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Electronic structure and electron-phonon interaction in aluminium hydrides

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Résumé. — Après implantation d'une forte dose d'hydrogène dans des échantillons d'aluminium, Lamoise *et al.* ont obtenu un accroissement de la température critique de passage à l'état supraconducteur. Puisque les observations expérimentales indiquent la possibilité d'un ordre de l'hydrogène, nous avons étudié la modification de la structure électronique et de l'interaction électron-phonon de Al pur par formation de AlH et AlH₂. A cet effet, le paramètre électronique η défini par McMillan a été obtenu à partir de nos résultats APW de structure de bande, en utilisant le modèle de Gaspari-Gyorffy. Les bandes s-p du métal sont fortement affectées par l'interaction métal-hydrogène. Pour le mono- et le dihydrure, nous trouvons à basse énergie une bande d'états liants métal-hydrogène ; de plus, pour le dihydrure, une bande antiliante due à l'interaction hydrogène-hydrogène apparaît en-dessous du niveau de Fermi E_F . Les deux hydrures sont métalliques ; leur densité d'états à E_F est de l'ordre de 25 % plus élevée que celle du métal pur. Les principaux résultats obtenus pour η peuvent être résumés comme suit : alors qu'au site de l'aluminium, pour le mono- et le dihydrure, η_{Al} décroît de 50 % à partir de sa valeur pour le métal pur, nous obtenons des valeurs élevées de η_H , plus fortes que celle de η_H dans PdH. Ceci est essentiellement dû à la valeur des densités d'état de symétrie s et p au site de l'hydrogène et fait de ces hydrures des métaux simples, de bons candidats à la supraconductivité.

Abstract. — The superconducting transition temperature of high dose H implanted Al samples has been found by Lamoise *et al.*, to be higher than that of pure Al. Since experimental observations indicate the possibility of H ordering, we have studied the changes in the electronic structure and the electron-phonon interaction of pure Al upon formation of AlH and AlH₂. For this purpose, the McMillan parameter η was determined from our augmented plane wave band structure results, using the Gaspari-Gyorffy model. The metal s-p bands are rather strongly affected by the metal hydrogen interaction. For both the mono- and the dihydride, a metal-hydrogen bonding band is found at the low energy side ; in addition, a hydrogen-hydrogen antibonding band appears in the dihydride, below the Fermi energy E_F . Both hydrides are metallic ; their density of states at E_F is of the order of 25 % higher than in the pure metal. The essential results obtained for η can be summarized as follows : while at the Al site, for both the mono- and the dihydride, η_{Al} decreases by about 50 % from its value in the pure metal, the values of η_H are found to be large, even larger than those of η_H in PdH ; this feature which can be essentially ascribed to the magnitude of the partial s and p densities of states at the H site makes these simple metal hydrides good candidates for superconductivity.

1. **Introduction.** — The ion implantation technique can be used to load aluminium samples with hydrogen. An enhancement of the superconducting transition temperature of Al over its bulk value $T_c = 1.2$ K has been observed by Lamoise *et al.* [1] at Orsay after ion implantation of H and D at low temperatures into Al thin films. A maximum value of $T_c = 6.75$ K was reached for high hydrogen concentrations in Al samples. Resistivity annealing results [2] of Al after high dose H implantation suggested that H ordering or a phase transformation occurs. Since high dose

implantation of hydrogen into palladium is known to lead to high values of T_c ($T_c^{\max} \simeq 8.8$ K) [3], it could be speculated that the high value of T_c in the Pd-H and Al-H systems has a common origin. In the case of the Pd-H system, it is now established from theoretical models [4-6] and experimental observation [7-9] that the electron-optical phonon coupling is responsible for the high value of T_c . Alternative explanations for the rise in T_c in H-implanted Al should also be considered since Lamoise *et al.* [1, 10] have also observed an increase in the T_c of Al by

implantation of heavier ions such as He, C, O, Al ($T_c^{\text{max}} = 4.2$ K for C implantation) which they ascribed to disordering in the Al lattice. Similar disorder effects on T_c have also been obtained on films prepared by quenched condensation of Al with O_2 [11]. The importance of lattice disorder on T_c has not yet been assessed in H-implanted Al samples; nevertheless, several experiments indicate that besides this possible effect, additional changes in the electron-phonon interaction due to the formation of ordered compounds should be considered; Lamoise *et al.* [1] have shown for instance that the T_c of a sample of H-implanted aluminium ($T_c^{\text{max}} = 6.75$ K) decreases to the limits found for Al-O and Al-He implantations when additional disorder is created by implantation of a low dose of Al. At the same time, the transition which was very sharp in the case of H-implanted Al samples becomes broad as in the case of disordered samples.

Motivated by the experimental results briefly summarized above, we attempted to approach the problem from a different point of view. Assuming, as suggested by the experimental results [2], that ordered compounds are formed, we have studied the modifications in the electronic structure brought about by the presence of high concentration of hydrogen in an Al f.c.c. lattice. We have then evaluated how these differences in the electronic structure affect the electronic contribution to the electron-phonon interaction.

The lattice location of hydrogen implanted in f.c.c. metals has been investigated [12, 13] by nuclear reaction analysis and channelling techniques. The results indicate that above 35 K the hydrogen occupies the tetrahedral interstices of the f.c.c. metal lattice and that this site occupation seems to be associated with the formation of monovacancies created by the implantation process. However, Bugeat and Ligeon [13] proposed that by analogy with other f.c.c. metals (Ag, Cu, Pd, Pt), the octahedral position for hydrogen in Al should be more stable at temperatures below 35 K. It is to be noted that the relative stability of the tetrahedral *versus* octahedral interstitial position of hydrogen in an aluminium lattice has not yet been fully ruled out by the theoretical models presently available [14, 15]. Thus, in this work, we considered the two possible site occupancies by studying the monohydride AlH with a rocksalt structure (in which H occupies the octahedral interstices) and the dihydride AlH_2 with the fluorite structure (in which H occupies the tetrahedral interstices). The remainder of this paper is organized as follows: in section 2, we describe the modification of the electronic structure of Al upon hydrogenation by a comparison of the energy bands and densities of states of AlH and AlH_2 obtained by the augmented-plane-wave (APW) method, to the corresponding results for Al. The changes in the characteristics of the states at the Fermi energy E_F are duly emphasized by means of a site and angular momentum analysis of the density of states (DOS)

at E_F . In section 3 the band structure results are used to calculate the McMillan [16] electronic parameter η with the Gaspari and Gyorffy [17] model, based upon the rigid muffin-tin approximation.

2. Electronic structure of AlH and AlH_2 . — 2.1 AlH. — Since the octahedral site occupancy is generally observed at low temperatures for f.c.c. metals and has also been found from theoretical models, we have investigated the electronic structure of rock-salt structure AlH assuming a lattice constant $a = 8.056$ a.u. which corresponds to a $\sim 5.3\%$ linear increase in the lattice parameter of pure f.c.c. Al ($a = 7.6527$ a.u.). The choice of this linear dilatation was guided by the experimental results for f.c.c. Ni and Pd hydrides. The APW method with warped muffin-tin potential was used as described previously for other metal hydrides [18, 19], to generate the energy eigenvalues at 89 k points in the 1/48th irreducible Brillouin zone (BZ). The energy bands of AlH along several high symmetry directions are plotted in figure 1. In figure 2, we plotted the energy bands of

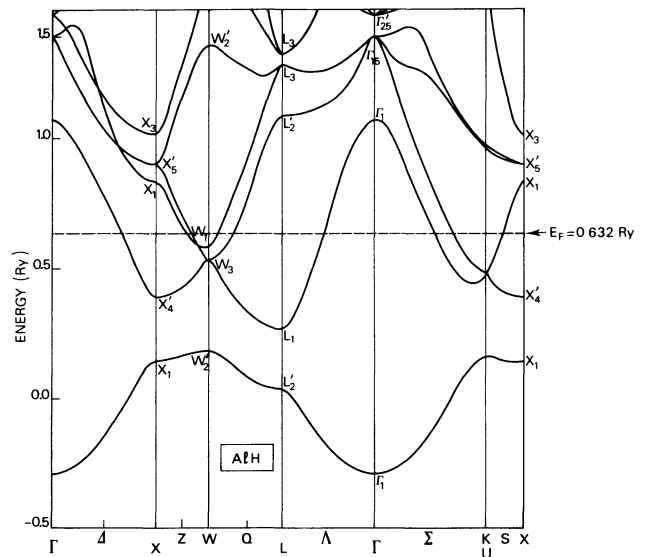


Fig. 1. — The energy bands of AlH along several high symmetry directions. Energies are in Rydberg.

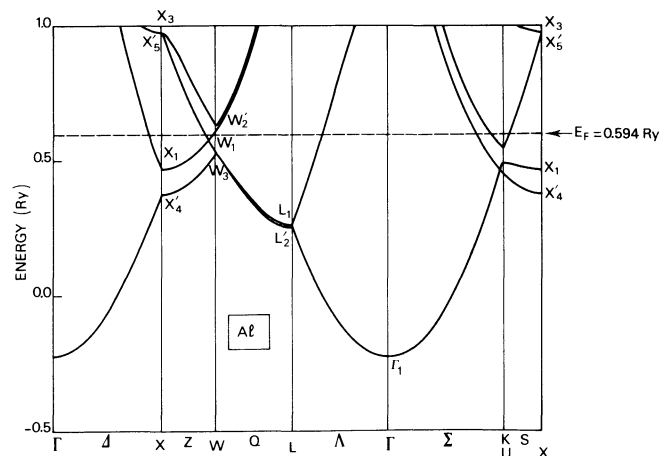


Fig. 2. — The energy bands of Al along several high symmetry directions. Energies are in Rydberg.

Table I. — Energy eigenvalues of AlH and angular momentum analysis of the charge (z_i^k) inside the Al and H muffin-tin spheres for some high symmetry points.

\vec{k}	Energy (Ry)	Al site				H site			
		$z_s^k(\ell = 0)$	$z_p^k(\ell = 1)$	$z_d^k(\ell = 2)$	$z_f^k(\ell = 3)$	$z_s^k(\ell = 0)$	$z_p^k(\ell = 1)$	$z_d^k(\ell = 2)$	$z_f^k(\ell = 3)$
Γ	-0.2921	0.4094	0.0	0.0	0.0	0.2472	0.0	0.0	0.0
	1.0753	0.2398	0.0	0.0	0.0	0.6234	0.0	0.0	0.0
	1.3954	0.0	0.6851	0.0	0.0309	0.0	0.1072	0.0	0.0026
X	0.1471	0.1483	0.0	0.1105	0.0	0.4952	0.0	0.0011	0.0
	0.3914	0.0	0.4821	0.0	0.0047	0.0	0.0637	0.0	0.0
	0.8384	0.6834	0.0	0.0162	0.0	0.1709	0.0	0.0145	0.0
	0.9000	0.0	0.5561	0.0	0.0328	0.0	0.0904	0.0	0.0011
W	0.1814	0.0	0.0998	0.0907	0.0059	0.5565	0.0	0.0002	0.0001
	0.5314	0.0	0.4351	0.0560	0.0029	0.0	0.0611	0.0026	0.0
	0.5801	0.7102	0.0	0.0156	0.0144	0.0	0.0384	0.0075	0.0002
K	0.1593	0.0188	0.1134	0.0818	0.0045	0.5241	0.0003	0.0004	0.0009
	0.4614	0.0	0.4566	0.0304	0.0029	0.0	0.0623	0.0014	0.0
	0.4912	0.4976	0.0901	0.0452	0.0081	0.0007	0.0483	0.0045	0.0001
	0.9684	0.0	0.5222	0.0427	0.0249	0.0	0.0861	0.0027	0.0009
L	0.0351	0.0	0.2726	0.0	0.0074	0.4105	0.0	0.0011	0.0
	0.2677	0.5402	0.0	0.0599	0.0	0.0	0.0551	0.0	0.0001
	1.0859	0.0	0.2360	0.0	0.0695	0.3713	0.0	0.0092	0.0
	1.2857	0.0	0.7288	0.0	0.0263	0.0	0.0	0.0252	0.0

pure f.c.c. Al. If we compare the two sets of results, the first remarkable feature is the presence in the case of AlH of a split-off band at the low energy side of figure 1. The composition of the states forming this low-lying band is shown in table I where we give, for some high symmetry points, an analysis of the charge into its angular momentum components inside the muffin-tin Al and H spheres. Note that the corresponding wavefunctions are normalized in the unit cell volume; the analysis given in table I does not include the charge in the interstitial region. The results listed in table I reveal the importance of the hydrogen-s and metal states in the split-off band. Similar analysis is given in table II for pure f.c.c. Al. The Γ_1 state of pure s symmetry in f.c.c. Al is found to be a bonding combination of H-s and Al-s states in AlH. The admixture of metal and H states in the low-lying band is also very clear for other high symmetry points analysed in table I; their energies have been lowered by the metal-hydrogen interaction.

The existence of low-lying metal-hydrogen bonding states in rocksalt structure transition metal hydride PdH was first emphasized by Switendick [20] and also in subsequent work [18, 21]; the photoelectron spectroscopy data of Eastman *et al.* [22] for PdH and more recent data on other transition [23] and rare earth [24] metal hydrides consistently show the formation of such H-derived states. The present calculation

Table II. — Energy eigenvalues of Al and angular momentum analysis of the charge (z_i^k) inside the Al muffin-tin sphere for some high symmetry points.

\vec{k}	Energy (Ry)	$z_s^k(\ell = 0)$	$z_p^k(\ell = 1)$	$z_d^k(\ell = 2)$
Γ_1	-0.225	0.7133	0.0	0.0
x_4'	0.374	0.0	0.7005	0.0
x_1	0.465	0.5366	0.0	0.1976
x_5'	0.976	0.0	0.7227	0.0003
w_3	0.527	0.0	0.5968	0.1142
w_1	0.614	0.0	0.3671	0.2385
w_2'	0.630	0.8150	0.0	0.0275
κ_3	0.450	0.0	0.6463	0.0610
κ_1	0.490	0.1450	0.4364	0.1230
κ_1	0.545	0.5236	0.0601	0.1579
L_1	0.257	0.0	0.6534	0.0
L_2'	0.258	0.6535	0.0	0.1318

shows that similar metal-hydrogen bonding band exists also in s-p metal hydrides like AlH.

Two structures are observed in the DOS of the low

lying bands of AlH around $E = 0.035$ Ry and $E = 0.147$ Ry as can be seen in figure 3. They correspond respectively to a flat band around L_2' and to a flat band between X_1 and K_1 . As observed for other

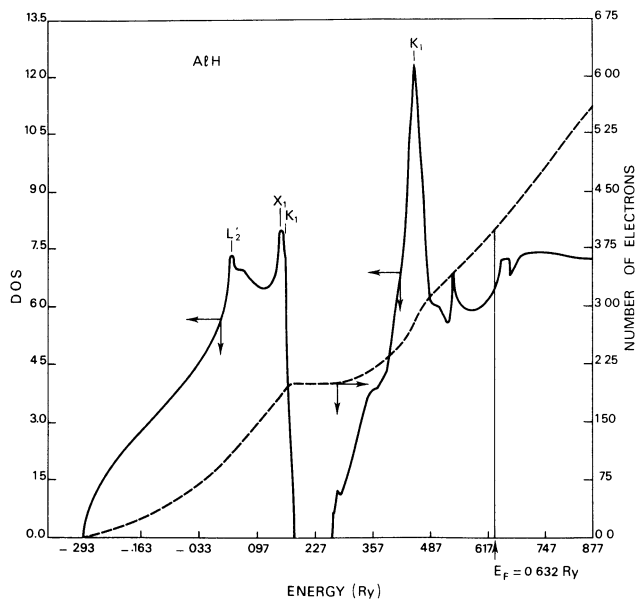


Fig. 3. — The total DOS of AlH, full line curve, left-hand side scale ; units are states of both spin/Ry unit cell. The total number of electrons, dashed line and right-hand side scale.

metal hydrides, the position of the low-lying band depends upon the strength of the metal-hydrogen interaction which is directly related to the metal-hydrogen distance. With the present choice of lattice constant, the low-lying band of 6.44 eV width is separated by a gap of 1.17 eV from the next band complex. A partial wave analysis of the DOS inside the Al and H muffin-tin spheres is given respectively in figures 4 and 5. We can see that the low-lying band is globally dominated by the hydrogen's contribution ; nevertheless, the Al-s component is particularly important at the bottom of the band, where it is even larger than the H-s contribution ; at higher energies, the Al-p component and to a lesser extent, the Al-d contribution are also important. It can be seen clearly that the Al-p partial DOS gives an important contribution to the peak in the total DOS observed around L_2' at $E = 0.035$ Ry, while the structure in the total DOS found around K_1 and X_1 at $E \sim 0.15$ Ry is mostly due to H-s states with a much smaller contribution from the metal site. From a rapid glance at figure 3, we can notice that the overall parabolic shape of the total DOS of pure Al is very much altered in AlH.

If we examine the partial wave DOS analysis we can see from figures 4 and 5 that the bands above the energy gap $E > 0.268$ Ry are mostly composed of metal s and p states ; the magnitude of the H-s and p components is however important in this energy range since it is comparable to the metal-d contribution. This feature is specific to the simple metal hydrides ;

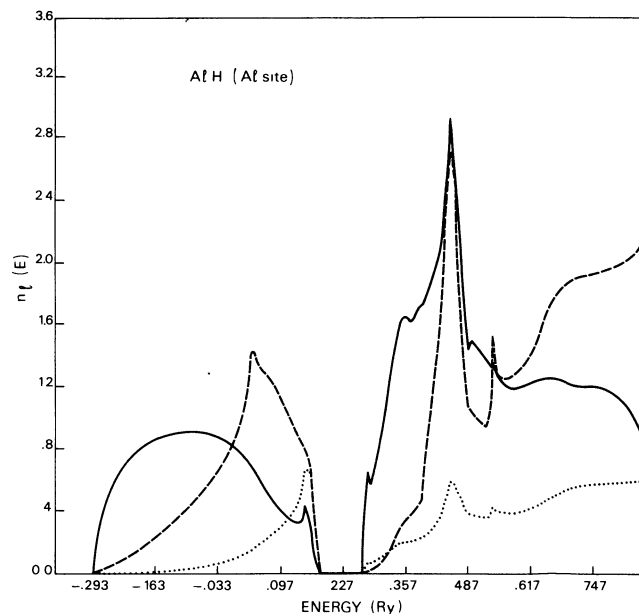


Fig. 4. — The angular momentum DOS analysis n_l of AlH inside the Al muffin-tin sphere $R_{Al} = 2.4596$ a.u. ; $l = 0$ (full line) ; $l = 1$ (dashed line) ; $l = 2$ (dotted line). Units are states of both spin/Ry unit cell.

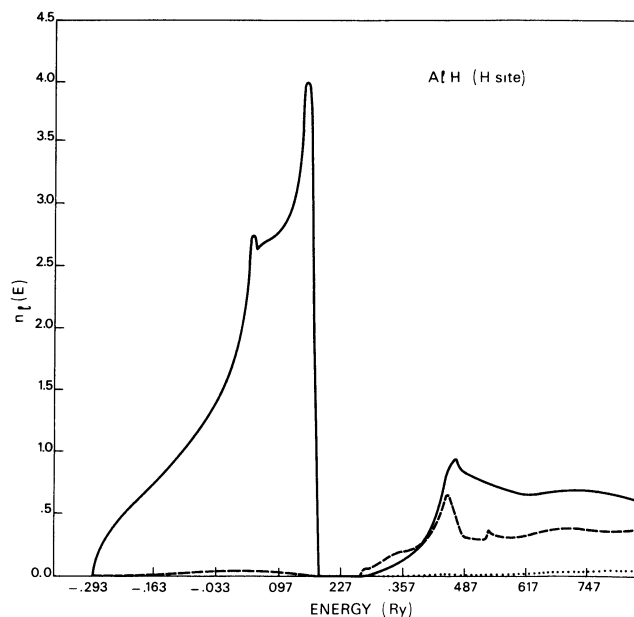


Fig. 5. — The angular momentum DOS analysis n_l of AlH inside the H muffin-tin sphere $R_H = 1.5683$ a.u. ; $l = 0$ (full line) ; $l = 1$ (dashed line) ; $l = 2$ (dotted line). Units are states of both spin/Ry unit cell.

it is very different from what we obtained for the transition metal (TM) hydrides of the beginning or of the middle of the TM series for which the partial DOS of s type at the hydrogen site was found to be very small. As we shall see in section 3, the presence of sizeable hydrogen s and p components plays an important role in the strength of the electron-phonon matrix elements. The reader is referred to table I for an analysis of the charge at the points of high symmetry above

Table IV. — Energy eigenvalues of AlH_2 and angular momentum analysis of the charge (z_l^k) inside the Al and the two hydrogen muffin-tin spheres, for some high symmetry points.

\vec{k}	Energy (Ry)	Al site				2 H sites			
		$z_s^k(\ell = 0)$	$z_p^k(\ell = 1)$	$z_d^k(\ell = 2)$	$z_f^k(\ell = 3)$	$z_s^k(\ell = 0)$	$z_p^k(\ell = 1)$	$z_d^k(\ell = 2)$	$z_f^k(\ell = 3)$
Γ	-0.3729	0.2810	0.0	0.0	0.0	0.2935	0.0	0.0	0.0
	0.6428	0.0	0.0	0.0	0.0607	0.7311	0.0	0.0	0.0
	1.3149	0.0	0.0	0.3302	0.0	0.0	0.1526	0.0007	0.0008
	1.3831	0.0	0.6574	0.0	0.0040	0.0	0.0105	0.0227	0.0004
X	0.0055	0.0	0.2023	0.0	0.0049	0.4208	0.0	0.0013	0.0
	0.3311	0.0	0.0	0.1260	0.0	0.5772	0.0	0.0017	0.0
	0.4234	0.4223	0.0	0.0426	0.0	0.0	0.0713	0.0005	0.0001
	0.8482	0.0	0.4183	0.0	0.0123	0.0	0.0988	0.0003	0.0004
	1.1350	0.2882	0.0	0.1369	0.0	0.0	0.0004	0.0199	0.0
W	0.1247	0.0	0.1546	0.0357	0.0030	0.4415	0.0047	0.0011	0.0001
	0.5219	0.5787	0.0	0.0064	0.0054	0.0	0.0700	0.0029	0.0001
	0.6008	0.0	0.2171	0.0656	0.0007	0.0	0.0739	0.0006	0.0
K	0.0667	0.0	0.1804	0.0169	0.0041	0.4285	0.0030	0.0011	0.0001
	0.1581	0.0529	0.1036	0.0528	0.0014	0.4180	0.0106	0.0008	0.0001
	0.4907	0.3859	0.0479	0.0338	0.0017	0.0037	0.0704	0.0014	0.0
	0.8466	0.1553	0.0756	0.0928	0.0083	0.1363	0.0557	0.0044	0.0001
	0.9120	0.0	0.4092	0.0191	0.0103	0.0	0.0952	0.0020	0.0004
L	-0.0030	0.2451	0.0	0.0415	0.0	0.3349	0.0135	0.0004	0.0
	0.0176	0.0	0.2076	0.0	0.0046	0.3530	0.0125	0.0001	0.0001
	1.0437	0.4156	0.0	0.0628	0.0	0.2913	0.0355	0.0052	0.0005
	1.1534	0.0	0.0509	0.0	0.0582	0.3080	0.0369	0.0029	0.0002
	1.1778	0.0	0.5474	0.0	0.0128	0.0	0.0776	0.0103	0.0003

energy which are formed of metal-hydrogen bonding states and hydrogen-hydrogen antibonding combinations. From the results listed in table IV we can see that the lowest Γ_1 point is a bonding combination of metal-s and the two hydrogen s states while Γ'_2 is an antibonding combination of the two H atom s states, with a residual metal f contribution. The two low-lying bands of width 13.8 eV overlap the hybridized metal s-p bands located above the X_1 point (see Fig. 6). The position of the two low-lying bands and their width which is given by the energy difference between the bonding Γ_1 and antibonding Γ'_2 states, depend sensitively upon the metal-hydrogen and the hydrogen-hydrogen distances.

As already mentioned for AlH the total DOS of AlH_2 plotted in figure 7 shows strong deviations from the parabolic shape of the pure metal DOS. Several structures are observed : the large value of the DOS around $E = 0.0$ Ry corresponds to flat bands around L_1 and X'_4 and also L'_2 as we can see in figure 6 ; another peak structure around $E = 0.12$ Ry arises from flat bands around W_3 and from the crossing of the Σ_1 and Σ_3 branches in this energy range. The value of the total DOS of the two low-lying bands then drops

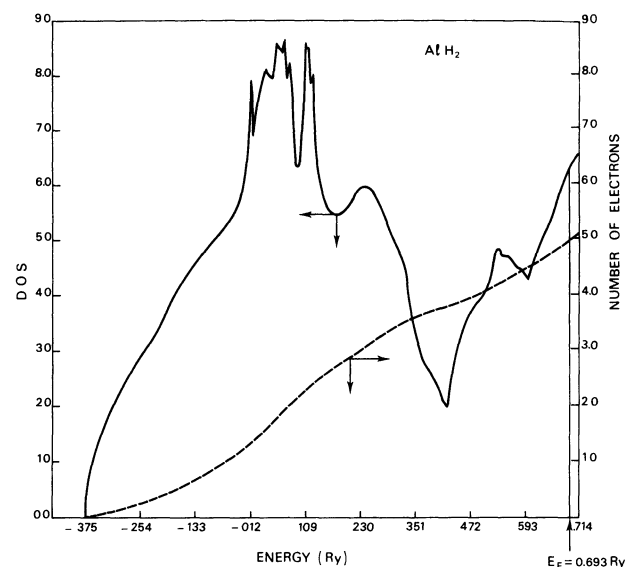


Fig. 7. — The total DOS of AlH_2 , full line curve, left-hand side scale ; units are states of both spin/Ry unit cell. The total number of electrons, dashed line and right-hand side scale.

as E increases and starts rising again for $E > 0.423$ Ry, above the X_1 point which marks the bottom of the third band. The partial DOS analysis inside the muffin-

tin Al sphere (see Fig. 8) shows the importance of the metal s contribution in the first low-lying metal-hydrogens bonding band, while the metal p states play an important role in the energy range spanned by the second band. The two structures previously described in the total DOS appear clearly in the partial Al-p DOS plotted in figure 8. A metal d contribution is also found

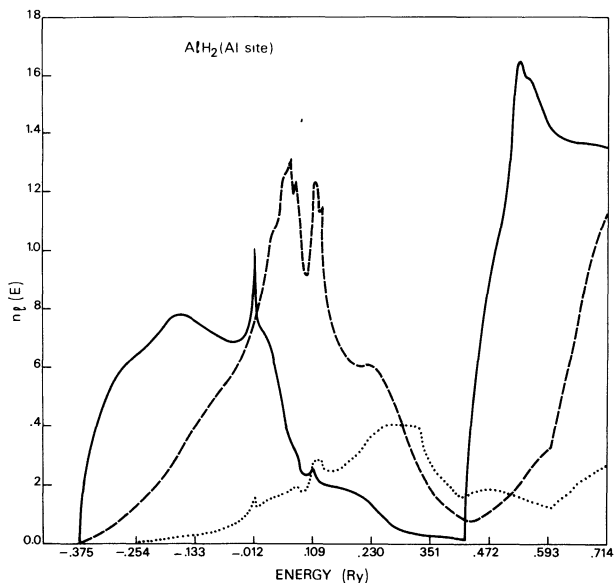


Fig. 8. — The angular momentum DOS analysis n_l of AlH_2 inside the Al muffin-tin sphere $R_{\text{Al}} = 2.2255$ a.u. ; $l = 0$ (full line) ; $l = 1$ (dashed line) ; $l = 2$ (dotted line). Units are states of both spin/Ry unit cell.

in the DOS of band 2 essentially. Figure 9 shows that the s component at the H sites gives the major contribution to the total DOS of the two low-lying bands. The contribution of H-p and H-d components to the first two bands is extremely small.

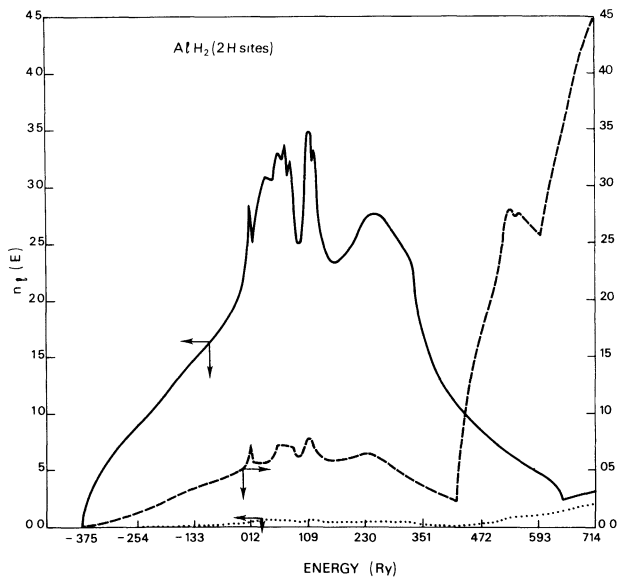


Fig. 9. — The angular momentum DOS analysis n_l of AlH_2 inside the H muffin-tin sphere $R_{\text{H}} = 1.3499$ a.u. ; $l = 0$ (full line, left-hand side scale) ; $l = 1$ (dashed line, right-hand side scale) ; $l = 2$ (dotted line, left-hand side scale). Units are states of both spin/Ry unit cell.

Above the point X_1 , the total DOS is dominated by the metal-s states. For energies larger than $E = 0.6$ Ry which marks the bottom of band 4, the metal-p contribution is found to rise very sharply and, although it remains smaller than the metal s component, it gives a very important contribution at the Fermi energy. The metal d states have a much smaller contribution. At the H site, the partial DOS decreases sharply in bands 3 and 4 from its large value in the two low-lying bands. On the contrary, band 3 and band 4 are marked by a sharp increase of the H-p contribution to the total DOS.

As can be seen in figure 7, the two metal-hydrogen low-lying bands are filled by 4 electrons and the remaining electron fills the bottom of bands 3 and 4 which accommodate respectively 87 % and 13 % of an electronic charge. Like the monohydride, the dihydride is metallic ; the Fermi level lies at 1.066 Ry above the bottom of the bands ; this is to be compared to the values 0.924 Ry and 0.819 Ry respectively obtained for AlH and pure Al. The total value of the DOS at E_F for AlH_2 is 6.3 states of both spin/Ry unit cell which is very close to the value obtained for AlH and of the order of 25 % higher than the DOS of pure Al.

The values of the partial DOS at E_F resulting from an analysis inside the muffin-tin Al and the two hydrogen spheres are listed in table III. As for AlH and pure Al the metal s and p components are dominant at E_F . Nevertheless, the hydrogen-s and p contributions at E_F are not negligible since they are larger than the metal d component. From the results listed in table III we can see that for AlH_2 the partial DOS of s type at the H sites is ~ 50 % smaller than for AlH. In the case of AlH_2 the two hydrogen atoms-p partial DOS is slightly larger than the two hydrogen-s contribution ; for AlH, on the contrary, the s component is larger than the p term at the H site.

We also give in table III the detailed contribution to the DOS from the two bands crossing the Fermi level. The H-s contribution is provided mostly by the third band ; however, this band has a dominant metal s character (with a smaller metal p contribution) ; it is very different from band 2 of AlH which was formed of antibonding metal-hydrogen states and thus was giving a much larger H-s character at E_F . In the case of AlH_2 , band 2 which at Γ'_2 is formed of antibonding s states of the two H atoms in the unit cell, has a larger s character ; this can be seen clearly in figure 9, in the energy range spanned by band 2. Since before starting the calculation, we did not possess any experimental information on the lattice parameter of Al hydrides, one could surmise that, with a smaller lattice expansion of the Al lattice, the Γ'_2 point could lie above E_F and in that case, band 2 could give a larger H-s contribution at E_F . This remark should be kept in mind for the discussion of the value of the electron-phonon interaction in Al hydrides which is given in the next section.

3. Electron-phonon interaction. — The electron-phonon coupling constant can be expressed in the following way [16] in terms of the electron-phonon spectral function $\alpha^2(\omega) F(\omega)$

$$\lambda = 2 \int \alpha^2(\omega) F(\omega) \omega^{-1} d\omega \quad (1)$$

where :

$$\begin{aligned} \alpha^2(\omega) F(\omega) &= \frac{1}{(2\pi)^3} \int d\mathbf{k} \int d\mathbf{k}' \times \\ &\times \sum_v \frac{|\langle \psi_{\mathbf{k}} | \boldsymbol{\varepsilon}_{\mathbf{k}-\mathbf{k}',v} \cdot \nabla V | \psi_{\mathbf{k}'} \rangle|^2}{2M\omega_{\mathbf{k}-\mathbf{k}',v}} \delta(\omega - \omega_{\mathbf{k}-\mathbf{k}',v}) \\ &\times \delta(\varepsilon_{\mathbf{k}} - \varepsilon_F) \delta(\varepsilon_{\mathbf{k}'} - \varepsilon_F) \Big/ \int d\mathbf{k} \delta(\varepsilon_{\mathbf{k}} - \varepsilon_F). \end{aligned} \quad (2)$$

In eq. (2), $\boldsymbol{\varepsilon}_{\mathbf{q},v}$ and $\omega_{\mathbf{q},v}$ are respectively the eigenvector and frequency of a phonon of wavevector \mathbf{q} and branch index v ; ∇V is the gradient of the screened potential and $\psi_{\mathbf{k}}$ the electron Bloch function where \mathbf{k} stands for both the wavevector \mathbf{k} and the band index. Direct calculation of λ using eq. (2) is a formidable task since they involve a double integration on the Fermi surface (FS) which requires a detailed knowledge of the phonon dispersion curves and electronic wavefunctions. McMillan [16] proposed an approximate expression for λ :

$$\lambda \simeq \frac{N_{\uparrow}(E_F) \langle I^2 \rangle}{M \langle \omega^2 \rangle} = \frac{\eta}{M \langle \omega^2 \rangle} \quad (3)$$

in which the mean square phonon frequency is defined by :

$$\langle \omega^2 \rangle = \frac{\int \alpha^2(\omega) F(\omega) \omega d\omega}{\int \alpha^2(\omega) F(\omega) \omega^{-1} d\omega} \quad (4)$$

$\langle I^2 \rangle$ is the square of the electron-phonon matrix element averaged over the FS and N_{\uparrow} is the DOS per spin at E_F . In eq. (3) λ is defined as the ratio of an electronic contribution η to an effective phonon force constant. The approximation $\alpha^2 = \text{constant}$ is often used in eq. (4) to evaluate $\langle \omega^2 \rangle$. Using the rigid muffin-tin approximation which ignores the screening of the crystal potential associated with a lattice vibration, Gaspari and Gyorffy [17] have shown that η can be easily calculated using the results of band structure calculations :

$$\begin{aligned} \eta &= \frac{1}{N_{\uparrow}(E_F)} \sum_{\mathbf{K}} \frac{E_F}{\pi^2} \sum_l 2(l+1) \times \\ &\times \sin^2(\delta_{l+1}^{\mathbf{K}} - \delta_l^{\mathbf{K}}) \frac{n_l^{\mathbf{K}}(E_F) n_{l+1}^{\mathbf{K}}(E_F)}{n_l^{\mathbf{K}(1)}(E_F) n_{l+1}^{\mathbf{K}(1)}(E_F)}. \end{aligned} \quad (5)$$

In eq. (5) the summation on \mathbf{K} runs on all the atoms in the unit cell; $\delta_l^{\mathbf{K}}$ is the phase shift of the muffin-tin

potential for site \mathbf{K} , calculated at the Fermi energy; $n_l^{\mathbf{K}}$ is the partial DOS with angular momentum l at site \mathbf{K} and $n_l^{\mathbf{K}(1)}$ is the single site DOS defined by :

$$n_l^{\mathbf{K}(1)} = \frac{\sqrt{E_F}}{\pi} (2l+1) \int_0^{R_{\text{MT}}^{\mathbf{K}}} \mathcal{R}_l^{K^2}(r, E_F) r^2 dr \quad (6)$$

where \mathcal{R}_l is the radial wavefunction with angular momentum l . The integration is carried out inside the muffin-tin sphere of radius R_{MT} at site \mathbf{K} . Important contributions to η from site \mathbf{K} are expected when the difference between the l and $l+1$ phase shifts is close to a resonance, provided that the ratios of the l and $l+1$ partial DOS to their single site values are not small.

As we can see from the results listed in table V, the s phase shift at the H site is large in both AlH and AlH₂; it is close to a resonance while the phase shifts of higher

Table V. — Value of several parameters entering the calculation of λ . The phase shifts of the scattering muffin-tin potentials δ_l are given in radians; the McMillan electronic parameter η is given in eV/Å²: (a) from Papaconstantopoulos et al. [26]; (b) from Gupta and Burger [27].

		δ_0	δ_1	δ_2	η (eV/Å ²)
AlH	Al site	0.336 5	0.401 4	0.052 8	0.294
	H site	1.185 6	0.040 4	0.001 2	2.292
AlH ₂	Al site	0.253 6	0.371 4	0.055 6	0.224
	H site	1.173 8	0.037 9	0.001	0.744
Al (a)		0.344	0.436	0.065	0.558
PdH (b)	Pd site	-0.511 5	-0.109 4	2.806 6	0.886
	H site	1.193 1	0.028 0	0.000 6	0.641

angular momentum are much smaller. The strong scattering of the conduction electrons by the hydrogen potential is also found in the case of transition and rare earth metal hydrides such as PdH, NiH, TiH₂, LaH₂ [27]. Thus, the strength of the H site contribution to the electron-phonon matrix elements in hydrides is expected to be essentially governed by the magnitude of the s and p type partial DOS values. As we mentioned previously in section 2, these values are relatively important in the case of the simple metal mono- and dihydrides presently studied since in both cases the Fermi level falls in a portion of the metal s - p bands where the hybridization with H- s and p states is quite important. Particularly, we mentioned that for AlH, the antibonding metal-hydrogen band which crosses the Fermi energy is responsible for the enhanced value of the H- s partial DOS at E_F . In view of these remarks, we expect η_{H} to be quite large for the Al hydrides. We also give in table V, for comparison, the values of the parameters entering the calculation of η in the case of PdH. For AlH₂, the value of η_{H} for each hydrogen atom is slightly larger than that found in PdH. At the H site, the s - p scattering is dominant since it gives 98 % of the total contribution while the p - d mechanism gives

only 2 %. In the case of AlH, the value of η_H , which is also dominated by the s-p scattering term is found to be very large ; it is a factor of 3.5 larger than η_H in PdH. The magnitude of this term is due to the large value of the H-s type partial DOS at E_F and to the magnitude of the H-p partial DOS which is only 50 % smaller than n_s ; this is in contrast to the case of PdH where the p-type DOS at the H site is an order of magnitude smaller than n_s . For AlH₂, as we can see in table III, the values of n_s and n_p per H site are smaller than in AlH and lead to a smaller value of η_H .

The contribution to η provided by the scattering at the metal site is found to be small for both AlH and AlH₂. The results listed in table V show that, at the metal site, the p and s phase shifts largely dominate the d phase shift, as it is the case for simple metals. The values for pure f.c.c. Al from the work of Papaconstantopoulos *et al.* [26] are listed in table V for comparison. Since at the Al site the p and s phase shifts are of the same order of magnitude we can see from eq. (5) that the s-p scattering term is expected to be small ; the dominant term at the Al site is given by the p-d scattering in both the mono- and the dihydride, where it represents respectively ~ 92 % and ~ 79 % of the values of η_{Al} , the values of η_{Al} found for AlH and AlH₂ are about 50 % smaller than η_{Al} obtained for pure f.c.c. Al using the same approximations. It should however be noted that for simple metals, the expressions of λ given by eq. (3) in terms of the ratio of an electronic to a phonon contribution underestimates λ as has been shown by Allen and Cohen [28], and that for simple metals, the screening is expected to be more effective than in transition metals and consequently the rigid muffin-tin approximation is not expected to be as good. The values of η_{Al} obtained by means of Gaspari and Gyorffy's model are too small [26]. Nevertheless, the decrease in η_{Al} from the pure metals [26] to the metal hydrides is meaningful since the same model has been used consistently. This decrease suggests that the metal lattice may not be responsible for the increase of T_c , unless the decrease of the electronic contribution η_{Al} is accompanied by an even larger decrease in the phonon contribution ; in spite of the lattice expansion of the hydrides, such a drastic decrease in the effective phonon force constant seems to be doubtful [29]. Our results point out the importance of the electron-phonon matrix elements at the H sites in the aluminium hydrides since the total value of η_H is 1.49 eV/Å² for AlH₂ and 2.29 eV/Å² for AlH compared to 0.64 eV/Å² for PdH. If the optic

modes are not too hard, the large values presently found for η_H should result in a substantial contribution to the electron-optical phonon coupling constant λ_H . Sufficient information on the phonon DOS of the aluminium hydrides is not yet available and precludes further estimate of λ , and calculation of T_c . Tunnelling data have been obtained for D implanted Al samples [29] which seem to indicate that the optic modes do not play a role for energies smaller than 50 meV. Further investigations of the tunnelling characteristics at higher energies, now underway at Orsay will provide further insight on the origin of the high value of T_c in the aluminium hydrides.

4. Conclusion. — The study of the electronic structure of the mono- and dihydrides of aluminium shows that upon hydrogenation substantial deviations from the overall parabolic shape of the DOS of the pure f.c.c. metal, occur. As for transition and rare earth metal mono- and dihydrides, we observe the formation of a low-lying metal-hydrogen bonding band and in the case of AlH₂, of an additional band due to the hydrogen-hydrogen interaction. The new feature is the importance of the admixture of hydrogen s and p states in the metal bands. This hybridization, which is particularly large in the case of AlH at the Fermi energy, is responsible for the large value of the electron-phonon matrix elements evaluated at the H sites ; this feature makes these compounds good candidates for superconductivity and should lead to an important electron-optical phonon coupling provided that the optic modes do not have a too high energy. Further conclusion concerning the increase of T_c over its value in pure Al cannot be drawn prior a better knowledge of the vibrational properties of the Al-hydrides. As mentioned previously, the rise in T_c could also be partially due to the lowering of the acoustic phonons due to disorder in H-implanted Al samples. Tunnelling experiments now in progress at Orsay should provide a further clue to this interesting problem. The thrust of the present paper was to emphasize the changes in the electronic structure and the electron phonon matrix elements of Al, upon formation of AlH and AlH₂.

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