

# Bonding in Group IIIb Hydrides: an Empirical Approach

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The hydrides of scandium and yttrium<sup>1</sup> and the lanthanides<sup>2</sup> have been extensively studied, and much is known concerning their structures and physical properties. Yet the question of bonding in these compounds is controversial. Though hydrogen is the simplest atomic system from a theoretical point of view, the controversy has centered on the nature of the hydrogen in these binary compounds. The hydrogen in metallic hydrides has been variously described as protonic, atomic, or hydridic.

This Account reviews, for group IIIb hydrides, the arguments which have been advanced for each of these widely divergent models. Recent experimental results which strongly favor the hydridic model are discussed and used to derive detailed, though schematic, band diagrams for these hydrides. These empirical band diagrams are found to agree with the results of recent theoretical calculations for these hydrides, thus providing a convincing argument for the hydridic model.

Scandium, yttrium, and the lanthanides except europium and ytterbium form dihydrides which have the fluorite structure. The metal atoms form a face-centered cubic (fcc) sublattice and the hydrogens occupy the tetrahedral interstices between the metal atoms. These dihydrides are metallic in character. With the exception of scandium, they absorb additional hydrogen up to nearly  $MH_3$ . Scandium dihydride is the only dihydride which is metallic and has the fluorite structure but does not absorb additional hydrogen.

The dihydrides of the lighter lanthanides are converted to hydrogen-deficient trihydrides without a phase change. The metal atoms remain fcc, the additional hydrogen progressively filling the octahedral interstices of this structure. For yttrium and the heavier lanthanides, conversion of the dihydride to the trihydride is accompanied by a phase change. The metal atoms of these trihydrides form a hexagonal sublattice and the hydrogens occupy positions slightly displaced from the tetrahedral and octahedral interstices.

Europium and ytterbium form orthorhombic dihydrides which are isostructural with calcium hydride. It is generally accepted that the latter is hydridic. The structural similarity suggests that europium and ytterbium dihydrides are also hydridic. The two orthorhombic lanthanide dihydrides are

hydrogen deficient and exhibit semiconductivity. Calcium hydride is an insulator. At high pressures, ytterbium does form a higher hydride, but europium does not.

The group IIIb trihydrides might be expected to be ionic in character on the basis of the relatively low electronegativity of these metals. The metallic dihydrides might then be considered to contain two hydride ions per formula unit, the metal atoms being present as trivalent cations whose extra valence electrons were delocalized in a conduction band. Just such a description of the dihydrides was suggested in 1956 by Libowitz and Gibb<sup>3</sup> who found good agreement between observed internuclear distances in the dihydrides of several lanthanides and the sum of the trivalent cation radius and the hydride ion radius. This model was extended to a larger number of metallic hydrides<sup>4,5</sup> and used by Gibb<sup>6</sup> to estimate lattice energies for a large number of hydrides. For group IIIb hydrides, first principle calculations<sup>7</sup> and a bonding model<sup>8</sup> derived from a variety of experimental results now both provide a description of the bonding which is in basic agreement with Libowitz and Gibb's early model. Between 1956 and the present, however, a very different viewpoint has been expressed by some authors: the hydrogen in these compounds has frequently been described as protonic. The two models being opposite in their description of the hydrogen, it is clear that if either the hydridic or protonic model is even approximately correct, the other must be wrong.

Differences in viewpoint concerning the bonding in group IIIb hydrides seem to arise from at least two sources. First, the bonding in group IIIb hydrides has often been discussed in relation to their magnetic properties. There is, however, an ambiguity in the interpretation of these properties. The nature of this ambiguity is discussed in the next section. Second, since there is some evidence that the bonding in some

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(2) W. M. Mueller in ref 1, pp 386-489, and references cited therein; see also W. L. Korst and J. C. Ward, *Inorg. Chem.* **5**, 1719 (1966); K. I. Hardcastle and J. C. Warf, *ibid.*, **5**, 1728 (1966); J. C. Warf and K. I. Hardcastle, *ibid.*, **5**, 1736 (1966).

(3) G. G. Libowitz and T. R. P. Gibb, Jr., *J. Phys. Chem.*, **60**, 510 (1956).

(4) T. R. P. Gibb, Jr., and D. P. Schumacher, *ibid.*, **64**, 1407 (1960).

(5) G. G. Libowitz, "The Solid State Chemistry of Binary Metal Hydrides," W. A. Benjamin, New York, N. Y., 1965.

(6) T. R. P. Gibb, Jr., *Progr. Inorg. Chem.*, **3**, 315 (1962).

(7) A. C. Switendick, *Solid State Commun.*, **8**, 1463 (1970). An important correction appears under Errata, *ibid.*, **8** (No. 23), xxiv (1970). A. C. Switendick, *Int. J. Quantum Chem., Symp.*, **5**, 459 (1971).

(8) See discussion under The Hydridic Model.

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other transition metal hydrides is metallic, it becomes important to recognize that the group IIIb hydrides differ from some other metallic hydrides in an important way. A large shift, similar to  $K$ , the Knight shift, has been observed for the hydrogen nmr in a number of transition metal hydrides,<sup>9,10</sup> though these shifts may arise, at least in part, from macroscopic susceptibility effects.<sup>11</sup> For metals  $K$  is attributed to the field created at the nucleus by conduction electrons.<sup>12</sup> Thus the hydrogen shifts suggest that the hydrogen in these transition metal hydrides is metallic. No hydrogen nmr shift is observed for scandium, yttrium, or lanthanum hydrides;<sup>13</sup> therefore the hydrogen species present in these hydrides is not metallic in nature. Hydrogen nmr shifts are observed for a number of hydrides of lanthanides with unpaired f electrons,<sup>14</sup> but these can be attributed to a mechanism other than that of the Knight shift.

Ebisuzaki and O'Keefe<sup>15</sup> have proposed a screened proton model for metallic hydrides. They consider the effect of introducing protons into a hypothetical metal in which the cation charge is smoothed out to neutralize the electron gas. The electrons in the vicinity of the protons would be conduction electrons and give rise to a Knight shift. For most transition elements, the screening of the proton would be large enough to prevent the formation of a bound state, but for the rare earth hydrides, a high density of states might lead to a charge buildup approaching that of a hydride ion.<sup>15</sup> If this is what occurs upon going from the transition metal hydrides to the rare earth hydrides, the change produces an important difference in the nature of the electrons centered on the hydrogens. Since no hydrogen shift is observed for scandium, yttrium, or lanthanum hydrides, those bands which place electrons on the hydrogens must be filled bands and not conduction bands.

### A Review of the Problem

In 1957, Stalinski<sup>16</sup> reported the magnetic susceptibility,  $\chi$ , of lanthanum hydrides. The weak paramagnetism of lanthanum metal is reduced somewhat in the dihydride and decreases with increasing hydrogen content beyond this composition. Samples of higher hydrogen content than  $\text{LaH}_{2.7}$  were diamagnetic. Stalinski pointed out that these results were consistent with either a protonic or hydridic model. Either

hydride ions form by the capture of electrons from the conduction band, which would then be empty at the composition  $\text{LaH}_3$ , or the hydrogens donate their electrons to the conduction band, filling it at the composition  $\text{LaH}_3$ . The latter interpretation would require that the 5d-6s band of the metal be split to give a lower subband with a capacity of six electrons per metal atom. Such splitting had been suggested earlier by Martin and Rees<sup>17</sup> for zirconium hydrides. Of the two models suggested by Stalinski, it was the split band protonic model that Schreiber and Cotts<sup>18</sup> chose to interpret the results of a nmr study of lanthanum hydrides. The decrease and eventual disappearance of the La  $K$  and the increase in  $T_1$ , the La spin-lattice relaxation time, with increasing hydrogen content were attributed to filling the conduction band. This interpretation was later extended<sup>13</sup> to scandium and yttrium dihydrides. Analogies with vanadium<sup>19</sup> and niobium<sup>10</sup> hydrides were emphasized.

For the hydrides of lanthanides with unpaired f electrons, the large moments due to the unpaired core electrons preclude the direct observation of the weak paramagnetism of conduction electrons.<sup>2</sup> An important indirect role is played by the conduction electrons: they provide the medium for exchange interactions by which ordering of the core moments occurs. The effect of hydride formation is to make the conduction electrons less available for this role. Ordering occurs at lower temperatures in the dihydrides than in the metals and at still lower temperatures, if at all, in the trihydrides. The reduced availability of the conduction electrons could be due to the formation of either protons or hydride ions.<sup>20</sup>

A similar question of interpretation arises with regard to the large hydrogen nmr shifts observed for cerium, praseodymium, neodymium, and gadolinium hydrides by Kopp and Schreiber.<sup>14</sup> They attribute these shifts to the effect of the large core moments on a small fraction of an electron in the hydrogen 1s orbitals. It is also possible, however, that the core moments act on hydride ion electrons by a spin polarization mechanism to produce these results.

The nature of the ambiguity in the interpretation of the magnetic properties can be most easily seen for those cases where there are no unpaired f electrons. The weak paramagnetism of the conduction electrons can then be measured and subjected to analysis. Only those conduction electrons within about  $kT$  of the Fermi energy can change their spins under the influence of an applied magnetic field.<sup>21</sup> Since the density of states diminishes toward either end of the band, the observed decreases in  $\chi$ ,  $K$ , and  $1/T_1$  upon dihydride formation are consistent with either the

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(10) D. Zamir and R. M. Cotts, *Phys. Rev.*, **134**, A666 (1964).

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(13) D. S. Schreiber, *ibid.*, **137**, 860 (1965).

(14) J. P. Kopp and D. S. Schreiber, *J. Appl. Phys.*, **38**, 1373 (1967); *Phys. Lett. A*, **24**, 323 (1967).

(15) Y. Ebisuzaki and M. O'Keefe, *Progr. Solid State Chem.*, **4**, 187 (1967).

(16) B. Stalinski, *Bull. Acad. Polon. Sci., Cl. Troisieme*, **5**, 997 (1957).

(17) S. L. H. Martin and A. L. G. Rees, *Trans. Faraday Soc.*, **50**, 343 (1954).

(18) D. S. Schreiber and R. M. Cotts, *Phys. Rev.*, **131**, 1118 (1963).

(19) D. Zamir, *Phys. Rev. A*, **140**, 271 (1965).

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protonic or hydridic model. According to the protonic model, the dihydride would have five electrons and the trihydride six electrons per metal atom in a band with a capacity of six. According to the hydridic model, there would be only one electron per metal atom left in the conduction band of the dihydride, and this electron would also be lost upon formation of the trihydride.

A more detailed analysis of the magnetic properties was given for lanthanum hydrides.<sup>22</sup> Distinct s-spin, d-spin, and d-orbital contributions to  $\chi$ ,  $K$ , and  $1/T_1$  were assumed. Of the nine terms thus defined, all depend directly upon the density of states for the respective type of electron at the Fermi energy except the d-orbital contributions of  $\chi$  and  $K$ . These depend on the term  $n(n' - n)$ , where  $n$  is the number of d electrons per metal atom and  $n'$  is the capacity of the d band or subband. Thus all nine terms tend toward zero for either a nearly filled or nearly empty band.

The protonic model requires that the conduction band be split to give a lower subband with a capacity of six electrons per metal atom. The use of crystal field theory<sup>23</sup> leads to the conclusion that the d orbitals of a metal atom would be split into a lower, triply degenerate set,  $T_{2g}$ , and a higher doubly degenerate set,  $E_g$ , by the cube of eight protons surrounding each metal atom in the dihydride. The  $T_{2g}$  set having a capacity of six electrons would be the subband required by the protonic model. This implies that the s band is higher in energy, separated by a gap from the  $T_{2g}$  band. An earlier suggestion had been that a d subband with a capacity of four electrons overlapped an s band.<sup>24</sup>

For the hydridic model the splitting of the d orbitals would be opposite in direction because of the negative sign of the ligands. The one electron per metal atom in the conduction band of the dihydride would occupy the  $E_g$  subband. The s band would be placed above the Fermi energy to account for the relatively long spin-lattice relaxation time observed for the Sc, Y, and La nuclei in their dihydrides. Because of their finite density at the nucleus, s electrons are especially efficient in promoting spin-lattice relaxation. Upon conversion of Y metal to  $YH_2$ ,  $\chi$  decreases<sup>25</sup> from  $184 \times 10^{-6}$  to  $104 \times 10^{-6}$  emu g atom<sup>-1</sup>;  $K$  decreases from 0.34<sup>25</sup> to 0.11%<sup>14</sup> and  $1/(T_1T)$  decreases<sup>26</sup> from 0.067 to 0.0018 sec<sup>-1</sup> deg<sup>-1</sup>. The application of crystal-field theory and the analysis of the magnetic properties do not provide a basis for selecting between the protonic and hydridic models, but do provide useful predictions concerning the character of the conduction band electrons. For the free metal, we take the conduction band to arise from the  $(n - 1)d^1ns^2$  electron configuration. The protonic model predicts  $(n -$

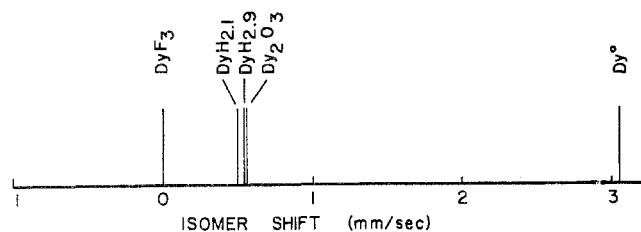


Figure 1. <sup>161</sup>Dy isomer shifts in the Mössbauer spectra of dysprosium metal and dysprosium compounds. See ref 27 for additional details.

1) $d^5ns^0$  and  $(n - 1)d^6ns^0$  configurations for the di- and trihydride, respectively. The hydridic model predicts  $(n - 1)d^1ns^0$  and  $(n - 1)d^0ns^0$  configurations for the di- and trihydride, respectively.

The electron configurations thus predicted for the protonic and hydridic models were used to interpret isomer shifts in the <sup>161</sup>Dy Mössbauer spectra of dysprosium metal and its hydrides.<sup>27</sup> The isomer shift,  $\delta$ , measures changes in nuclear energy level separations due to the chemical environment of the absorbing nucleus.  $\delta$  is proportional to the difference in electron density at the nucleus between a given compound and a standard, either the source material or some selected absorber. For <sup>161</sup>Dy the proportionality constant is positive, and a positive  $\delta$  indicates greater electron density at the nucleus in the absorber than in the standard. Increased electron density at the nucleus can result either from the addition of an s electron to the atom or from the removal of p, d, or f electrons. For example, the addition of electrons to the 6s level of dysprosium would give a positive  $\delta$  because these electrons have a finite density at the dysprosium nucleus. The removal of 5d electrons would also give a positive  $\delta$  since this would decrease the shielding of all of the s electrons in the dysprosium atom and increase their density at the nucleus.

Isomer shifts for Dy metal and several Dy compounds,<sup>27</sup> relative to  $DyF_3$  which was taken to represent the  $(Xe)4f^9$  electron configuration of the  $Dy^{3+}$  ion, are shown in Figure 1. The large positive  $\delta$  of Dy metal may be attributed to the dominant effect of the presence of 6s conduction electrons, the effect of the 5d conduction electrons being of opposite sign but of much smaller magnitude. The  $5d^5$  and  $5d^6$  electron configurations predicted by the protonic model for  $DyH_2$  and  $DyH_3$ , respectively, should give rise to negative  $\delta$ 's, but positive  $\delta$ 's are observed. In the first approximation, the hydridic model predicts a slightly negative isomer shift for  $DyH_2$  with a  $5d^1$  electron configuration and a isomer shift of zero for  $DyH_3$  with a  $5d^0$  electron configuration. On the basis of electronegativities, the hydrides would be expected to be appreciably more covalent than  $DyF_3$ . The positive  $\delta$ 's of the hydrides can be attributed to partial covalency of about 10% which places electron density back into the 6s orbitals of the  $Dy^{3+}$  ions. The  $\delta$ 's

(22) W. G. Bos and H. S. Gutowsky, *Inorg. Chem.*, **6**, 552 (1967).

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(24) M. F. Merriam and D. S. Schreiber, *J. Phys. Chem. Solids*, **24**, 1375 (1963).

(25) R. G. Barnes, F. Borsa, S. L. Segal, and D. R. Torgeson, *Phys. Rev. A*, **137**, 1828 (1965).

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(27) T. P. Abeles, W. G. Bos, and P. J. Ouseph, *J. Phys. Chem. Solids*, **30**, 2159 (1969).

indicate about the same degree of covalency for the hydrides as for  $\text{Dy}_2\text{O}_3$ . The difference in  $\delta$ 's between  $\text{DyH}_{2.08}$  and  $\text{DyH}_{2.90}$  is about equal to the experimental uncertainty. To the extent that it is real, it may be taken as indicative of the presence of 5d electrons in the dihydride conduction band.

The electrical properties<sup>2</sup> of rare earth hydrides have also been discussed in relation to bonding. Heckman<sup>28</sup> has reported an extensive study of the electrical properties of cerium and gadolinium hydrides.  $\text{CeH}_{1.6}$  and  $\text{GdH}_{1.8}$  were better conductors than their parent metals. With increasing hydrogen content beyond these compositions, the conductivity fell rapidly; hydrides of composition near  $\text{MH}_2$  were poorer conductors than the parent metals. Further increases in hydrogen content were accompanied by further decreases in conductivity. Negative Seebeck coefficients were observed for several fcc cerium and gadolinium hydrides. On this basis, Heckman argued that the charge carriers were electrons. This would be consistent with the hydridic model. Later, however, Heckman<sup>29</sup> reported that Hall coefficients for cerium hydrides were positive and increased with increasing hydrogen content from  $\text{CeH}_{2.0}$  to  $\text{CeH}_{2.8}$ . These results were consistent with the predictions of the protonic model: the charge carriers would be positive holes and the Hall coefficient would approach infinity as  $\text{H/Ce}$  approaches 3. Heckman concluded that these results supported the protonic model.

An alternate interpretation of the positive Hall coefficients of cerium hydrides has been suggested by Libowitz and Pack.<sup>30</sup> Conductivities for single-crystal cerium hydride specimens were reported in good agreement with Heckman's results. Libowitz and Pack assumed the bonding to be ionic and the stoichiometric trihydride to be an insulator. With the removal of hydrogen to form  $\text{CeH}_{3-x}$ , hydrogen vacancies form and act as electron donors in the band gap, giving rise to semiconductivity. As  $x$  increases, the concentration of vacancies would become great enough so that, at  $\text{H/Ce} = 2.8$ , their wave functions would overlap to form a defect conduction band. The defect band being half-filled, the shape of the density of states curve would determine whether electron or hole conductivity would predominate. Thus positive Hall coefficients, indicative of hole conductivity, are not in conflict with the hydridic model. An extension<sup>31</sup> of the model of Libowitz and Pack involves overlap of the vacancy orbitals with metal  $E_g$  orbitals to give rise to the defect conduction band.

Recent studies of the  $L_{\text{II}}$  ( $2p_{1/2}$ )<sup>32</sup> and  $L_{\text{III}}$  ( $2p_{3/2}$ )<sup>33</sup> X-ray emission edges in lanthanum hydrides provide very direct evidence for the hydridic model. The results of these studies are illustrated in Figure 2.

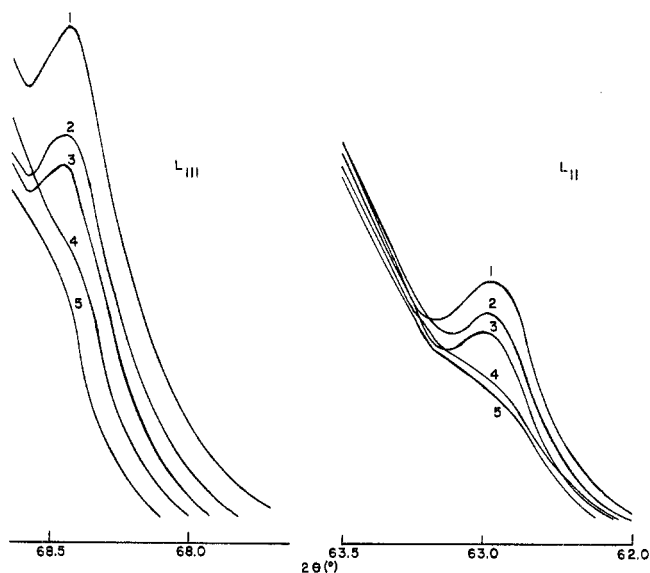


Figure 2. The lanthanum  $L_{\text{II}}$  and  $L_{\text{III}}$  X-ray emission edges of (1) La metal; (2)  $\text{LaH}_{2.09}$ ; (3)  $\text{LaH}_{2.49}$ ; (4)  $\text{LaH}_{2.90}$ ; and (5)  $\text{La}_2\text{O}_3$ . The spectra of the compounds have been normalized with respect to that of the metal. The peaks shown here have been assigned to transitions from the conduction band to the  $L_{\text{II}}$  and  $L_{\text{III}}$  levels of lanthanum, respectively. See ref 32 and 33 for additional details.  $2\theta$  values are for a LiF (200) analyzer crystal with  $2d = 4.028 \text{ \AA}$ .

To correct for concentration differences between different samples, the intensities of the curves for all of the other materials have been normalized to that of the metal using certain characteristic peaks below each emission edge. For lanthanum metal, the peaks shown in Figure 2 were assigned to transitions from the conduction band to the  $L_{\text{II}}$  and  $L_{\text{III}}$  levels, respectively. The intensities of these peaks decreased from the metal to the dihydride and with increasing hydrogen content from the dihydride to the trihydride. We attribute these decreases to the progressive depopulation of the conduction band through hydride ion formation. At each edge, the decrease in integrated intensity is smaller from La metal to  $\text{LaH}_2$  than from  $\text{LaH}_2$  to  $\text{LaH}_3$ . The hydridic model predicts that two 6s electrons are lost from La metal to  $\text{LaH}_2$  and one 5d electron is lost from  $\text{LaH}_2$  to  $\text{LaH}_3$ . Because of the smaller change in principal quantum number, the  $5d \rightarrow 2p_{1/2}$  and  $5d \rightarrow 2p_{3/2}$  transitions occur with greater intensity than the  $6s \rightarrow 2p_{1/2}$  and  $6s \rightarrow 2p_{3/2}$  transitions. Thus these changes in intensity support the hydridic model in which the dihydride conduction band is taken to contain one 5d electron per metal atom. The  $L_{\text{II}}$  and  $L_{\text{III}}$  emission edges of  $\text{LaH}_{2.9}$  closely resemble those of  $\text{La}_2\text{O}_3$ . The residual intensities for these compounds at the emission edges may be attributed to partial covalence such as that suggested earlier on the basis of the dysprosium Mössbauer results.

Angular correlations of the radiation from positron annihilations in cerium<sup>34</sup> and several other lanthanide<sup>35</sup>

(28) R. C. Heckman, *J. Chem. Phys.*, **40**, 2958 (1964).

(29) R. C. Heckman, *ibid.*, **46**, 2158 (1967).

(30) G. G. Libowitz and J. G. Pack, *ibid.*, **50**, 3557 (1969).

(31) W. G. Bos, *ibid.*, **53**, 855 (1970).

(32) A. C. Sarma and W. G. Bos, *J. Phys. Chem. Solids*, **33**, 935 (1972).

(33) A. C. Sarma and W. G. Bos, *ibid.*, **32**, 1423 (1971).

(34) M. P. Chouinard, D. S. Gustafson, and R. C. Heckman, *J. Chem. Phys.*, **51**, 3554 (1969).

(35) M. P. Chouinard and D. R. Gustafson, *ibid.*, **54**, 5082 (1971).

hydrides were interpreted in terms of a screened proton or metallic type of bonding. Positron annihilation rates in lanthanum hydrides<sup>36</sup> were, however, interpreted on the basis of a hydridic model. Thus positron annihilation results do not provide a clear answer to the question of bonding.

### The Hydridic Model: Band Structures

The data reviewed in the previous section not only provide a basis for selecting the hydridic model as providing the most accurate description of bonding in group IIIb hydrides but also provide information from which a detailed band diagram can be derived. The following points, in particular, should be noted. (1) The absence of Knight shifts for hydrogen in the nmr spectra of Sc, Y, and La hydrides precludes a metallic state for hydrogen. (2) The decreases in intensity with increasing hydrogen content of the peaks at the lanthanum  $L_{II}$  and  $L_{III}$  X-ray emission edges support the hydridic, rather than the protonic, model. (3) The long spin-lattice relaxation times of Sc, Y, and La nuclei in the dihydrides suggest that the dihydride conduction band is predominantly of d character. Changes in the  $L_{II}$  and  $L_{III}$  X-ray emission intensities from La to  $LaH_2$  and from  $LaH_2$  to  $LaH_3$  are also consistent with this view. (4) The positive Hall coefficients of cerium hydrides are consistent with the hydridic model provided that the hydride conduction band is always half-filled so that the sign of the charge carriers will be determined by the shape of the density of states curve. (5) The  $L_{II}$  and  $L_{III}$  X-ray emission edges for lanthanum hydrides of composition near  $LaH_3$  indicate covalent contributions to the predominantly ionic bonding. The  $^{161}Dy$  isomer shifts of dysprosium hydrides indicate that the s valence orbitals of the metal ions are involved here and that the covalent contribution is 10% or more.

These conclusions regarding bonding in group IIIb hydrides have been incorporated into the schematic dihydride band diagram shown in Figure 3. The free atom  $(n-1)d$  and  $ns$  energy levels of the metal are shown in column A. The eight hydride ions which form a cube around each metal atom split the d levels so that, in column B, the  $E_g$  set lies below and the  $T_{2g}$  set above the  $ns$  level.

Further splitting of the  $E_g$  orbitals is invoked to give, in column C, a single, lowest d level. Libowitz and Pack<sup>30</sup> suggested that the hydride conduction band was a defect band arising from the overlap of octahedral vacancy states. A later suggestion<sup>31</sup> was that overlap between the vacancy states and the metal  $E_g$  orbitals, whose lobes point directly toward the octahedral sites, gives rise to the conduction band, the number of vacancy states determining its capacity. We now suggest that each octahedral vacancy state may be described by a linear combination of the  $E_g$  orbitals of the six metal atoms which surround it. In the semiconducting, hydrogen-deficient trihydride, the

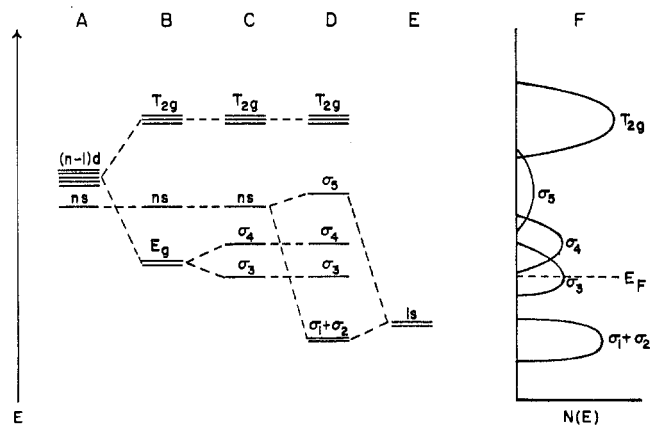


Figure 3. Derivation of a schematic band diagram for face-centered-cubic dihydrides of group IIIb metals. Column A shows the valence levels for a free metal atom. In column B, crystal field splitting of the metal d orbitals is taken into account. The further splitting of the  $E_g$  d orbitals, shown in column C, may be attributed to the formation of bonding and antibonding bands. In column D, the combination of hydrogen 1s orbitals from column E with the metal s orbitals is shown. A schematic density of states curve is shown in column F.

isolated vacancy states resemble f centers for which wave functions may be obtained in just this way.<sup>37</sup> The connection between the wave functions of adjacent vacancies then arises quite naturally *via* contributions from the same wave functions of the metal atom between them. The hydride conduction band corresponds to a network of vacancy states thus connected. In the dihydride there are  $N$  vacancies and  $N$  metal atoms with  $2N$   $E_g$  orbitals. The lobes of the  $E_g$  orbitals point toward each other across the octahedral sites;  $N$  bonding combinations of the  $E_g$  orbitals may be formed to give a conduction band with a capacity of  $2N$  electrons. This band would be half-filled in the dihydride. The band formed by taking  $N$  antibonding combinations of the  $E_g$  orbitals would lie higher in energy and remain vacant.

The basic assumption of the hydridic model is reflected in the diagram by placing the hydrogen levels in column E lower in energy than the lowest metal d level. The covalent contribution to the bonding is indicated by contributions from the metal  $ns$  orbital to  $\sigma_1$  and  $\sigma_2$  and from the hydrogen 1s orbitals to  $\sigma_5$  in column D. The degree of mixing being about 10%  $\sigma_1$  and  $\sigma_2$  are only slightly stabilized relative to the pure hydrogen 1s levels and  $\sigma_3$  is only slightly destabilized relative to the metal  $ns$  level. A refinement of this treatment is suggested by Switendick's calculations,<sup>7</sup> discussed more fully below. He finds two bands arising from the bonding and antibonding combinations of the 1s orbitals of the two hydrogens in the primitive unit cell. The metal  $ns$  orbitals mix with the bonding combination of hydrogen orbitals. These results imply that, in column D,  $\sigma_1$  should lie below and  $\sigma_2$  above the hydrogen levels of column E.

The levels of column D give rise to the highly

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schematic density of states profile shown in column F. Of the five valence electrons per metal atom in the dihydride, four are accommodated in the  $\sigma_1$  and  $\sigma_2$  bands. An energy gap separates these valence bands from the conduction band,  $\sigma_3$ . The latter is of metal d character and is half-filled. Since hole conductivity predominates in the dihydride, the  $\sigma_3$  profile is drawn so that  $E_F$  lies above its maximum.

As the dihydride takes up additional hydrogen, the octahedral lattice sites begin to fill. New hydrogen-like states, centered on the filled octahedral sites, are introduced below  $\sigma_3$ . For each hydride ion that forms, one electron is removed from  $\sigma_3$ , but  $\sigma_3$  remains half-filled because one state is also removed since the combination of d orbitals across one octahedral site is blocked. Eventually, most of the octahedral sites are occupied and only isolated, singly occupied vacancy states are left. These give rise to the semiconductivity of the hydrogen-deficient trihydride. The conversion of the dihydride to the trihydride is much less exothermic than the formation of the dihydride from the metal.<sup>1,2</sup> This suggests that the third hydride band of the trihydride is higher in energy than the hydride bands of the dihydride; there is also increased hydride ion-hydride ion repulsion resulting from the insertion of a third hydride ion into the somewhat crowded lattice.<sup>38</sup>

The band structure derived above does not take into account the transition to a hexagonal structure which accompanies the dihydride to trihydride conversion for yttrium and most of the heavier lanthanides. The great similarity in the other physical properties of the fcc and hexagonal hydrides<sup>1,2</sup> provides evidence that there is no major rearrangement of the energy bands on going to the hexagonal structure. This empirical conclusion is not surprising since the fcc and hexagonal arrangements of metal atoms in the structures are closely related. Metals whose structures are related to each other in the same way have generally similar density of states curves. For the hydrides there is a further structural difference: the hydride ions in the hexagonal hydrides are displaced from their ideal lattice position in such a way as to lessen repulsions between them.<sup>38,39</sup>

The stability of the dihydrides of europium and ytterbium toward the absorption of more hydrogen can be attributed to the presence of only two electrons per atom in the conduction bands of these metals. Thus in the stoichiometric dihydrides of these elements, the metal and hydrogen electrons would just fill two hydride valence bands.  $\text{EuH}_2$  and  $\text{YbH}_2$  might be expected to be insulators like  $\text{CaH}_2$  with which they are isostructural. The dihydrides formed by europium

and ytterbium are hydrogen deficient, however, and exhibit semiconductivity. Scandium also forms only a dihydride. We attribute the failure of scandium dihydride to absorb additional hydrogen to the excessive repulsion between hydride ions which would result from the insertion of additional hydride ions into the very compact scandium dihydride lattice.<sup>38</sup> In terms of band levels, this implies that, because of repulsions between the hydride ions, the third hydride band would be higher in energy than the conduction band. Thus scandium forms only a dihydride and it is metallic.

The major features of the group IIIb hydride band structures derived above are in good agreement with Switendick's augmented plane wave results.<sup>7</sup> For  $\text{YH}_2$ , he finds that the Fermi energy falls in a band derived from yttrium 4d states. Two hydride bands lie below, and are separated by a gap from, this conduction band. One of these bands is derived from bonding and the other from antibonding combinations of the Bloch sums of the 1s orbitals of the two dihydride hydrogens. The metal 5s levels mix to some extent with the bonding combination. In a sphere of such size that it would enclose 0.57 electron in a free hydrogen atom, these bands place 0.99 electron at each hydrogen site. Though Switendick originally interpreted this result differently, we feel that this 74% greater charge density is what might be expected for a hydride ion, allowance being made for expansion of the electron cloud due to interelectronic repulsion and for partial covalency.

Switendick also calculated a band structure for  $\text{PrH}_3$ . Here he found a third hydride band formed from a bonding combination of metal *ns* orbitals and 1s orbitals of the third hydrogen, with antibonding contributions from the 1s orbitals of the first two hydrogens. The Fermi energy lay in a gap just above this third hydride band. Switendick did not calculate the coefficients of the metal and hydrogen orbitals contributing to these bands. These coefficients would describe, in the terminology of our empirical model, the degree of covalency of the bonding. The antibonding character of the hydrogen 1s contributions to some of the hydride bands in Switendick's more rigorous treatment corresponds to the interionic repulsions in our more classical hydridic model.<sup>38</sup> Both approaches stress the importance of hydrogen-hydrogen separations in determining the relative stability of the hydride bands.

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