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Trends in the electron-phonon coupling parameter in some metallic hydrides

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We present an evaluation of the electron-phonon coupling parameter λ, using the McMillan formalism, for several classes of stoichiometric mono- and dihydrides with a metallic underlying fcc structure. We calculate the electronic term η and use experimental estimates for the phonon energies when available. We derive systematic trends concerning both contributions to η stemming, respectively, from the metallic site M and the hydrogen site H. We show that η_H is generally small, but it may become large if the Fermi energy is in the metal s-p band as in the filled d-band transition-metal (TM) hydrides such as PdH; η_H may also be large when a metal-hydrogen antibonding band crosses the Fermi level, a case which happens in AlH and may happen for some unstable dihydrides. The metallic contribution η_M is calculated to be small for all stable mono- and dihydrides like PdH, NiH, ZrH_2, NbH_2, etc., but nothing in principle prevents this contribution from becoming as large as in some pure TM, if one sweeps the Fermi level through the whole metallic d band. Good agreement with the available experimental data is obtained concerning the occurrence of superconductivity in the compounds considered.

I. INTRODUCTION

The discovery of superconductivity in thorium[1] and palladium hydrides[2] and the overall technological importance of metallic hydrides focused the attention on their electronic properties and on the values of the electron-phonon coupling parameter λ. As it is also known that the superconducting T_c may decrease upon the formation of the hydride phase [NbH_x with $x \simeq 1$ and 2 (Ref. 3) and LaH_2 (Ref. 4) are nonsuperconductors while pure Nb and La have rather high T_c], it becomes interesting to develop a more systematic approach to this problem and see if there are some systematic features which may favor or disfavor the occurrence of superconductivity in the metallic hydrides. The two main questions one would like to answer are the following: (i) Is the variation of T_c as one goes from the metal to the hydride, related to changes in the electronic and atomic (phonons) structure of the host metal through the presence of the H atoms? (ii) Is there a direct coupling of the electron manifold to the hydrogen optic vibrations?

There is indeed experimental evidence[5] for such a coupling in PdH, while of course it must be weak in all nonsuperconducting hydrides such as NbH_2. We use an extension of McMillan's formalism[6] in which λ is expressed in terms of the ratio of an electronic contribution η to a phonon contribution. We will focus, in our calculations, on the electronic term η since it is difficult to undertake, at this time, reliable first-principles calculations of the phonon vibration frequencies ω; we will thus use experimental values of ω if these are available. The lattice expansion observed upon hydrogenation and the drastic change in the electronic properties, which obviously affect the screening of the phonon field, lead to a modification of the acoustical host-metal phonons. Only detailed microscopic calculations can give an answer for the trends of such changes. Experimental results show that these effects lead either to a stiffening of the acoustic modes from pure metal to the hydride [this is the case for NbH_x (Ref. 7) and LaH_2 (Ref. 8)], or to a general lowering of the acoustic frequencies as observed between pure Pd and $PdH_{0.63}$.[9] The optical-phonon energies, on the other hand, depend on the nature of the occupied interstitial site (octahedral or tetrahedral). For compounds having essentially the same electronic structure, like all the rare-earth dihydrides, it is the metal-hydrogen distance which appears to control the position of the optical phonon.[10] The observation of low-energy optical-hydrogen phonon energies[9,11] in PdH is probably an important factor for the occurrence of a high value of λ in this system. But it is interesting to note that no superconductivity is reported for VH_x where the optical modes are as low in energy as in PdH when H occupies the octahedral sites. This could suggest that the electronic term η may be the determining factor in explaining the trends in T_c.

Another interesting feature of the hydrides is the possibility of varying the average electron-per-atom ratio either by alloying effects on the metallic matrix or by varying the concentration of hydrogen. Most hydrides exist, indeed, over a wide composition range, with a few stoichiometric compounds. Along this line, it is interesting to note the experimental data obtained by Robbins *et al.*[12] who investigated the superconducting properties of several transition-metal (TM) alloys charged with various concentrations of H.

In the present work we will discuss mainly stoichiometric monohydrides (with H in octahedral sites) and dihydrides (with H in tetrahedral sites), the structure of the underlying metallic host lattice being for all cases fcc. This encompasses a large number of existing mono- and dihydrides, some of which, like NbH_2, involve a change in the crystal structure of the metal-atom matrix from bcc in the pure metal to fcc in the dihydrides.

More precisely we will discuss the stable or nearly stable monohydrides of the end of the TM series such as PdH and NiH, as well as NbH, a nonstable monohydride which we studied because of the observed superconductivity[12] in some TM alloys charged with hydrogen where a change over from bcc to fcc symmetry seems to be favorable to superconductivity. We will then discuss the stable early-TM dihydrides of group IV- and V-like TiH_2, ZrH_2, NbH_2...; LaH_2 is also investigated as an example of a trivalent-metal dihydride. To simulate the effect of alloying we will use the rigid-band model since we will notice that the density of states of the metal *d* bands shows the same structure across a TM series. This procedure must be handled with care if one deals with the unstable dihydrides for which the antibonding H-H band crosses the Fermi level as one moves to the right of a series, making the rigid-band approximation very questionable. Finally, results concerning simple metal hydrides such as AlH_x ($x = 1$ and 2), which can be prepared by ion implantation,[13] will also be presented since rather high superconducting transition temperatures (T_c) up to 6.8 K are observed.

In Sec. II we discuss only briefly the method of calculation used, since it has been developed at length in previous work.[14,15] Section III is devoted to a classification of some systematic features of the band structure with an emphasis on those which are relevant to the calculation of η. Some of these features were already present in the earlier work of Switendick.[16] In Sec. IV we describe the trends in the variation of the phase shifts and the partial densities of states (DOS) which determine the electronic factor η. In Sec. V we discuss the values of η and λ and compare the electron-phonon coupling of the hydrides with the pure metals.

II. METHOD

The results presented below are obtained by means of augmented-plane-wave (APW) band-structure calculations performed at 89 $\vec{k}$ points in the $\frac{1}{48}$th irreducible wedge of the Brillouin zone (BZ). The DOS was accurately obtained in a 1-mRy mesh by means of the linear-energy tetrahedron scheme.[17]

Following the work of McMillan for transition metals,[6] an approximate expression of λ has been proposed for compounds with a large mass ratio between the constituent atoms[15,18]:

$$\lambda \simeq \frac{\eta_{\text{metal}}}{\mathfrak{M}_{\text{metal}}\langle\omega^2\rangle_{\text{acoustic}}} + \frac{\eta_{\text{H}}}{\mathfrak{M}_{\text{H}}\langle\omega^2\rangle_{\text{optic}}} = \lambda_M + \lambda_{\text{H}}\,, \tag{1}$$

where η is the "electronic" contribution, $\mathfrak{M}$ the atomic mass, and $\langle\omega^2\rangle$ the second moment of the renormalized phonon frequencies as defined by McMillan.[8] In Eq. (1), the so-called "interference" term[11] has been neglected. Using a simple model, it has been shown[11] that this term has a negligible effect on λ_{H} due to the large mass ratio between the metal and H, but it may affect more λ_M. Nevertheless, all the trends which we will discuss in relation with the band structure are expected to be essentially preserved. Using the rigid-ion approximation and expanding the Bloch functions into their angular momentum representation, Gaspari and Gyorffy[12] showed that the mean square of the electron-phonon matrix element $\langle I^2\rangle$ can be conveniently expressed in terms of quantities obtained from *ab initio* band-structure calculation. They have shown that

$$\eta \sim \sum_K \frac{E_F}{N_\uparrow(E_F)\Pi^2} \sum_l 2(l+1)\sin^2(\delta_{l+1}^K - \delta_l^K) \times \frac{n_l^K(E_F)\,n_{l+1}^K(E_F)}{n_l^{K^{(1)}}(E_F)\,n_{l+1}^{K^{(1)}}(E_F)}\,, \tag{2}$$

where the summation on K runs on all the atoms in the unit cell, δ_l^K is the single-site scatterer phase shift at the Fermi energy E_F, n_l^K the partial density of states of angular character l at the K site, $n_l^{K^{(1)}}$ is the corresponding partial DOS of a free scatterer, and $N_\uparrow(E_F)$ is the total DOS per spin at E_F.

III. BAND STRUCTURE OF HYDRIDES

A. Monohydrides

a. PdH; NiH. We will first consider the stable or nearly stable monohydrides of the end of the TM series, such as PdH and NiH. As illustrated in Fig. 1, the DOS is characterized as follows: (i) by the formation at low energy of metal-hydrogen bonding states. This is an expected feature since it has been long known that the metal-ligand interaction in other interstitial compounds such as carbides, nitrides, etc., leads to structures at low energies. The general position of the metal-hydro-

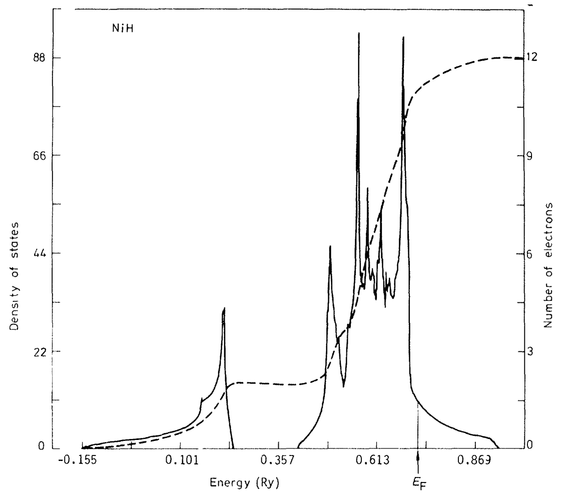

FIG. 1. The total density of states (DOS) of NiH (full line curve, left-hand-side scale) units are states of both spin per rydberg unit cell; the number of electrons (dashed line and right-hand-side scale).

gen induced states in the hydrides could be predicted by a simple model taking into account the atomic-level positions. (ii) By the filling of the pure-metal d-band holes, the Fermi energy of the monohydrides PdH and NiH being in the metal s-p band. The large decrease in the DOS at E_F from the pure metal to the hydride found in the calculation is in agreement with electronic specific-heat[19] and magnetic-susceptibility data.[20]

Less than one electron is nevertheless accommodated at the top of the metal d bands since a branch of metal p states in the [111] direction, previously empty in the pure metal, is drastically lowered by the H potential and forms in the hydride part of the low-lying metal–hydrogen bonding band.[21-23] This feature has important consequences for the electronic states at the Fermi level. This level is closer to the top of the d bands in PdH and NiH than it is in the corresponding noble metals Ag and Cu. The wave functions at the Fermi energy retain in PdH and NiH an important d character,[22] an effect which is more pronounced for NiH because the number of d holes is larger for pure Ni (0.6 holes) than for pure Pd (0.36 holes).

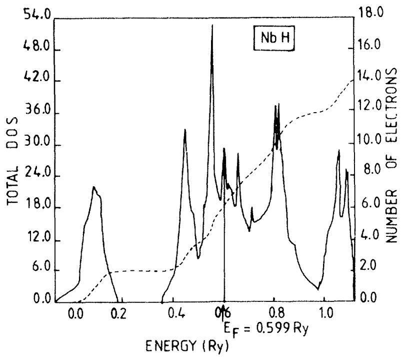

FIG. 2. The total DOS of NbH (full line curve, left-hand-side scale) units are states of both spin per rydberg unit cell; the number of electrons (dashed line and right-hand-side scale).

b. NbH. We will consider now the compound NbH, with the same NaCl structure as PdH and NiH. This compound is not stable within this structure, but the experimental data of Robbins *et al.*[12] suggest that such a symmetry occurs in some superconducting TM alloys based on Nb with the hydrogen probably occupying the octahedral sites. In order to simulate this situation as closely as possible, we calculated the DOS of NbH which is represented in Fig. 2. The overall band structure is essentially the same as for PdH with two differences: The Fermi level is now well inside the d bands and there appears a new metal-hydrogen antibonding band at the top of the d bands responsible for the structure observed at the high-energy side in Fig. 2 (this band exists also in PdH but is well above the top of the d band in that case). The similarity of the d bands of PdH and NbH suggests the possibility that a rigid-band model may be not too bad an approximation if one switches from one hydride to another hydride in the same TM series, a point which will be discussed in more detail below.

c. AlH. Since superconductivity with a fairly high value of $T_c = 6.8$ K was observed[13] in hydrogen-rich aluminum samples prepared by the ion implantation technique, we have also studied the mono- and dihydride of Al. Indeed, the stability of the octahedral versus tetrahedral occupancy of the hydrogen in the Al lattice has not yet fully been ruled out either by theoretical calculations[24] or by experimental investigations.[25] We thus studied the two possible phases. Our calculation for AlH shows the parabolic s-p bands of pure Al are drastically modified by the metal-hydrogen interaction; the DOS of AlH is shown in Fig. 3. We obtain, as discussed previously for the rocksalt-structure monohydrides, a metal hydrogen bonding band at low energy. Three bands cut the Fermi level. The lowest one, which contains the majority of the two electrons to be accommodated, has a strong admixture of H s states.[26] Indeed, at the BZ center, the corresponding state is an antibonding combination of metal and H s states. The large hybridization with H s states at E_F is a new feature of the simple metal hydrides. Such hybridization is not observed in the TM hydrides. This H s character of the states at E_F has important consequences on the value of the electron–optical-pho-

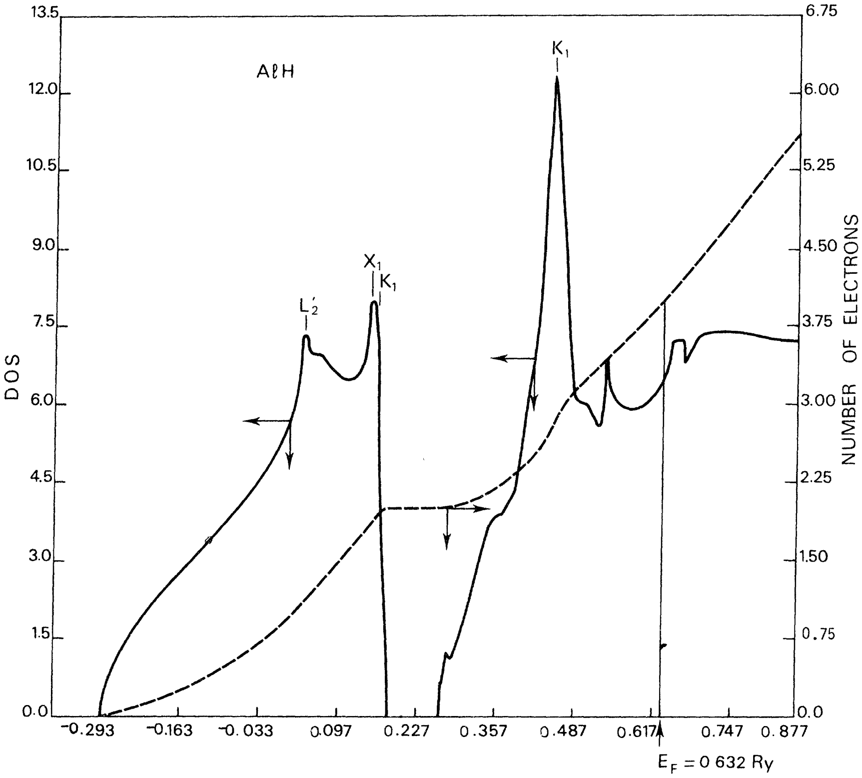

FIG. 3. The total DOS of AlH (full line curve, left-hand-side scale) units are states of both spin per rydberg unit cell; the number of electrons (dashed line and right-hand-side scale).

non coupling, as we shall discuss in the next sections.

B. TM, rare-earth, and simple metal dihydrides

a. TM and La dihydrides. As illustrated in Figs. 4 and 5, the DOS of the cubic CaF_2 structure dihydrides is characterized by a structure at low energy which is due to two bands: a metal-hydrogen bonding band, already found in the case of monohydrides and, in addition, a second band which at the Brillouin-zone (BZ) center is formed

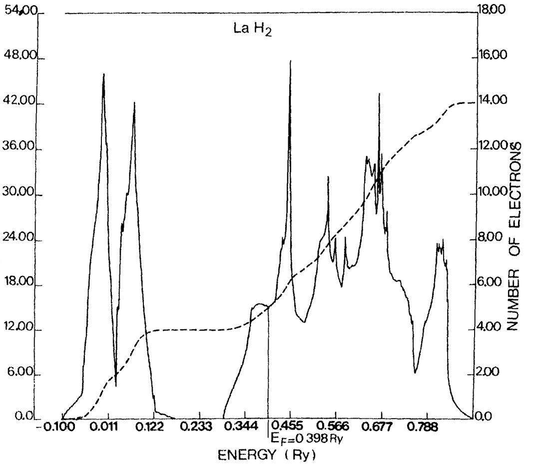

FIG. 4. The total DOS of LaH_2 (full line curve, left-hand-side scale) units are states of both spin per rydberg unit cell; the number of electrons (dashed line and right-hand-side scale).

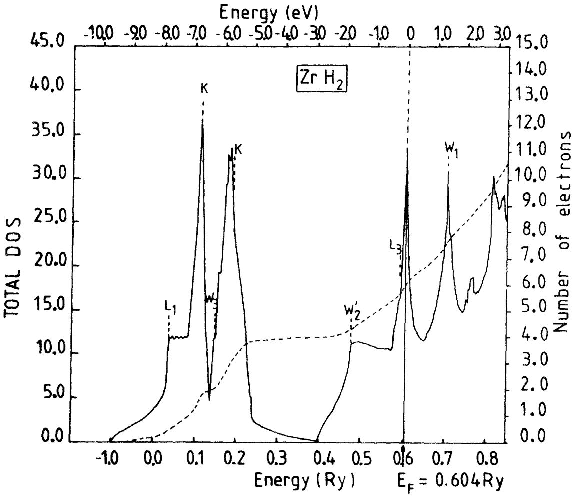

FIG. 5. The total DOS of ZrH_2 (full line curve, left-hand-side scale) units are states of both spin per rydberg unit cell; the number of electrons (dashed line and right-hand-side scale).

of hydrogen antibonding states. In the stable dihydrides of the early members of the TM series, this second band is always observed below E_F.[27-30] However, its position relative to the metal *d* bands is sensitive to the position of the metal atom in the Periodic Table and to the H-H distance through the lattice constant of the hydride. Thus in the lanthanide, dihydrides which have large lattice constants, the low-lying bands do not overlap the metal *d* bands located at higher energies.[29] Figure 5 shows that in the case of ZrH_2 an overlap is obtained.

For the transition metals of the end of the series, such as Ni and Pd, the dihydrides do not form. Switendick has shown[21] that in PdH_2, assuming a lattice constant equal to that of pure Pd, the antibonding H-H band is much above the top of the metal *d* bands; this feature is not favorable to the stability of the compound. Switendick proposed an empirical criterion for the stability of the dihydrides in the TM 3*d* and 4*d* series which is based upon the H-H distance (the critical distance proposed being ~2.1 Å). Our calculations show that this criterion is not sufficient. Indeed, the antibonding H-H band in PdH_2 does not fall below the metal *d* bands even when large H-H distances are used. This indicates, as we will show elsewhere,[31] that the distance is not a unique determining stability factor.

The position of this antibonding band relative to E_F which controls the stability of the dihydride, controls also the hydrogen *s* character of the states at the Fermi level, which may be important in determining the value of the electron–optical-phonon coupling constant. For the stable dihydrides of the early TM series, such as TiH_2, ZrH_2, and NbH_2, the two low-lying metal-hydrogen induced bands are filled and, respectively, one, two, and three electrons occupy the bottom of the metal *d* bands for the group III, IV, and V dihydrides.

We wish to caution the reader at this point that, although in these compounds the metal *d* bands appear to have been depopulated in favor of the two low-lying bands, this feature should by no means be understood in a rigid-band-model sense since we have shown with emphasis the considerable deformation of the low-lying portion of the metal *d* states upon dihydride formation, a large portion of the metal *d* states being found at lower energies, in the metal-hydrogen-induced bands. The large hybridization with metal states of the low-energy structures appears clearly in the partial DOS analysis of Figs. 6 and 7.

b. AlH_2. In addition to the low-lying metal-hydrogen bonding band found in Al-H, the interaction of the two H atoms leads to a second band at low energy. The two bands are filled and the Fermi level falls in the metal *s*-*p* band which is also hybridized with H *s* states but to a lesser extent than in the case of the monohydride.

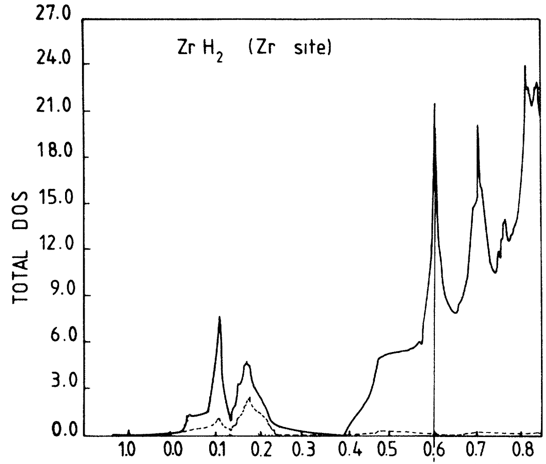

FIG. 6. The angular momentum DOS analysis of ZrH_2 and n_l inside the Zr muffin-tin sphere; $l = 0$ (dotted curve), $l = 1$ (dashed curve), and $l = 2$ (full curve) contribution. Units are states of both spin per rydberg unit cell.

C. Rigid-band model applied to hydrides

An interesting feature of the electronic structure of the stable dihydrides is the similarity in the shape of the DOS of the metal *d* states, a point which we noticed also for PdH and NbH. As shown in Figs. 4 and 5, the metal *d* DOS of LaH_2 and ZrH_2

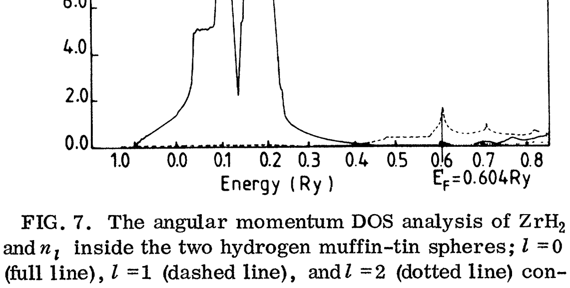

FIG. 7. The angular momentum DOS analysis of ZrH_2 and n_l inside the two hydrogen muffin-tin spheres; $l = 0$ (full line), $l = 1$ (dashed line), and $l = 2$ (dotted line) contributions. Units are states of both spin per rydberg unit cell.

consistently present the same structure. Thus, with the filling of the d bands by 1 electron (for trivalent-metal dihydrides such as YH_2, ScH_2, and LaH_2), the Fermi level falls at the bottom of the d states in a shoulder of the DOS where the DOS is rather low. For group-IV dihydrides such as TiH_2, and ZrH_2, the Fermi level falls in a sharp peak of the DOS (Ref. 28), as also found by a rigid shift of the Fermi level from the DOS of LaH_2 (Ref. 29) or NbH_2. This feature plays an important role in the cubic-to-tetragonal distortion consistently observed in the group-IV dihydrides. For the group-V dihydrides such as NbH_2, the Fermi level falls near the next valley in the DOS. Thus, in spite of the difference in the width of the metal d states, the main characteristic of the position of the Fermi level can be predicted by a rigid-band model applied to the d bands of another dihydride crystallizing within the same structure. In contrast, the position and width of the low-lying metal-hydrogen-induced states shows a large sensitivity to the compound under study.

It seems thus reasonable to apply the rigid-band model in order to simulate the effect of metal alloying on the mono and dihydrides. We caution the reader, however, that this model is good if limited to alloying on the metal lattice of the hydride. This model cannot be applied to simulate the variation of the H-to-metal ratio except perhaps in the very near vicinity of the full stoichiometry. This later limitation of the rigid-band model is due to the peculiar role played by the hydrogen atoms, namely, in the lowering of states previously empty in the pure metal and in the deformation of the d band. The effect of metal-atom alloying on a dihydride should also be limited to the stable hydrides because, for the unstable dihydrides to the right of molybdenum, one expects the antibonding H-H band to cross the Fermi level, a feature which should result in drastic changes in the character of the states at E_F.

IV. TRENDS CONCERNING PHASE SHIFTS AND PARTIAL DENSITIES OF STATES

The value of the electronic term η is determined by the phase shifts δ_l and the partial density of states n_l taken at the Fermi energy, as shown by Eq. (2). In order to get a better insight concerning the variation of η, we will try to derive some systematic features governing δ_l and n_l as a function of the nature of the site involved (metallic M or hydrogen H), the filling of the d band, and the position of the M-H and H-H bonding and antibonding states compared to E_F.

A. Phase shifts

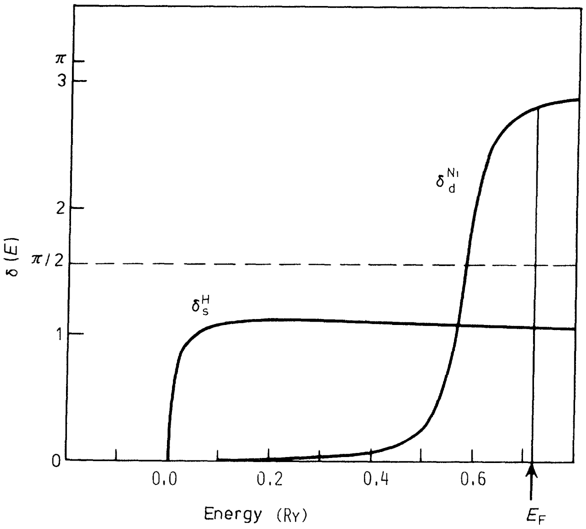

FIG. 8. The d-phase shift of the Ni potential and the s-phase shift of the H potential in NiH as a function of energy. Phase shifts are in radians.

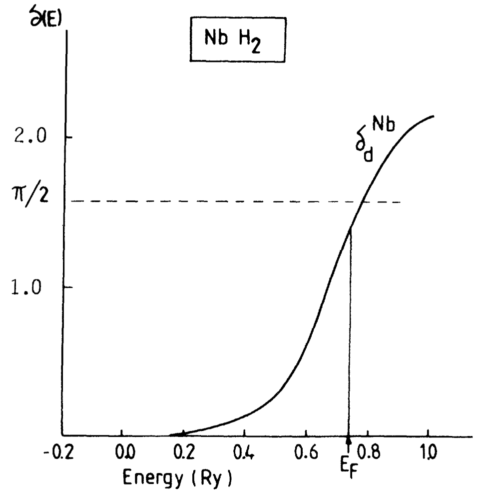

FIG. 9. The d-phase shift of the Nb potential in NbH_2 as a function of energy. Phase shifts are in radians.

a. Metallic site. For the TM hydrides, the s and p phase shifts at the metal site at E_F are negative. This indicates a repulsive character of the metal potential for the s and p waves due to the orthogonalization conditions to the corresponding core states. The d-phase shifts at E_F are positive and they increase with the filling of the metal d bands. Thus δ_2^{metal} is small for the hydrides whose Fermi energy falls at the bottom of the metal d bands (like LaH_2), it increases and reaches a resonance, $\delta_2^{metal} \sim \pi/2$ in the middle of the d bands; it is large and close to the value of π for the hydrides with filled d bands. Typical energy dependence of δ_2^M in hydrides is illustrated by the plots of the d-phase shifts as a function of energy for Ni in NiH and Nb in NbH_2 given in Figs. 8 and 9. These plots also show the differences in sharpness of the resonance, which is related to the width of the d bands. The resonance of the $3d$ metal is narrow compared to the much wider resonance of the $4d$ TM hydrides. Since the value of the d-phase shift at E_F varies considerably with the filling of the d bands, we expect the relative importance of the p-d and d-f scattering mechanisms, and thus the value of η_M given by Eq. (2), to vary considerably in a series.

In contrast to the TM hydrides, only the s and p phase shifts at the Al site are large at E_F. Nevertheless, the s-p scattering term will be small at the metal site due to a near cancellation of the phase-shift-dependent term in Eq. (2). The d-phase shift is, as expected, small for simple metal hydrides.

b. Hydrogen site. The hydrogen potential strongly scatters the s waves so that the $s(l=0)$ scattering phase shift δ_0^H is large at the Fermi energy for all the metal hydrides; δ_0^H is always close to a resonance $\delta_0^H \sim \pi/2$. Figure 8 shows a typical plot of δ_0^H in NiH as a function of energy. In the energy range spanned by the metal d bands, the δ_0^H phase shift remains large and is a very slowly varying function of energy; the same behavior is observed for dihydrides. This indicates that all metal hydrides of the beginning as well as of the middle and of the end of the series will have large values of δ_0, no matter where the Fermi energy lies in the metal d bands. All other phase shifts of higher angular momentum are very small. Very similar results hold also for the simple-metal hydrides like AlH and AlH_2.

B. Partial densities of states and scattering mechanism

The angular momentum representation of the Bloch waves leads to the introduction of partial DOS n_l of given angular momentum l and to the appearance of different contributions to the scattering of the electrons. We will try now to explain the physical origin and meaning of these partial DOS and to derive the main contribution to the total scattering.

a. Metal site. For the TM hydrides the density of states at E_F is dominated, of course, by the $l=2$ term and this is true even for the full band monohydrides like PdH and NiH because of the proximity of the Fermi level to the top of the d band.[22] Thus, one expects the p-d and d-f scattering mechanism to be dominant. This is indeed the case for both PdH and NiH. More than 80% of the value of η_{metal} is provided by the d-f scattering mechanism. We wish to remind the reader at this point that in the angular momentum representation used here, the d-f scattering should not be considered as an intra-atomic effect since the partial DOS of f type at a given metal site is provided by the tails of the metal d functions of the neighboring sites. Thus, the physical origin of this term should rather be understood in terms of a metal d-d interaction in a tight-binding picture.[32]

For the early TM dihydrides and for LaH_2, we find that, although the d-f scattering mechanism gives an important contribution to η_M, it is the p-d scattering term which dominates. This is due mainly to the variation of the d-phase shift δ_2 at E_F with the filling of the d band. As an example, in LaH_2 60% of the contribution of η_{La} arises from the p-d scattering term and 37% from the d-f contribution. Similar importance of the p-d scattering term has been obtained in the pure La metal[33] where it represents 58% of the total η_{La}.

For simple-metal hydrides like AlH_x both s and p densities of states are important at E_F, but in spite of this it is the $p \rightarrow d$ scattering term which provides ~80% of η_M in AlH and AlH_2: this is due to the near cancellation of the s and p phase shifts in Eq. (2). The origin of the d density of states is again related to the tails of the wave functions coming from neighboring atoms.

b. H site. The value of η_H is dominated here by the s-p scattering mechanism, and its variation across a series of metal hydrides is controlled by the magnitude of the partial s and p DOS at E_F. n_s is found to be sizable for the TM hydrides at the end of the series,[22] especially for PdH. The Fermi level is not high enough to fall in the antibonding hydrogen-metal band, nevertheless in this energy range some metal p (and to a lesser extent, some metal s) states, of s symmetry at the H site, have been lowered by the H potential but not enough to fall below the d band. The value of n_s increases with increasing energies if one applies the rigid-band model to PdH or NiH, and this may explain the initial increase of T_c in the Pd-noble-metal-H_x system.[34] The p-type DOS at the H site is, on the other hand, small.

For the early-TM dihydrides one has just the contrary. The s-type DOS at E_F is vanishingly small because all states with s-type symmetry are pushed down below the d band in the hydrogen-metal and hydrogen-hydrogen bands but there is a non-negligible p-type DOS arising from the metal d states having a p symmetry at the H site and which is not much perturbed by the H potential. Nevertheless, η_H remains small for most of these dihydrides.

Of course, if the antibonding H-H band crosses the Fermi level, one expects very sizable s-type DOS at the H site which may considerably increase η_H. This may be the case for all unstable dihydrides to the right of Nb, beginning with MoH_2.

TABLE I. The partial-wave analysis n_l of the DOS inside the muffin-tin metal and hydrogen spheres at the Fermi energy. $N_\uparrow(E_F)$ is the total DOS at E_F.

		n_s	n_p	n_d	n_f	$N_\uparrow(E_F)$
AlH	Al	0.621	0.757	0.217	0.037	3.203
	H	0.325	0.168	0.011	0.000_5	
AlH_2	Al	0.684	0.520	0.124	0.016	3.155
	1 ×H	0.073	0.107	0.005	0.000_3	
LaH_2	La	0.017	0.168	3.250	0.014	7.550
	1 ×H	0.017	0.154	0.0168	0.000_7	
TiH_2	Ti	0.0015	0.0590	18.7405	0.035	23.519
	1 ×H	0.015	0.8755	0.0535	0.0015	
ZrH_2	Zr	0.004	0.073	10.805	0.035	16.460
	1 ×H	0.008	0.432	0.021	0.000_8	
NbH_2	Nb	0.004	0.051	4.369	0.034	6.440
	1 ×H	0.016	0.119	0.010	0.001_2	
NbH	Nb	0.0925	0.3555	9.3800	0.066	12.425
	H	0.0202	0.3049	0.0283	0.004	
NbH_0	Nb	0.337	1.464	11.405	0.1652	15.41
PdH	Pd	0.058	0.163	2.618	0.012	3.405
	1 ×H	0.255	0.029	0.001_6	0.001	
NiH	Ni	0.048	0.133	4.741	0.009	5.390
	H	0.161	0.035	0.002_5	0.001	

One should, along this line, keep in mind that such unstable dihydrides could eventually be prepared either by very high pressure or by the ion implantation technique. It is also necessary at this stage to remember that large η_H does not mean always large λ_H, the absolute value of the phonon energies ω_H being of importance in determining the value of λ_H. For the simple-metal hydrides, in contrast to the early-TM and RE hydrides, the value of the H s DOS is rather large. This is due to a larger hybridization of the s-p metal states with the H s states. In the case of AlH the presence of a metal-hydrogen antibonding band at E_F is responsible for the large value of n_s^H which may lead to an enhancement of the electron-optical phonon coupling.

V. DISCUSSION OF THE VALUES OF η AND λ

The values of the phase shifts, partial DOS as well as the values of η, $\mathfrak{M}\langle\omega^2\rangle$, and λ, are gathered together in Tables I and II. We will now discuss mainly the resulting values of η and λ for the different classes of hydrides considered and compare them with their values in the pure metal.

TABLE II. Values of the various parameters entering the calculation of λ. Symbols are defined in Eqs. (1) and (2). The angular-momentum-dependent phase shifts δ_l are given in radians.

		δ_0	δ_1	δ_2	δ_3	η (eV/Å^2)	$\mathfrak{M}\langle\omega^2\rangle$ (eV/Å^2)	λ
AlH	Al	0.3365	0.4014	0.0528	0.0015	0.294		
	H	1.1856	0.0404	0.0012	0.0	2.292		
AlH_2	Al	0.2536	0.3714	0.0556	0.0018	0.224		
	1 ×H	1.1738	0.0379	0.0010	0.0	0.744		
LaH_2	La	−1.1006	−0.4556	0.5326	0.0006	0.753	7.35	0.103
	1 ×H	1.5290	0.0400	0.009	0.0	0.043	3.35	0.013
TiH_2	Ti	−0.7913	−0.2262	0.3156	0.0016	3.898		
	1 ×H	1.2502	0.0374	0.0009	0.0	0.067		
ZrH_2	Zr	−0.9504	−0.3662	0.9042	0.0049	2.352 (3.87)[a]	6.24	0.377
	1 ×H	1.2462	0.0373	0.0009	0.0	0.088	4.92	0.018
NbH_2	Nb	−1.0219	−0.4075	1.3749	0.0067	2.975 (7.39)[a]		
	1 ×H	1.1593	0.0408	0.0011	0.0	0.102		
NbH	Nb	−0.8077	−0.2852	1.3732	0.0054	2.855		
	H	1.2413	0.0405	0.0012	0.0	0.0898		
NbH_0	Nb	−0.5105	−0.1402	1.3396	0.0032	3.6848		
PdH	Pd	−0.5115	−0.1094	2.8066	0.0030	0.886	5.971	0.15
	H	1.1931	0.0280	0.0006	0.0	0.641	1.062	0.60
NiH	Ni	−0.3857	−0.0235	2.7916	0.0025	0.810	10.0	0.08
	H	1.0604	0.0318	0.0008	0.0	0.275	3.44	0.08

[a] Theoretical values obtained by Butler (Ref. 35) for the corresponding transition metals.

A. The monohydrides PdH and NiH

Pure Ni which is ferromagnetic, and pure Pd, probably because of magnetic fluctuations, are not superconducting. But η_M and λ_M have been calculated in Pd by methods similar to ours[35,36] and it appears that η_M is at least a factor of two smaller than that of the pure metal. This decrease results from the drastic change in the Fermi-level position which no longer falls below the top of the d bands in a region of high DOS, but rather in the metal s-p band. The lattice expansion and the increased localization of the d orbitals at the end of a TM series contribute also to a decrease of the d-d interaction at neighboring sites and lead to a small value of η_M. A lowering of the acoustic-phonon frequencies[10] by about 20% from pure Pd to $PdD_{0.63}$ has been observed. This decrease of the denominator of Eq. (1) is not sufficient to compensate for the small value of η_M in PdH. We thus obtain small values for the electron-acoustic phonon coupling in the two compounds as shown in Table II. For PdH the value of $M_{Pd}\langle\omega^2\rangle_{\text{acoustic}}$ listed in this table has been obtained from the experimental phonon DOS of Rowe *et al.*[7] Since similar data are not available for NiH, we have used the approximation $\mathfrak{M}\langle\omega^2\rangle \simeq \frac{1}{2}\mathfrak{M}\Theta_D^2$ with $\Theta_D = 366$ K.[37]

Although the Debye temperature Θ_D does not provide an entirely reliable value of the average phonon frequency, we used this estimate whenever neutron scattering data were not available. The small values of λ_M obtained for both PdH and NiH show that superconductivity in these hydrides cannot be due to the electron-acoustic phonon coupling.

One has thus to invoke the value of λ_H in order to explain the superconductivity of PdH. Indeed, superconducting tunneling experiments,[38] and normal-state phonon resistivities[39] reveal a coupling of electrons to the optical phonons. In Table II, we see that η_H is indeed nearly as large as η_M. The absolute value of λ_H is in fact large enough to explain the occurrence of superconductivity in PdH. It appears thus that the decisive factors for superconductivity are twofold: an appreciable s-type Fermi-level DOS n_0 at the H site, and a low value of the optical phonon energy.[9] Both circumstances are less favorable in the case of NiH. The Fermi level is closer to the top of the d band,[22] thus decreasing n_0, and from the experimental resistivity data[37] it follows also that the phonon energies are more than two times larger in NiH than in PdH in relation probably with the smaller lattice parameter of NiH. It is probable also that the sensitivity of T_c in PdH_x to deviation from stoichiometry ($x < 1$) and to the alloying with noble metals is also in close relation with the two factors mentioned.

B. NbH_0 and NbH

In order to understand the origin of the disappearance of superconductivity between bcc Nb and the hydrides of Nb having an fcc metal lattice, we calculated η for pure Nb assuming an fcc phase which we will call hereafter NbH_0 since it corresponds to the NbH_2 lattice where the H atoms have been removed. The results are summarized in Tables I and II. We obtained a strong reduction of η_M as one goes from the bcc to the fcc structure, in spite of the fact that the total DOS at E_F varies the other way. This reduction can be ascribed, in fact, to the lattice expansion effect (we assumed the same lattice constant for fcc Nb and NbH_2) which leads to an increase of the Nb-Nb nearest-neighbor distance from 5.369 a.u. in the bcc phase to 6.088 a.u. in the fcc phase, and thus reduces the strength of the d-d interaction, and to the structural change itself which induces a different orientational dependence of the interacting lobes of the neighboring d orbitals. A further decrease of η_M is observed as one goes from fcc Nb to NbH which is due to the change in electronic structure induced by the formation of the monohydride, namely the deformation of the metal d band and the change in the position of the Fermi-level position due to the additional electron in the unit cell. The value of η_H is also very small, an effect due to the very small value of the s-type density of states at the H site. Nothing is known, of course, concerning the phonon modes of fcc Nb and of NbH, but one would need a rather large softening of the acoustical phonons in order to compensate for the decrease of η_M as one goes from bcc Nb to fcc Nb and NbH. The available neutron scattering data indicate rather a hardening of the acoustical phonons in bcc hydrides[7] compared to bcc Nb. All this put together points towards the conclusion that fcc Nb and NbH are probably not good candidates for superconductivity.

C. Dihydrides

We will first discuss the case of LaH_2, a hydride which is not superconducting[4] above 1 K. As shown in Table II, the value of η_{La} in LaH_2 is 0.753 eV/Å^2. This value is much smaller than that obtained for the pure fcc metal $\eta_{La} = 2.62$ ev/Å^2 using similar approximations.[33] It is also smaller than η_{metal} in trivalent pure metals like Y and Sc.[35] The decrease of η_{La} from the pure metal to the dihydride is due to the following: (i) the reduction of the DOS at E_F from 13.74 states/per rydberg spin unit cell to 7.55 states/per rydberg spin unit cell. We have previously emphasized the deformation of the lower portion of the metal d band and its apparent depopulation in favor of low-lying metal-hydrogen states in the dihydrides. (ii) The 6.7% increase in the lattice constant which leads to a decrease in the width of the *d* bands and thus to a change in the metal *d-d* interaction. A similar effect is observed in the pure metal since η_{La} increases under pressure. (iii) The low value of δ_2, the Fermi level being to the left of the *d* resonance.

The drastic decrease in η_{La} from the pure metal to the dihydride is further accompanied by a hardening of the frequencies of the acoustic phonons. Inelastic neutron scattering data are not available for LaH_2, nevertheless, the low-temperature specific-heat data show a large increase in the Debye temperature from 140 K in pure La (Ref. 40) to $\Theta_D = 243$ K in $LaH_{2.03}$.[41] To give an estimate of the phonon contribution at the La site we used the approximate value $\mathfrak{M}_{La}\langle\omega^2\rangle_{La} \simeq \frac{1}{2}\mathfrak{M}_{La}\Theta_D^2$. With this estimate, we obtain a very small value of $\lambda_{La} = 0.103$ compared to $\lambda_{La} = 1.42$ in the pure metal.[33] Thus, our results show that the change in the electronic structure upon dihydride formation leads to a small electron acoustic-phonon coupling which is not favorable to superconductivity in LaH_2.

An interesting problem is the nonoccurrence of superconductivity above 1 K in the early group-IV and group-V dihydrides[42,3] TiH_2, ZrH_2, VH_2, and NbH_2. Concerning TiH_2 and ZrH_2, we obtain larger values of the DOS in the dihydrides than in the pure metals,[35,36] nevertheless the values of η_M in the dihydrides are smaller. For NbH_2, we have approximately the same value of η_M as for ZrH_2 in spite of the fact that the total DOS is now much smaller. This again shows that the values of η_M do not follow the values of the DOS, a result which we found also for the monohydrides. In fact, η depends rather sensitively upon the detailed characteristics of the states at E_F which can be related to the bonding or antibonding nature of the eigenfunctions at E_F and to the Fermi-surface anisotropies, as shown recently by Varma *et al.*[43] for transition metals. Not much is known on the acoustic-phonon modes in these dihydrides, but if one admits in a first approximation that they do not change much, one ends up with a small value of λ_M. On the other hand, η_H is very small compared to η_H in PdH, for instance, while the optical-phonon energies are much higher (≃50 MeV in Pd and ≃140 MeV in NbH_2) so that λ_H becomes small.

From this we may conclude that all these early

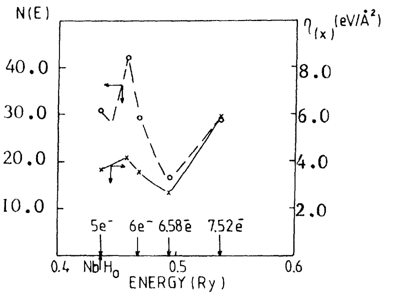

FIG. 10. The electronic contribution η at the metal site in MH_0 [(x) and full line, right-hand-side scale]. The total DOS [(o) and dashed line, left-hand-side scale] units are states of both spin per rydberg unit cell. The number of electrons is indicated by the arrows on the horizontal scale.

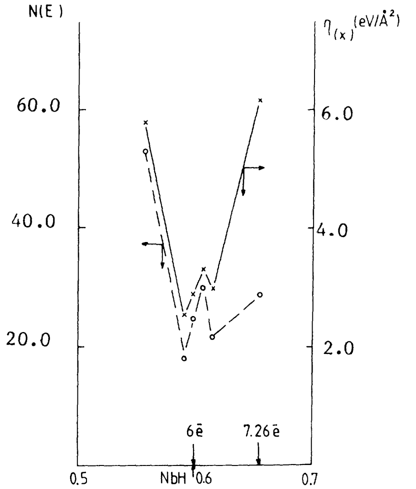

FIG. 11. The electronic contribution η at the metal site in MH [(x) and full line, right-hand-side scale]. The total DOS [(o) and dashed line, left-hand-side scale] units are states of both spin per rydberg unit cell. The number of electrons is indicated by the arrows on the horizontal scale.

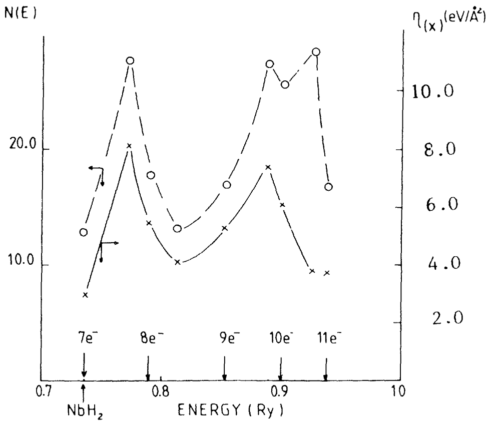

FIG. 12. The electronic contribution η at the metal site in MH_2 [(x) and full line, right-hand side scale]. The total DOS [(o) and dashed line, left-hand-side scale] units are states of both spin per rydberg unit cell. The number of electrons is indicated by the arrows on the horizontal scale.

dihydrides are not superconducting. One can thus wonder if the low values obtained for η_M are not in some way accidental because we are making overly large steps in the electron-to-atom ratio as one goes from one hydride to the other. As we have shown, on the other hand, that inside a hydride family it is rather well justified to use the rigid-band model, we will present also data on η_M for some TM alloys hydrided to the desired H-to-metal ratio.

D. Hydrides of TM alloys and the rigid-band model

We are also motivated along this line by the results of Robbins *et al.*,[12] who investigated several hydrides based on alloys such as Nb-Pd, Nb-Pd-Mo, and Nb-Ru. Their x-ray diffraction studies showed the existence of a fcc phase for alloys with e/at.>5.8. A sizable value of $T_c \sim 5.5$ K was reached for alloys such as $Nb_{0.8}Ru_{0.2}H_{0.5}$. In Figs. 10 to 12 we show the variation of η_M for the fcc pure metals and for the mono and dihydrides as a function of e/at. Indeed, we see that η_M does not vary in a monotonous way and shows peak which do not necessarily scale with the DOS factor. This result clearly indicates that it is interesting to look for superconductivity more carefully.

For the dihydrides our results include data well to the right of Nb and Mo and these results must be taken with caution because we have admitted that the H-H antibonding band remains below the d band as is the case for NbH_2. A proper calculation would probably indicate that this band sweeps through the d band as one goes to the right of a series. Indeed, in PdH_2 this band is well above the d band. This has two consequences: First, the d band will be deformed and second there will be an appreciable value of η_H because of a much larger value of the s-type density of states at the H site. This may be a favorable circumstance for superconductivity in dihydrides if the optical phonons are not too high.

E. Simple metal hydrides like AlH and AlH_2

Here we find for both hydrides a reduction of η_{Al} compared to the pure metal.[36] It should be mentioned that it is generally admitted that the rigid muffin-tin approximation is not expected to be as good as in TM metals. Nevertheless, the decrease in η_{Al} from the pure metal to the hydrides is meaningful since the same model has been consistently used in all cases. This decrease suggests that the metal lattice may not be responsible for the increase in T_c. Tunneling data[44] indicate that the acoustical phonons are not changed in a first approximation. Our calculation leads to large values of η_H (see Table II) and suggests that, in this case, there may be a contribution from the electron-optical-phonon coupling. The large value of η_H is due to the large hybridization of the metal states with H s states which results in an appreciable s- and p-type DOS at the H site and at the Fermi level. This is particularly the case for AlH as we can see from the results listed in Tables I and II. Unfortunately, no information on the optical phonons are yet available in the hydrides so that it is impossible to draw a further conclusion. Nevertheless one must be reminded that simple-metal hydrides may be good candidates for superconductivity.

VI. CONCLUSIONS

From the results obtained in the present work, we find that the values of the electronic parameter η_H are sizable for transition-metal hydrides with filled d bands, especially when the Fermi energy is not too close to the top of the d bands. η_H is especially large for simple-metal hydrides. These compounds appear to be particularly favorable for a large electron-optical-phonon coupling, provided that the energies of the optic phonons, which are not known experimentally, are not too high. The dihydrides of the beginning of the series and LaH_2 have small values of η_H. The values of η_H increase for the TM dihydrides of the middle of the series but remain small. Moreover, for these compounds, the energies of the optic phonons are high and this leads to small values of the electron-optical-phonon coupling. For the hydrides of Nb-based alloys, with a H-octahedral occupancy for which there is experimental evidence of low optic phonons, we also obtained small values of η_H. Thus, except for hydrides with filled d bands and their alloys, and possibly for the simple-metal hydrides, the electron-optical-phonon coupling is not expected to lead to high values of T_c. We should nevertheless mention that η_H is expected to be high for unstable dihydrides of the middle or the end of the TM series, since in this case the antibonding H-H band cuts E_F and gives a large density of H s states at the Fermi level. For these compounds, which could eventually be obtained by the ion implantation technique, one could expect sizable values of T_c provided that the optic-mode frequencies are not too high.

At the metal site, we obtained in most cases a sizable decrease of the electronic parameter from its value in the pure metal. This decrease is not compensated by a sufficient softening of the acoustic modes in most of the hydrides for which experimental data are available, and thus the electron-acoustic-phonon-coupling mechanism does not lead to superconductivity in these compounds.

Our simulation of the effect of alloying for Nb-based alloys shows, nevertheless, that sizable values of η_{metal} can be reached. The lack of data on the energies of the acoustic phonons of these alloys precludes further speculation on the values of T_c.

The theoretical results obtained here are in satisfactory agreement with available experimental results on the search of superconductivity in metal hydrides.[44] We have shown that the difference in the electron–optical-phonon coupling between PdH and NiH explains the experimental data of McLachlan *et al.*[37] who did not observe superconductivity down to 1 K in NiH. We have shown that the superconductivity of the high-T_c metals of group V such as Nb, and the superconductivity of La disappear upon formation of a dihydride, in agreement with the data of Satterthwaite and Peterson.[3] This is due to a large decrease of the electronic contribution at the metal site and a hardening of the acoustic mode. This decrease of λ_{metal} is not compensated by the contribution from the electron–optical-phonon coupling since we found this term to be small for these dihydrides. In agreement with the experimental data of Matthias *et al.*[42] we did not find the group-IV dihydrides TiH_2 and ZrH_2 to be superconducting. Recently an increase of the T_c of pure Zr ($T_c = 0.7$ K) has been reported by Stritzker[45] after implantation of small concentration of H and D at low temperature with values of $T_c = 3.14$ K for H and 4.65 K for D. Nevertheless, this experimental result is not in contradiction either with Matthias *et al.*'s data or with the present theoretical results since it concerns disordered dilute hcp structures where the changes in the electronic structure are expected to be drastically different from those obtained upon formation of a stoichiometric hydride. Finally, our results on the simple-metal hydrides such as the hydrogen-implanted Al samples can provide an explanation for the increase in T_c in these compounds.[13]

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