 895. (b) Daou, J. N.; Vajda, P.; Lucasson, A.; Lucasson, P. *J. Phys. C: Solid State Phys.* 1981, 14, 3155. (c) Khata-mian, D.; Stassis, C.; Beaudry, B. *J. Phys. Rev.* 1981, B23, 624. (d) Danielou, R.; Daou, J. N.; Ligeon, E.; Vajda, P. *Phys. Status Solidi A* 1981, 67, 453. (e) Bonnet, J. E.; Juckum, C.; Lucasson, A. *J. Phys. F: Met. Phys.* 1982, 12, 699. (f) Saw, C. K.; Beaudry, B. J.; Stassis, C. *Phys. Rev. B* 1983, 27, 7013. (g) Burger, J. P.; Daou, J. N.; Lucasson, A.; Lucasson, P.; Vajda, P. *Z. Phys. Chem. (Munich)* 1985, 143, 111. (h) Blaschko, O.; Krexner, G.; Daou, J. N.; Vajda, P. *Phys. Rev. Lett.* 1985, 55, 2876. (i) Weaver, J. H.; Peterson, D. T.; Butera, R. A.; Fujimori, A. *Phys. Rev. B* 1985, 32, 3562. (j) Anderson, I. S.; Rush, J. J.; Udovic, T. J.; Rowe, J. M. *Phys. Rev. Lett.* 1986, 57, 2822. (k) Khatanian, D. *J. Less-Common Met.* 1987, 129, 153. (l) Lichty, L.; Schoenberger, R. J.; Torgeson, D. R.; Barnes, R. G. *J. Less-Common Met.* 1987, 129, 31. (m) Bonnet, J. E.; Ross, D. K.; Faux, D. A.; Anderson, I. S. *J. Less-Common Met.* 1987, 129, 287. (n) Han, J. W.; Chang, C.-T.; Forgeson, D. R.; Seymour, E. F. W.; Barnes, R. G. *Phys. Rev. B* 1987, 36, 615. (o) McK-ergow, M. W.; Ross, D. K.; Bonnet, J. E.; Anderson, I. S.; Schaerph, O. *J. Phys. C: Solid State Phys.* 1987, 20, 1909. (p) Anderson, I. S.; Berk, N. F.; Rush, J. J.; Udovic, T. *J. Phys. Rev. B* 1988, 37, 4358. (q) Lichty, L.; Han, J.-W.; Ibanez-Meier, R.; Torgeson, D. R.; Barnes, R. G.; Seymour, E. F. W.; Sholl, C. A. *Phys. Rev. B* 1989, 39, 2012. (r) Blaschko, O.; Krexner, G.; Pleschitschnig, J.; Ernst, G.; Daou, J. N.; Vajda, P. *Phys. Rev. B* 1989, 39, 5605. (s) Blaschko, O.; Pleschitschnig, J.; Ernst, G.; Pintschovius, L.; Burger, J. P.; Daou, J. N.; Vajda, P. *Phys. Rev. B* 1989, 40, 907. (t) Blaschko, O.; *Phys. Rev. Lett.* 1990, 65, 1168. (u) Udovic, T. J.; Rush, J. J.; Anderson, I. S.; Barnes, R. G. *Phys. Rev. B* 1990, 41, 3460. (v) Daou, J. N.; Vajda, P.; Lucasson, A.; Lucasson, P.; Burger, J. P. *Philos. Mag. A* 1986, 53, 611. (w) Vajda, P.; Daou, J. N.; Burger, J. P.; Kai, K. A.; Schneider, G.; Beaudry, B. *J. Phys. Rev. B* 1986, 34, 5154. (x) Daou, J. N.; Vajda, P.; Burger, J. P.; Lucasson, A. *Phys. Status Solidi A* 1986, 98, 183. (y) Vajda, P.; Daou, J. N.; Lucasson, A.; Burger, J. P. *J. Phys. F: Met. Phys.* 1987, 17, 1029. (z) Daou, J. N.; Vajda, P. *Ann. Chim. Fr.* 1988, 13, 567. (aa) Blaschko, O.; Krexner, G.; Pintschovius, L.; Vajda, P.; Daou, J. N. *Phys. Rev. B* 1988, 38, 9612. (bb) Blaschko, O.; Pleschitschnig, J.; Vajda, P.; Burger, J. P.; Daou, J. N. *Phys. Rev. B* 1989, 40, 5344. (cc) Vajda, P.; Daou, J. N.; Moser, P.; Remy, P. *J. Less-Common Met.* 1991, 172, 522.

(2) See for example: (a) Liu, F.; Challa, M.; Khanna, S. N.; Jena, P. *Phys. Rev. Lett.* 1989, 63, 1396. (b) Minot, C.; Demangeat, C. *Z. Phys. Chem. (Munich)* 1989, 163, 547. (c) Koudou, C.; Minot, C.; Demangeat, C. *Phys. Rev. Lett.* 1990, 64, 1474. (d) Koudou, C.; Minot, C.; Demangeat, C. *Europhys. Lett.* 1990, 13, 263.

(3) (a) Switendick, A. C. *Z. Phys. Chem. (Munich)* 1979, 117, 89 and references therein. (b) Westlake, D. G. *J. Less-Common Met.* 1983, 90, 251 and references therein. (c) Rao, B. K.; Jena, P. *Phys. Rev.* 1985, B31, 6726.

can predict a lack of long-range order (the so-called "proton glass") by considering only small clusters. Last but not least, this proton glass can be excluded in view of all neutron-scattering experiments available.¹⁴

The effect of the size of the supercell on the stability of the different hydrogen-hydrogen pairs in YH_x systems has been investigated.^{2d} The results, obtained for an $\text{H}\cdots\text{H}$ distance less than c , show that, in a supercell containing 38 atoms ($36\text{Y} + 2\text{H}$), the most stable pair is found to lie along the c axis, for hydrogen atoms separated by a metal atom. However, other pairs are found in an energy range of a few tenths of electronvolts.

The so-called "Switendick criterion",³ which has been established on the basis of band-structure calculations and compilation of experimental structures, is rationalized in the following manner: when the $\text{H}\cdots\text{H}$ separation is forced to be lower than ~ 2.1 Å, the fully occupied states which have significant $\text{H}\cdots\text{H}$ out-of-phase character become significantly antibonding so that the structure is destabilized.^{3a} However, one can imagine that the two H atoms could come very close to each other, in such a way that the $\text{H}\cdots\text{H}$ antibonding states, strongly destabilized, would rise above the Fermi level and leave their electrons to non-bonding or bonding metallic levels. At first sight, this situation of a stable structure containing H_2 "dimers" buried inside a metallic matrix might appear somewhat fanciful. However, no less strange a decade ago was the idea that H_2 , dihydrogen, could act as a simple two-electron ligand. Since the discovery by Kubas et al. of the first H_2 molecular complex,⁴ numerous similar compounds, most of them of the $d^6 \text{ML}_5(\text{H}_2)$ type, have been synthesized and characterized.⁵ Indeed, this type of molecule has become rather common in organometallic chemistry. Moreover, the recent discovery of a solid-state compound containing isolated neutral Br_2 units, namely CsFBr_2 ,⁶ gives new impetus to the search for unusual coupling of atoms in extended as well as in molecular compounds.⁷

One of the aims of this paper is to explore, by means of simple theoretical molecular orbital calculations, the possibility—or impossibility—of existence of solid-state equivalents of molecular H_2 complexes and to give an orbital explanation of the "Switendick criterion" for metal hydrides. Our second goal is to provide a rationalization of the observed through-atom hydrogen pairing in low-concentration metal hydrides such as $\alpha\text{-YH}_{0.2}$ and to analyze the various factors favoring or disfavoring this pairing. The details of the calculations of extended Hückel type^{8,9} are provided in the Appendix.

General Conditions for Through-Space Hydrogen Pairing

Before entering upon the analysis of the possibility of direct $\text{H}\cdots\text{H}$ coupling in extended metal hydrides, let us recall briefly the factors favoring this coupling in molecular L_nMH_2 complexes.¹⁰ The important molecular orbital

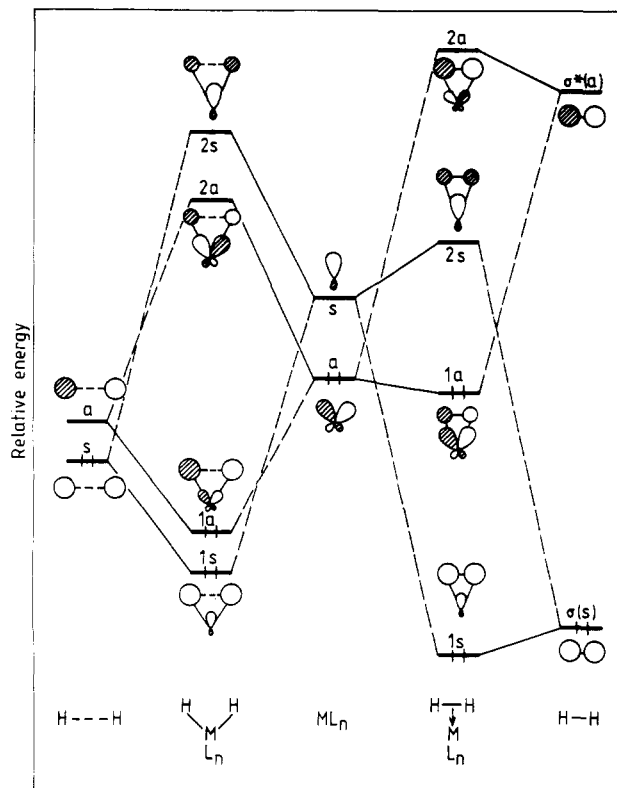


Figure 1. Schematic MO interaction diagram for ML_nH_2 , in its H_2 complex form (right) and its dihydride form (left).

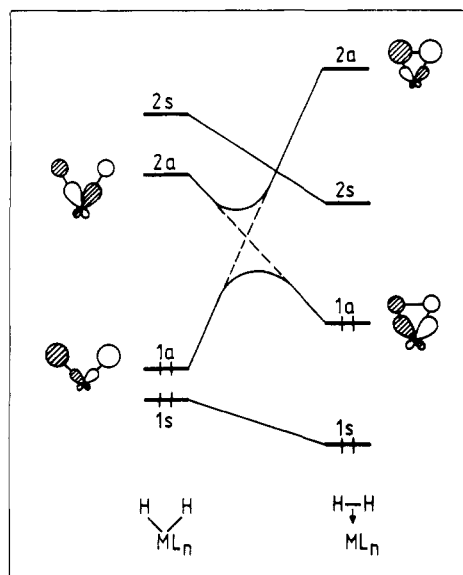


Figure 2. Correspondence between the crucial MO levels of ML_nH_2 , in its H_2 complex form (right) and its dihydride form (left).

(MO) levels of a stable complex are represented schematically in Figure 1, for an H_2 complex (right) and for its dihydride form (left). In both cases, these four levels result from the interaction of the σ and σ^* orbitals of the $\text{H}\cdots\text{H}$ entity with two frontier orbitals of proper symmetry

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(5) (a) Kubas, G. J. *Acc. Chem. Res.* 1988, 21, 120. (b) Kubas, G. J. *Comm. Inorg. Chem.* 1988, 7, 17.

(6) DesMarteaux, D. D.; Greblig, T.; Hwang, S.-H.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* 1990, 29, 1448.

(7) It is interesting to note that so far no transition-metal complex of any dihalogen is known.

(8) (a) Hoffmann, R. *J. Chem. Phys.* 1963, 39, 1397. (b) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* 1978, 100, 3686.

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(10) (a) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* 1984, 106, 2006. (b) Hay, P. J. *Phys. Rev. Lett.* 1984, 103, 466. Hay, P. J. *J. Am. Chem. Soc.* 1986, 108, 705. (c) Jean, Y.; Lledos, A. *New J. Chem.* 1986, 10, 635. (d) Volatron, F.; Jean, Y.; Lledos, A. *New J. Chem.* 1987, 11, 651. (e) Jean, Y.; Eisenstein, O.; Volatron, F.; Maouche, B.; Sefta, F. *J. Am. Chem. Soc.* 1987, 109, 6587. (f) Burdett, J. K.; Phillips, J. R.; Pourian, M. R.; Poliakov, M.; Turner, J. J.; Upmacis, R. *Inorg. Chem.* 1987, 26, 3054. (g) Burdett, J. K.; Pourian, M. R. *Organometallics* 1987, 6, 1684. (h) Saillard, J.-Y. In *Topics in Physical Organometallic Chemistry*; Gielen, M. F., Ed.; Freud Publishing House: London, 1988; Vol. 2.

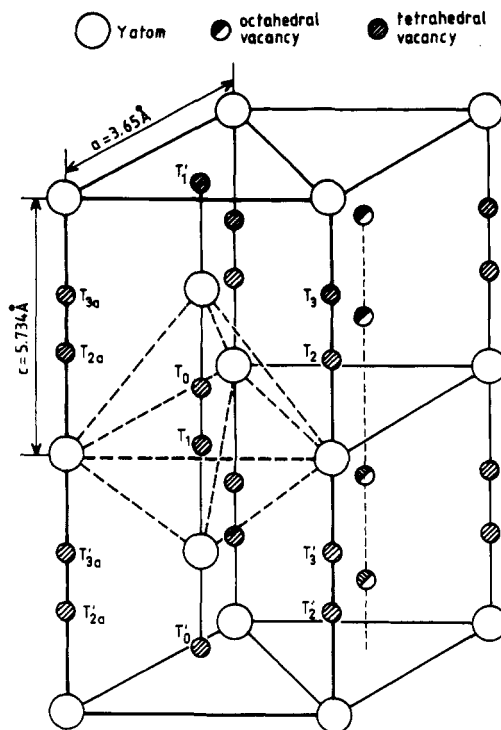


Figure 3. Crystal structure of nonstoichiometric hcp YH_x . An Y_5 trigonal bipyramid surrounding two adjacent tetrahedral vacancies is dashed.

of the ML_n fragment.^{10a} Note that these two metallic frontier orbitals lie generally at an energy which is significantly above that of the $1s(H)$ atomic orbital (AO) and far below the σ^* MO of free H_2 . The main difference between the two diagrams comes from the nature of the occupied $1a$ MO; in the case of the H_2 complex this orbital is nonbonding and mainly metallic in character, while in the dihydride form it can be better identified as the $\sigma^*(H_2)$ level, now at low energy because of the large $H\cdots H$ distance and its dominant M-H bonding character. This situation induces an avoided level crossing between the two antisymmetrical levels when going from one isomer to the other, as indicated in Figure 2. This crossing reflects the redox character of these isomerization reactions.^{10a}

The important antisymmetric interaction in the H_2 complex arises from the presence of two electrons in a d-type metallic frontier orbital of π symmetry, which is stabilized by $\sigma^*(H_2)$. Because of the H-H antibonding character of the resulting occupied $1a$ MO, this interaction is dissociative with respect to H_2 , favoring the transformation toward the dihydride form. This antisymmetric interaction, also present in all the isolable complexes of molecular hydrogen,^{5,11} helps to stabilize the dihydrogen complex but should remain weak to prevent H_2 dissociation.¹⁰ The symmetrical interaction is also, at least to some extent, dissociative; indeed, the occupied $1s$ MO of the H_2 complex corresponds to partial delocalization of $\sigma(H_2)$ to the metal atom and therefore to a decrease in H-H bonding upon complexation. Its dissociative strength depends on the relative magnitudes of the H-H and M-H interactions; the stronger the latter the longer the H-H distance.

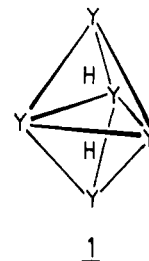
An Y_5H_2 Model

Having this molecular system in mind, we start our

analysis by considering the low-concentration yttrium hydride α - $YH_{0.2}$. The metal is in a hexagonal-closed-packed (hcp) arrangement. This generates octahedral and tetrahedral holes, marked by half-filled and filled circles in Figure 3. These holes are of substantial size, large enough to accommodate H atoms. No assumption is made as to whether the latter are cationic, neutral, or anionic in nature.

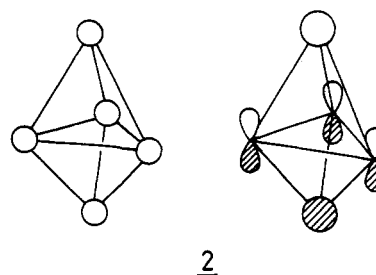
We will consider the choice the interstitial hydride makes among the tetrahedral and octahedral sites later. For the moment, wishing to study the feasibility of direct H-H bonding, we locate two hydrogen atoms on the c axis, in two adjacent tetrahedral voids labeled T_0 and T_1 in Figure 3. Their local environment is a trigonal bipyramidal cluster of metal atoms (depicted with dashed lines in Figure 3). Note that if the H atoms are right in the middle of their tetrahedra, their internuclear separation is only 1.43 Å, a value only ca. 0.7 Å longer than in the free H_2 molecule.

Let us begin modeling the solid by the molecular cluster Y_5H_2 (1). We allow the H positions to vary, keeping D_{3h} symmetry. The relative energy of 1 as a function of the



H-H separation is shown in Figure 4a for different hypothetical electron counts; all the metal electron counts (from d^0 to d^{10}) were considered. For all of them, except for the two-electron case (not shown in Figure 4a), the minimum energy is found in the range of H-H separations larger than 2.2 Å. For instance, the minimum energy is reached at ca. 2.3 Å for the d^0 count. Note that the energy difference between the various minima is not significant as it depends on the arbitrarily set zero-energy points. We chose to set the energies for electron counts equal at an H-H distance of 0.8 Å.

Figure 5 shows simplified frontier molecular orbital (FMO) interaction diagrams of 1 for a short H-H distance (0.8 Å) at right and for a long separation (2.3 Å) at left. Remarkably, only two frontier orbitals of the Y_5 metallic fragment dominate the interaction with the σ and σ^* orbitals of the H_2 fragment. These orbitals, labeled $1a'_1$ and $1a''_2$ in Figure 5, are the two lowest of the Y_5 moiety. They are shown in 2. Both are strongly bonding between the



metal atoms and have significant $5s$ and/or $5p$ character ($1a'_1$ is 95% $5s$; $1a''_2$ is 53% $5s$ and 28% $5p$). Among all the Y_5 FMOs, these two orbitals are the ones which provide the largest overlap with the $\sigma(H_2)$ and $\sigma^*(H_2)$ orbitals, for any of the H-H separations considered. At short H-H distances (Figure 5, right), $1a'_1$ stabilizes the $\sigma(H_2)$ and $1a''_2$

(11) Note that a d^0 organolanthanide complex of dihydrogen has been spectroscopically detected: Nolan, S. T.; Marks, T. J. *J. Am. Chem. Soc.* 1989, 111, 8538.

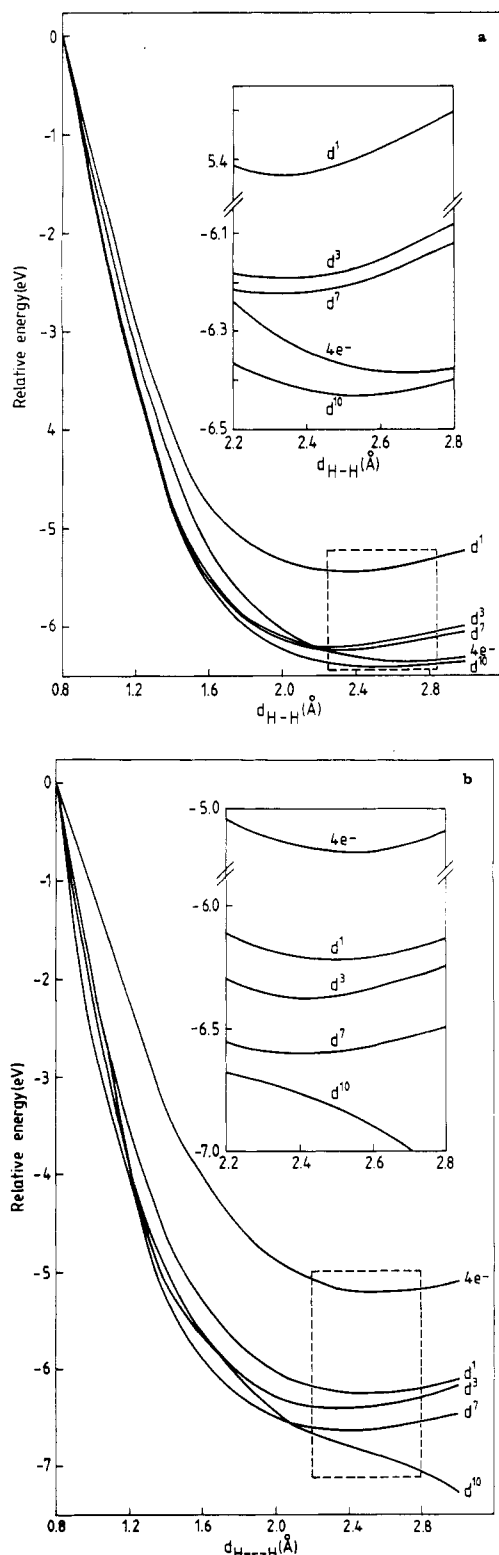


Figure 4. Variation of the relative energy as function of the H-H separation for different electron counts of the Y_5H_2 cluster model (a) and the Y_5H_2 3-D solid (b). A zoom-in on the region around the minima is shown in each inset. For all the electron counts considered, the zero energy is arbitrarily set to the H-H = 0.8 Å case.

is stabilized by the high-lying $\sigma^*(H_2)$. The resulting MO pattern resembles the one of a molecular H_2 complex (Figure 1, right). At large H-H separations (Figure 5, left) both low-lying $\sigma(H_2)$ and $\sigma^*(H_2)$ are stabilized by $1a'_1$ and $1a''_2$, leading to a situation qualitatively similar to the one of the molecular dihydride complex (Figure 1, left). There are, however, some differences between the diagrams of

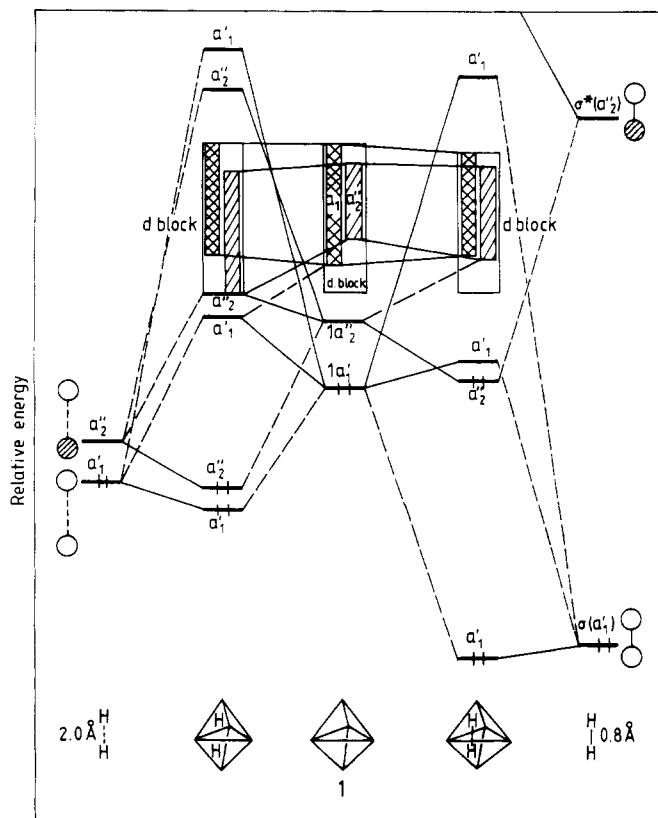


Figure 5. MO interaction of the Y_5H_2 cluster model for the H-H separation of 0.8 Å (right) and 2.0 Å (left). The high-lying H_2 σ^* (a''_2) level on the upper right-hand side, being largely destabilized after interaction with the Y_5 fragment, is not represented. Note that the level occupation in the different fragments is arbitrary.

Figures 1 and 5. In the Y_5H_2 case, because of the large number of metallic levels, second-order interactions occur with the a'_1 and a''_2 metallic levels. Consequently, there is a significant mixing of the $1a'_1$ and $1a''_2$ FMOs of the Y_5 moiety with the other metallic FMOs of the same symmetries all across the d-band.

When only two electrons are present in the Y_5H_2 system, the lowest a'_1 MO of this cluster is occupied. This favors H-H bonding. When four electrons are present, one has a pair of two-electron/two-orbital stabilizing interactions, as in the L_nMH_2 system of Figure 1. Contrary to the L_nMH_2 systems where the two possible isomers are often observed, it appears from Figure 4a that the structure corresponding to a "trapped" H_2 molecule is unstable with respect to its dissociation inside the Y_5 core, the unique energy minimum being found for H-H = 2.7 Å. The reason for this lies in the relative strength of the two (symmetric and antisymmetric) interactions. At short H-H distances, the symmetrical interaction is weak. Indeed, the overlap between the Y_5 $1a'_1$ FMO and $\sigma(H_2)$ is maximal for a rather large H-H separation (2.0 Å). Although the overlap between the $1a''_2$ of Y_5 and $\sigma^*(H_2)$ is maximal for a very large H-H separation, the antisymmetrical interaction is already rather strong for H-H = 0.8 Å. This is due to the relative proximity in energy of $1a''_2$ and $\sigma^*(H_2)$. Therefore, when H-H = 0.8 Å in the four-electron Y_5H_2 model, the charge transfer from $\sigma(H_2)$ to the Y_5 cluster is very small (0.02 electron), while the back-donation from Y_5 to $\sigma^*(H_2)$ is significant (0.53 electron). Clearly, for this hypothetical four-electron count, the through-space H-H coupling is highly disfavored, mainly because of the very weak symmetrical interaction at short H-H separation.

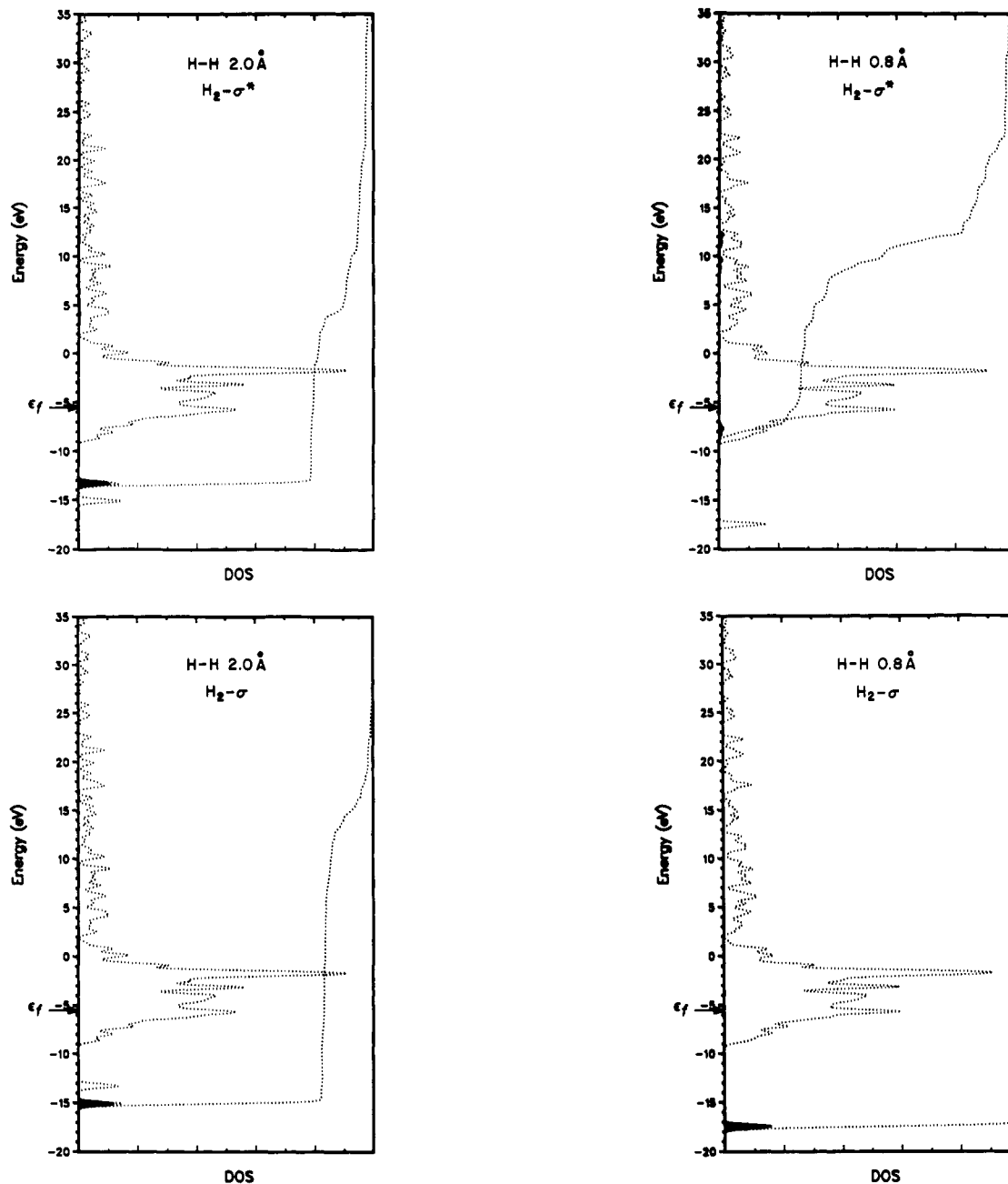


Figure 6. Total density of states (dashed line) and H₂ σ and σ* FMO contributions (dark area) in Y₅H₂ solid with H...H separations of 0.8 Å (right) and 2.0 Å (left).

Adding more electrons on the Y₅H₂ cluster leads to occupation of the metallic d-band. Only those levels of a₁' and a₂'' symmetry have some (small) hydrogen character. When these levels are occupied, new Y₅ FMOs of higher energy than 1a₁' and 1a₂'' are allowed to interact in an attractive or repulsive way with σ(H₂) and σ*(H₂). These new interactions, a consequence of the second-order mixing in the d-band, are not very strong and modify only slightly the position of the minimum on the energy curve (Figure 4a), which in any case remains larger than 2.2 Å.

Hydrogen in an Extended YH_{0.2} Structure

We proceed to an extended structure. A suitable model appears to be a hexagonal-closed-packed (hcp) network of yttrium with a unit cell doubled in the *a* and *b* directions and containing two H atoms along the *c* axis in neighboring tetrahedral sites. The stoichiometry is then YH_{0.25}, a value close to that of α-YH_{0.2} for which hydrogen pairing has been reported.¹ Varying the H...H distance and the elec-

tron count in the same way as in the Y₅H₂ cluster leads to the energy curves shown in Figure 4b. Except for the largest M = d¹⁰ electron count, the curves look very similar to the ones obtained in the cluster case, with minima lying in the range of H...H = 2.2–2.6 Å. This similarity between the molecular and the extended models may be easily understood by comparing the diagrams of Figure 5 with the density of states (DOS) curves shown in Figure 6. In Figure 6 the total DOS and the projections of the σ and σ* FMOs of the H...H fragment for H-H = 0.8 Å (right) and H-H = 2.0 Å (left) are plotted. One can see that at short H-H separation, the σ(H₂) FMO generates a narrow low-lying band situated far below the metal d band. This band corresponds to the lowest a₁' MO of Figure 5 (right). The σ*(H₂) levels are spread out over a larger energy range, mainly above the metal d band. One can note also the presence of a small peak in the σ*(H₂) projection, situated at the bottom of the d-band. This feature may be correlated to the lowest a₂' MO of Figure 5 (right). Except for

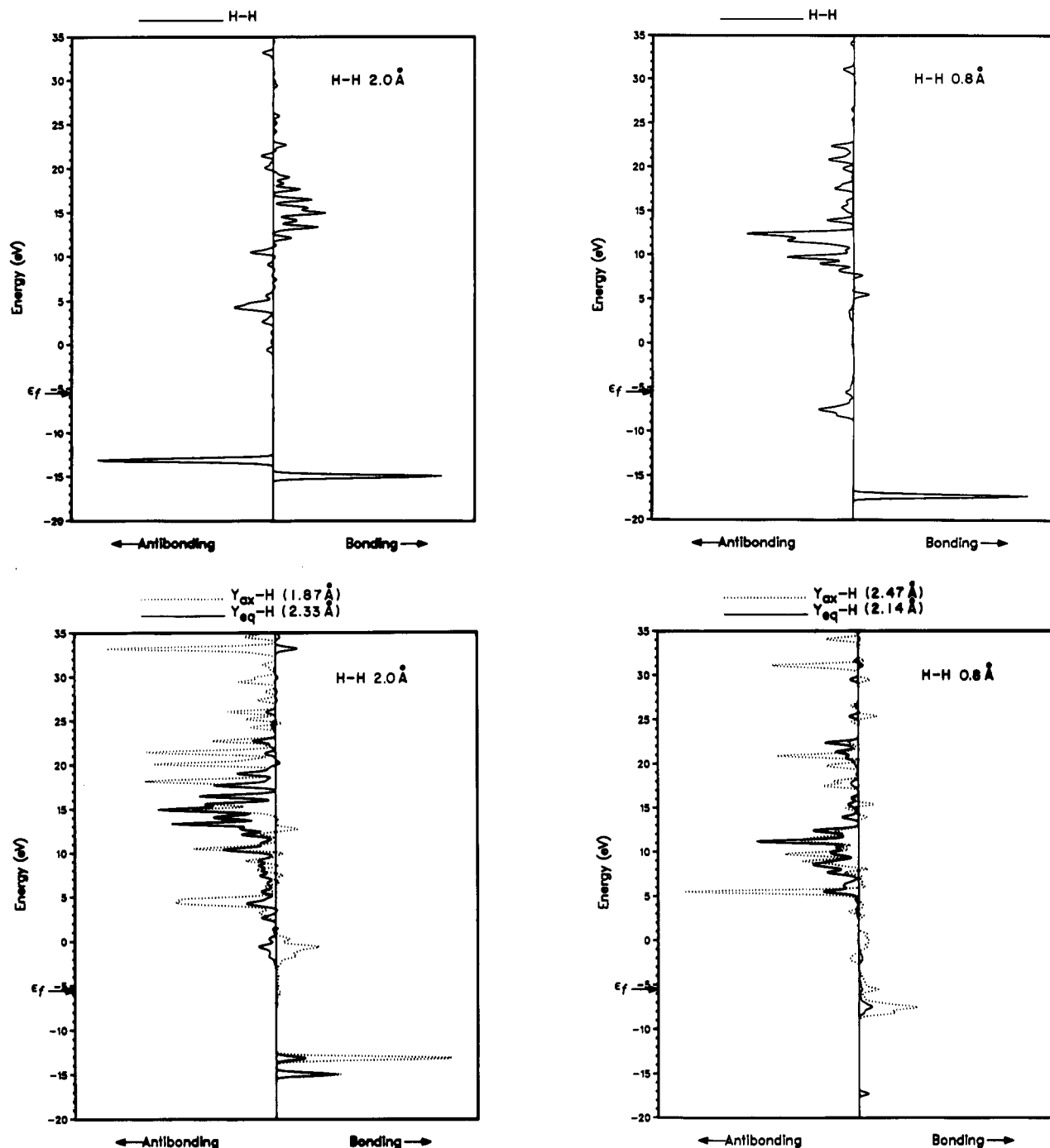


Figure 7. COOP curves for H...H and Y-H contacts in Y_8H_2 solid for H...H distances of 0.8 Å (right) and 2.0 Å (left).

this larger dispersion of the $\sigma^*(H_2)$ states, the situation appears similar to the corresponding one in the Y_5H_2 cluster. This similarity persists at large H...H separation. This time, the σ and σ^* FMOs of H_2 generate a pair of bands situated below the metal d band, corresponding to the lowest a'_1 and a''_2 MOs of Figure 5 (left). One can note some σ/σ^* intermixing, allowed by symmetry in the extended structure.

As in the cluster model, the hydrogen orbitals mix with metallic states, in particular in the energy range above the d-band. The analogy is confirmed by analysis of the COOP curves (overlap populations as a function of energy)¹²

shown in Figure 7. Peaks in the projected DOS of σ and σ^* of H_2 in Figure 6 correspond to positive and negative peaks in the H...H overlap curves of Figure 7. At H-H = 0.8 Å (right), one can note some Y-H bonding character in the $\sigma(H_2)$ band, as well as in the bottom of the d band. At H-H = 2.0 Å (left), the low-lying bands associated with σ and σ^* of H_2 have larger Y-H bonding character. For example, in the hypothetical case of a four-electron system, the averaged M-H overlap population is 0.035 at H-H = 0.8 Å, while it becomes 0.181 at H-H = 2.0 Å. In the real case of a "d³" metal (Y) the corresponding values are 0.129 and 0.186, respectively. An orbital by orbital analysis of the contribution to these peaks shows that the metallic states involved in the interaction with the σ and σ^* FMOs of H_2 have significant 5s and 5p character. They look very much like the molecular orbitals drawn in 2, except that they have greater 4d character, reflecting the larger sec-

(12) COOP was introduced for extended systems in: (a) Hughbanks, T.; Hoffmann, R. *J. Am. Chem. Soc.* 1983, 105, 3528. (b) Wijeyesekera, S. D.; Hoffmann, R. *Organometallics* 1983, 3, 949. (c) Kertesz, M.; Hoffmann, R. *J. Am. Chem. Soc.* 1984, 106, 3453.

ond-order mixing between the metallic states in the extended structure.

A Strategy for Stabilizing H₂ in Extended Materials

It is clear that our molecular and extended models lead to the same conclusion: through-space H-H coupling is unfavored in nonstoichiometric hcp metal hydrides. This preference derives from the fact that the overlap between $\sigma(\text{H}_2)$ and the metallic states of suitable local symmetry is small and far from maximal at short H-H separations.

Supposing one wanted, nevertheless, to stabilize such H₂ pairs. From the above analysis, one can suggest the following orbital criteria for the stabilization of H₂ pairs in solid-state metallic compounds:

(i) The geometry of the vacancy in which the H₂ pair might lie should be such that it provides orbitals able to overlap strongly with $\sigma(\text{H}_2)$ for short H-H distances. Therefore, a cavity of small size (tetrahedron, square-based pyramid, etc.) appears favorable. Calculations on the optimization of the cavity size are in progress. It is interesting to note that calculations on the potential energy surface of the cluster Ni₃₈H₂,¹³ modeling H₂ dissociation in fcc nickel, found a local minimum corresponding to the presence of an H₂ molecule (H-H = 0.85 Å) lying inside an octahedral cavity. This secondary minimum is computed to lie only 1 eV above the lowest energy minimum, which corresponds to a spatial arrangement where the H atoms occupy different octahedral sites.¹³ In this case, the small size of the cavity is a consequence of the short metal-metal separation. Analogous results obtained in calculations on the Li₁₀H₂ edge-sharing bioctahedral cluster might have the same origin.^{3c} Although various theoretical studies of through-space H...H interaction in Pd point to repulsive interactions,¹⁴ when the two H atoms were forced to lie inside the same octahedral vacancy, an H-H equilibrium distance of ~0.9 Å was calculated,^{14a} a value close to the one found in the above-mentioned¹³ calculations on nickel hydride.

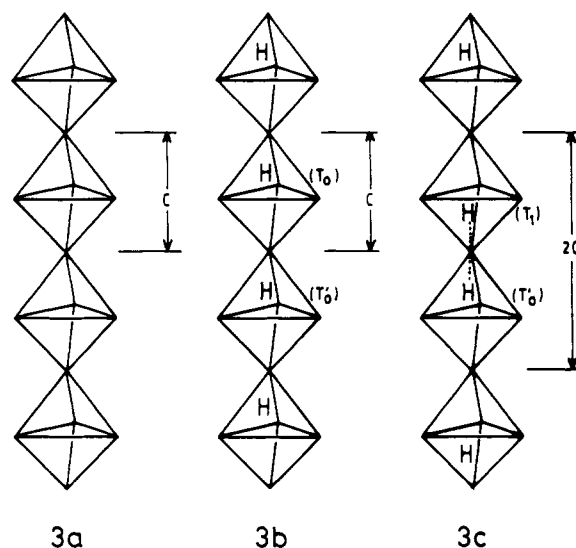
(ii) Another way of favoring the H₂ bond is to destabilize the noncoupled hydrido structures by removing electrons from the metallic d-band. Indeed, if there are no (or perhaps few) electrons in the metallic FMOs, the reduction of H₂ is not possible. This situation corresponds to the two-electron case discussed above. The metallic host can be considered as isolobal¹⁵ to H⁺ and the compound becomes analogous to H₃⁺ or to the still unisolated d⁰ L_nM(H₂) molecular complexes.¹¹ Perhaps an analogous situation occurs in CsFBr₂,⁶ where no electrons are present on the metallic cations to reduce Br₂ to two bromide ions. In the case of hydrogen in a metallic host, one might guess that a way of depopulating the d-band would be to introduce a third element in the compound, more electronegative than the metal. From this point of view, it is interesting to note that the structure of Th₂AlD₄¹⁶ presents short D-D contacts (1.79 Å) within pairs of deuterium atoms located inside tetrahedra of thorium atoms sharing a triangular face. Unfortunately, the low accuracy of this

experimental structure does not allow one to reach any judgment on through-space D-D coupling.¹⁷

(iii) It is also possible to disfavor the hydride structures by making unlikely the transfer of electrons from the metal atoms to the hydrogens, i.e., by rendering nonoxidative or even reductive the nature of the addition of H₂.^{10h,18} This can be done by choosing a metal whose Fermi level lies at a lower energy than the 1s(H) atomic orbital, or at least as low as possible.^{10h} Highly electronegative metal is necessary, and from this point of view it is not surprising that the above mentioned calculations on nickel hydride¹³ found a local minimum corresponding to through-space H-H coupling.

Through-Atom Hydrogen Pairing

We turn now to an analysis of the pairing of hydrogen through a metal atom, along the *c* axis, which is the observed pairing mode in nonstoichiometric hcp trivalent metal hydrides.^{1,2} To provide an orbital explanation for why the H atoms prefer to be bonded to the same rather than to different metal atoms, we first consider the one-dimensional polymers shown in 3, modeling a chain of face-



and vertex-sharing tetrahedra of yttrium atoms as it runs parallel to the *c* axis in the real hcp metal (see Figure 3). **3a** represents pure yttrium, **3b** models a hydride without through-atom coupling, and **3c** corresponds to the hydride in which through-atom coupling is present. The unit cell is Y₄ for **3a** (one tetrahedron) and Y₄H for **3b**, but it is Y₈H₂ for **3c**, since there are now two types of vertices shared by two tetrahedra. To compare the band structure of the three polymers, we are driven to consider the same cell size in the three cases, i.e., Y₈ for **3a** and Y₈H₂ for **3b,c**. For the three models, the local symmetry is C_{3v} at any *k* point between Γ and X. Since bands of e and a₂ symmetry cannot have any hydrogen character, the three band structures will differ only in the bands of a₁ symmetry.

The lowest bands of the three polymers are plotted in Figure 8. They correspond to the bottom of the metallic d-band and in addition, in the case of the hydrides, to the hydrogen bands. In the Y₈ system (Figure 8a) the bands are folded back at *k* = X, since the cell considered is twice the unit cell. The four lowest a₁ branches are relatively dispersive, reflecting significant variation of Y-Y bonding

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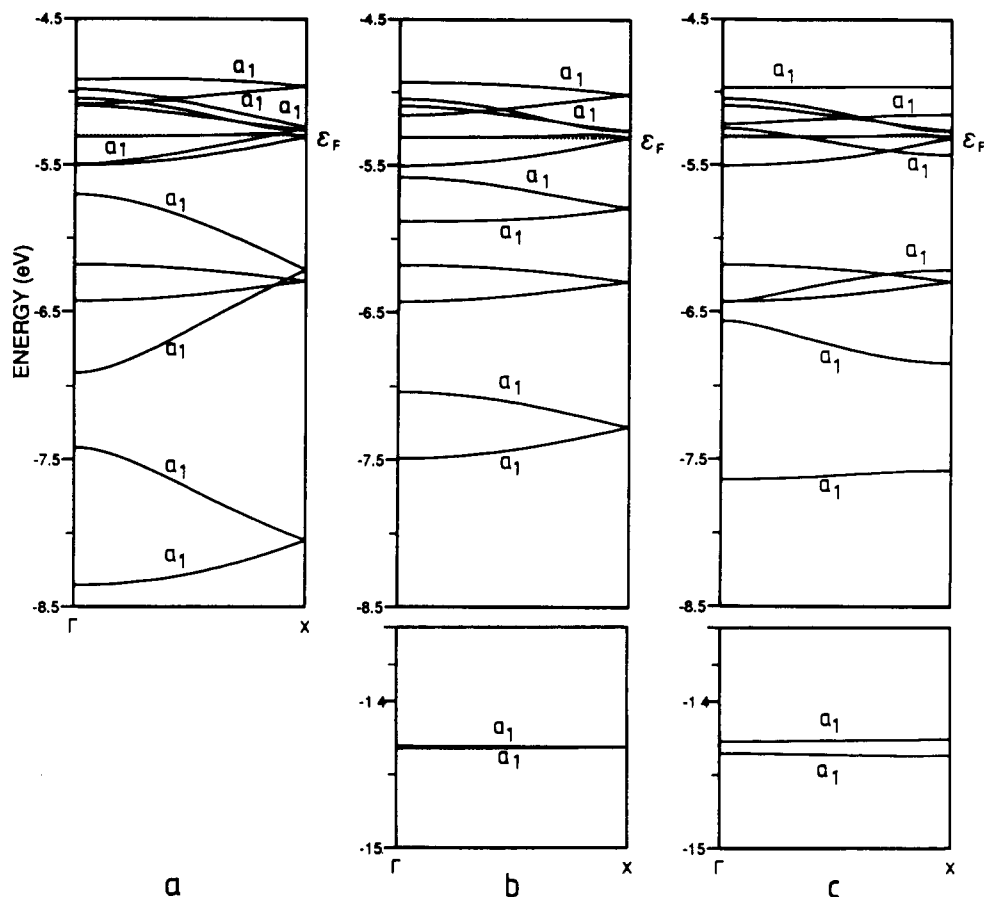
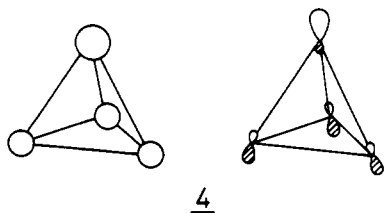


Figure 8. One-dimensional band structure for (a) 3a (Y_8), (b) 3b (Y_8H_2), and (c) 3c (Y_8H_2). The Fermi levels shown correspond to the real yttrium ($M = d^3$) case.

depending on k . Indeed, these a_1 bands are composed primarily of the tetrahedral MOs shown in 4. These MOs,



mainly 5s and 5p, are strongly bonding around the metal tetrahedra and can be related to the orbitals shown in 2, which have similar composition, nodal properties, and position in energy.

When two hydrogen atoms are introduced, as in 3b, these four a_1 bands are pushed up in energy by the two a_1 hydrogen bands (Figure 8b). In addition, significant second-order mixing occurs with upper a_1 bands, primarily of 4d character. One can note that here also the bands are folded back at $k = X$, since the cell considered is twice the elementary unit cell. In 3c (Figure 8c), destabilization and second-order mixing also occur, but the major change is the degeneracy splitting which occurs at $k = X$. Indeed, this time the elementary unit cell corresponds to a Y_8H_2 unit.

The through-atom pairing may be viewed as a Peierls distortion. Because of the distinction in the local symmetry around the axial Y atoms, the a_1 second-order mixing occurs in a different manner in 3b and 3c. Consequently, the position in energy of the four metallic a_1 branches is quite different. It appears that the through-atom coupling will be preferred for certain electron counts and unfavored for other electron counts, at least for low

Table I. a_1 Electron Counts and Energy Differences between the One-Dimensional H_2 Coupled and Uncoupled Structures of Y_8H_2 and $Y_{16}H_2$ for Different Electron Counts

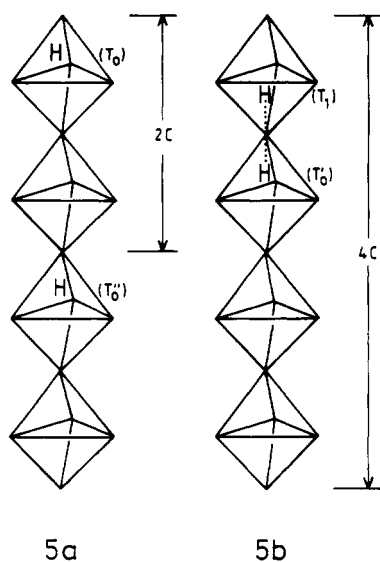
total e count	4	6	d^1	d^2	d^3	d^4	d^5
a_1 e count in 3c	4	6	8	10	12	12.8	16
a_1 e count in 3b	4	6	8.3	10	11.3	13.3	16
$E(3c) - E(3b)$	0.00	-0.38	0.42	-0.46	0.16	0.10	0.01
a_1 e count in 5b	4	6	13.2	18	20	24	32
a_1 e count in 5a	4	6	14	18	22	24.8	32
$E(5b) - E(5a)$	0.00	-0.31	-0.07	-0.01	0.05	0.02	0.00

Table II. Comparison of the Relative Energies (ΔE) of $Y_{32}H_2$ ($M = d^3$) for Various Hydrogen Occupation Sites. The Most Stable $T_0T'_0$ Structure Is Taken as a Reference

occupation site	d_{H-H}	ΔE , eV
$T_0T'_1$	$a\sqrt{6}$	1.27
$T_0T'_2$	$a\sqrt{2}$	0.21
$T_0T'_3$	a	0.39
$T_3T'_{3a}$	a	0.04
$T_3T'_{2a}$	$a\sqrt{7/6}$	0.06
$T_0T'_1$	$a\sqrt{3/2}$	0.02
$T_1T'_3$	$a\sqrt{11/6}$	0.29
$T_3T'_{3a}$	$a\sqrt{5/2}$	0.02
$T_0T'_0$	$a\sqrt{8/3}$	0.00
$T_3T'_{2a}$	$a\sqrt{11/3}$	0.01

occupancies of the d-band. This is illustrated in Table I, which gives the energy difference between 3b and 3c for different electron counts. Note that for the four-electron case there is no structural preference, the pairing being mainly related to second-order mixing between metallic levels in the lowest part of the d-band. We have also made band calculations on similar one-dimensional chains of

$Y_{16}H_2$ units, i.e., with a doubled metal cell size, as shown in 5. They lead to similar results; through-atom coupling, 5b, is favored over several specific electron counts (see Table I).



We think that our one-dimensional models provide a satisfactory rationalization of the pairing. The hydrogen 1s orbitals interact preponderantly with metallic FMOs which are bonding all over the tetrahedral holes. These orbitals, mainly 5s and 5p in character, are at the bottom of the d-band. When pairing occurs, first- and second-order mixing will induce, among these metallic FMOs, specific combinations which are bonding in two tetrahedra sharing a vertex and which will be more strongly destabilized by the σ and σ^* orbitals of the H...H pair. Since these levels are not uniformly distributed in the bottom of the d-band, their destabilization by the hydrogen FMOs will induce the preference for pairing at some specific electron counts (and/or temperature range).

The number and the position in energy of the spectator bands of e and a_2 symmetry play a crucial role in determining the electron counts favoring the pairing. We have also undertaken calculations on model clusters of various sizes, confirming the importance of the e and a_2 spectator orbitals. Moreover, one can see in Table I that the energy differences between the two structures are not very large. Therefore, we have also undertaken calculations on the three-dimensional extended structure, considering metallic supercells of various dimensions and various types of site occupation for the hydrogen atoms.

When the size of the cell considered is small, the distance between the two hydrogen atoms inside the cell may be larger than that of the two hydrogen atoms obtained by translation. To isolate a hydrogen pair, it is therefore necessary to increase the cell volume. Calculations were performed using a 36 yttrium atom supercell with $a\sqrt{3}$, $a\sqrt{3}$, and $2c$ cell vectors. Partial results have already appeared in the literature.^{2c,d} Using here the notation

referring to sites specified in Figure 3, the complete results are now given in Table II. The largest distance ($T_3T'_{2a}$ in Figure 3, $T_0T'_4$ in ref 2c,d), $a\sqrt{(11/3)}$, is smaller than the length of the cell vectors. The structures $T_0T'_0$, $T_3T'_{2a}$, and $T_0T'_1$ are the most stable. In two of them, $T_0T'_0$ and $T_0T'_1$, the hydrogen atoms are located on the c axis, in agreement with the experimental results. These two pairings correspond to the regular arrangement 3b and to the through-atom pairing 3c, respectively, which have been already discussed above. The difference between them is very small (0.02 eV) for the "d³" (real yttrium) electron count. As for the one-dimensional system, this difference varies with the electron count. It exhibits smooth oscillations. The $T_0T'_1$ structure is preferred for certain electron counts ["d¹" (38 electrons), "d²" (74 electrons), "d⁵" (182 electrons)]. On the other hand, the $T_0T'_0$ structure is preferred for the "d³" (110 electrons) and "d⁴" (146 electrons) counts. On the contrary, the energy difference does not vary for an intermediate number of electrons. In a simple ionic model, the number of metal electrons is reduced by one unit per H atom to generate each hydride and should vary with the number of hydrogen atoms. In the range 100–120 electrons, close to the real yttrium case, the $T_0T'_0$ structure is always preferred by more than 0.01 eV, the largest difference (0.02 eV) being for 114 electrons.

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Appendix

All calculations were performed using the molecular and tight-binding extended Hückel method.^{8,9} The yttrium parameters were taken in order that they reproduce the band dispersion of the pure metal.^{2b-d} The exponent (ζ) and the valence shell ionization potential (H_{ii} in eV) were respectively 1.30, -13.60 for H(1s); 1.39, -5.70 for Y(5s); 1.39, -3.80 for Y(5p). The H_{ii} value for Y 4d was set equal to -4.30 eV. A linear combination of two Slater-type orbitals was used to represent the atomic d orbitals of Y ($\zeta_1 = 4.34$, $c_1 = 0.67$; $\zeta_2 = 1.05$, $c_2 = 0.67$).

In model 1, Y-Y distances identical to that encountered in yttrium metal, i.e., $Y_{ax}-Y_{eq} = 3.56$ Å and $Y_{eq}-Y_{eq} = 3.65$ Å, were taken leading to the following Y-H separations (Å): $Y_{ax}-H = 2.47$ and $Y_{eq}-H = 2.15$ for H-H = 0.8; $Y_{ax}-H = 1.87$ and $Y_{eq}-H = 2.33$ for H-H = 2.0.

In 3-D calculations, different sets of k points, related to each other, were chosen according to the symmetry of the reciprocal lattice for the different H...H pairings. 12 for $T_0T'_1$ and $T_0T'_1$, 24 for $T_0T'_0$, 54 for $T_3T'_{2a}$ and $T_3T'_{3a}$, and 60 k points for T_0t_2 , $T_0T'_3$, $T'_1T'_3$, $T_3T'_{3a}$, and $T_3T'_{2a}$ were used.¹⁹

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