ON THE CHANGES OF THE ELECTRONIC STRUCTURE OF EARLY-TRANSITION-METAL-SYSTEMS AT HYDROGENATION*

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Abstract

The hydrogenation effect on Sc, Y, La, Cd and Eu has been investigated by XPS. The stability, the charge transfer as well as the microscopic behaviours of the processes have been discussed.

Introduction

The dihydrides of the lanthanide elements and of several of the transition metals are metallic. Generally there have been two opposing theories to account for the metallic properties of hydrides. Both involve H-ions in the metal-hydrogen bonding. The first is the so-called alloy theory in which the hydrogen atoms are regarded as donating an average fraction of their valence electrons to the conduction band of the metal having fractionally changed H^+ species which take up positions in the hydrogenated lattice. Theoretical support of this model in the case of some of the transition metal hydrides, has been given by Swittendick (1970) and Tammerman and Pindor (1982). The second is the 'hydridic' theory in which it is postulated, that the fractionally positive H^+ species can exist as excited states of both the negative ion H^- and the neutral atom H. In this model, introduced originally by Gibb (1962), the metallic properties are explained in terms of "residual" metallic bonding which involves the valence electrons that remain after formation of the H^- species. If a hydride MH_x is formed by a metal having n valence electrons, then XH^- ions are formed per metal-atom and $n-x$ 'metallic' electrons remain. The ionic hydrides are simply those for which $n=x$; which provides a natural explanation for the gradual disappearance of the metallic properties as the metal hydrides approach, e.g. in the lanthanides the composition LaH_3.

For the solution of the problems above, one of the important factor the charge transfer between the host metal and hydrogen introduced into it.

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* Dedicated to Prof. J. Giber on the occasion of his 60th birthday.

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Unfortunately there are also two opposit observations supporting both of the above described models; there was observation (Skala et al. (1982)) concluding that the charge transfer occurs from the hydrogen to metal-ion (supporting alloy theory) and there are some observation for the charge transfer direction in opposit conclusion (Osterwalder (1985)).

The other not clear behaviour, that according to the observations and considerations of Ducastelle et al. (1970) and Nagel and Goretzki (1975) there are different changes at the Fermi level depending on the actual phases of the hydrogenated material.

Several experimental results can be cited that favour the alloy theory including measurements of hydrogen mobility, magnetic susceptibility, hydrogen migration in a magnetic field and Knight-shifts. However the evidence is by no means conclusive and to-date no experiment has possibility eliminated one or other of the two theories. The overall properties of the hydrides are also affected by the size and thermodynamics of the H^+ and H^- species. The structure of the lanthanium hydrides remains cubic up to the composition LaH_2. The tetrahedral sites fill at random state stoichiometric composition is reached. With same of the transition metals a small proportion of sites remain unoccupied, giving limiting compositions much as $ScH_{1.98}$. Ittrium, lanthanum and gadolinium can all form semi-metallic trihydrides. The metallic dihydrides of Sc, Y, La and Gd characterised by high stability, which implies for equilibrium hydrogen pressure. Thus at room temperature are stable even in vacuum. This was exploded in previous (Gimzewski et al. (1977)) paper in which we made XPS measurements on ScH_2 formed by explosure of pure scandium metal to hydrogen gas at 10^{-4} torr pressure and studied the shift of plasmon energy-loss satellite peaks on hydriding under high-vacuum conditions. The plasmon shift for Sc on fraction of ScH_2 corresponded to donation of the H valence electrons to the conduction band of the metal, supporting the alloy theory for the formation of this hydride. In the present which we have made a more careful study of scandium hydride XPS plasma shifts and have extended the investigation to its isoelectron neighbourhood in the Periodic Table.

In our recent paper the electronic structure is investigated by the observing changes in the valence band and in the plasmon energy loss peaks as hydriding occurs.

The plasmon energy changes refer to the valence band structure at the vicinity of the Fermi level. The information having from these data are complete the observations of the core levels and valence band spectra.

Experimental

The XPS instrument used for both preparation and analysis of the hydrides was a VG ESCA3 Spectrometer, with specially modified gas inlet system that allows accurate hydrogen exposure to be made routinely. The analyzer base pressure is normally 5×10^{-10} torr or better, and the sample preparation chamber is also evacuated to this pressure or lower before contamination-free metal samples are deposited by evaporation. The cleanliness of a prepared metal film is checked by observing the O 1s, C 1s core level peaks and also the metal valence band at 7 eV below the Fermi level. When residual contamination is negligible, clean metal spectra are recorded.

The dihydrides of the isoelectronic metals Sc, Y, La and Gd were prepared by exposing clean evaporated films of the elements to pure hydrogen at 10^{-4} torr in the sample chamber of a VG ESCA3 photoelectron spectrometer. The surface hydrides produced were studied by XPS and their electronic structure investigated by observing changes in the valence band and in the Sc 2p plasmon energy-loss peaks as hydriding occurred, following the method of Gimzewski et al. (1977).

Hydrogen gas used for preparation of the surface hydrides is purified in a liquid-nitrogen cold trap and allowed to equilibrium with the clean metal film at 10^{-4} torr for various exposure times, until a saturation exposure is reached. Digital summing and processing of spectra is performed with a PDP 8E computer control.

Results

Scandium: Measured core-level binding energies for scandium metal are listed in Table I. These agree well with the values reported previously by Gimzewski et al. (1977) and by Kowalczyk (1976). The scandium 2p core-level (Figure 1) shows an intense plasmon energy-loss feature which is observed during the progressive surface hydriding of the metal.

Table I

Scandium core-level binding energies (eV)$^{+}$

Core level	2s	$2p^{3/2}$	$2p^{1/2}$	3s	3p
Metal	498.3 ± 0.3	398.6 ± 0.2	403.4 ± 0.2	51.2 ± 0.2	29.0 ± 0.2
ScH_2	—	398.8 ± 0.2	403.6 ± 0.2	51.3 ± 0.2	29.3 ± 0.2
Sc_2O_3*	502.8 ± 0.3	403.2 ± 0.2	407.8 ± 0.2	54.8 ± 0.2	33.1 ± 0.2

$^{+}$ Referred to Au $4f^{7/2}$ at 83.8 eV

* Evaporated oxide, O ls binding energy 530.7 ± 0.2 eV

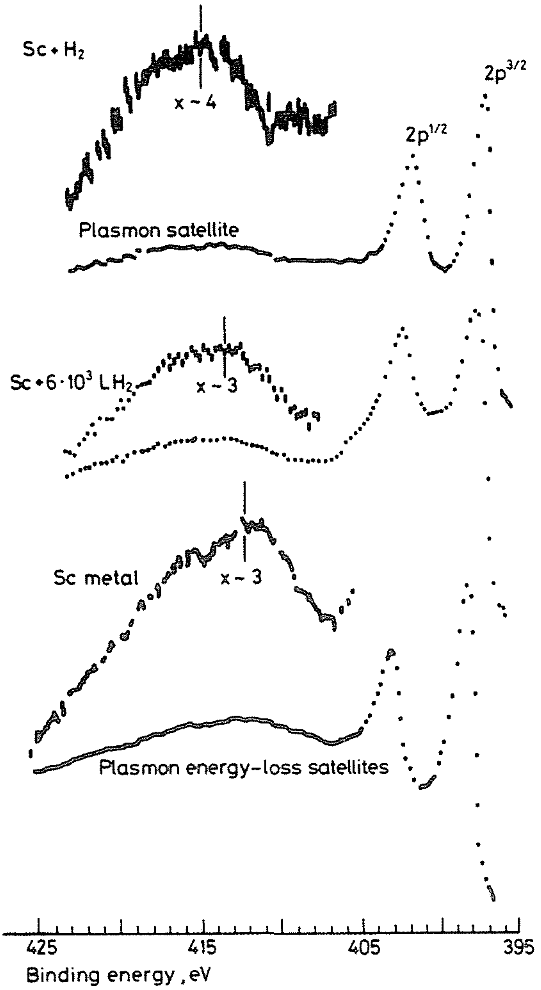

Fig. 1. The 2p XPS Core-level Spectra of Sc

The plasmon peak shifts from a position 13.0 ± 0.3 eV below the parent 2p peak to $16.8 + 0.8$ eV below on saturation exposure to 3×10^4 Langmuirs of hydrogen. The shifts of the peaks on intermediate hydriding are listed in Table II for some typical exposures to hydrogen.

The XPS valence band spectra for scandium metal and its surface hydrides are shown in Figure 2. The hydride shows a new approximately symmetrical band 6 eV below the Fermi level (FWHM $\simeq$ 3.5 eV).

Yttrium, lanthanum and gadolinium: In addition to their metallic dihydrides, the metals Y, La and Gd can form also the trihydrides YH_3, LaY_3 and GdH_3 Gibb (1962), which are semimetallic. In each case the plasmon shift

Table II

Scandium 2p core-level plasmon satellite shift with exposure to hydrogen
(Initial plasmon energy-loss peak at 13.0 ± 0.3 eV below parent peak)

Exposure (L)	0	10^2	5×10^2	10^3	5×10^3	10^4	5×10^4
Plasma shift	0	0.3	1.5	2.0	2.8	3.6	3.8

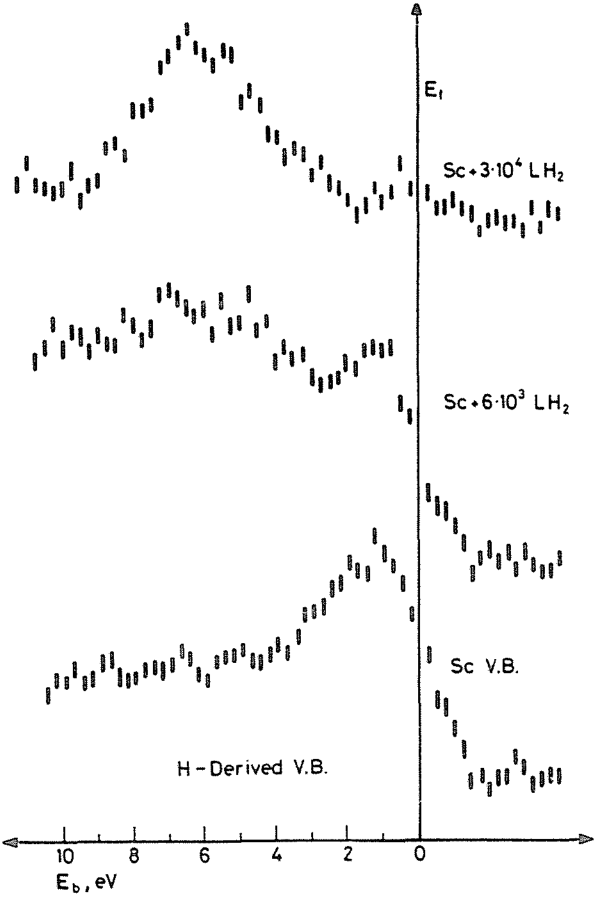

Fig. 2. The XPS valence band spectra of hydrogenated Sc

obtained, corresponds to an addition of two electrons to the metallic conduction band. The core-level binding energies and plasmon energies are given in Tables III and IV, together with the calculated plasmon energies.

The yttrium *3d* core-level peaks show distinct plasmon energy-loss satellites in their inelastic electron-scattering tail (Figure 3) located at 13.1 ± 0.3 eV

Table III

Core level binding energies for Y, La and Gd

Y	$3d^{5/2}$	$3d^{3/2}$	$3p^{3/2}$	$3p^{1/2}$	4p	4s	3s	
$E_B \pm 0.2$(eV)	155.5	157.6	299.0	311.0	24.0	45.0	393.6	
La	$5p^{3/2}$	$5p^{1/2}$	5s	$4d^{5/2}$	$4d^{3/2}$	4s	$3d^{5/2}$	$3d^{3/2}$
$E_B \pm 0.3$(eV)	17.6	19.0	33.0	102.8	105.2	271.1	835.1	852.5
Gd	4f	5p	5s	$4p^{3/2}$	$4p^{1/2}$	$4d^{5/2}$	$4d^{3/2}$	
$E_B 0.3$(eV)	7.7	20.7	26.5	271..4	290.2	141.1	146.1	

Table IV

Core-level plasmon satellite shifts for Y, La and Gd, on saturation exposure to H_2

Metal core-level		Measured plasmon-shift (eV)	Calculated energy-loss shift (eV) for 2 extra valence electrons
Y 3d	10^4	$13.1-16.4=3.3$	$11.1-14.3=3.2$
La 4d	$5 \cdot 10^3$	$12.0-13.8=1.8$	$10.6-12.5=1.9$
Gd 4d	$5 \cdot 10^3$	$11.5-14.2=2.7$	$11.3-13.7=2.4$

below the mid-point of each of the $3d^{3/2}$ and $3d^{5/2}$ peaks. These satellite peaks move to 16.4 ± 0.3 eV below their respective parent peaks (a shift of $\simeq 3.3$ eV) on exposure to more than 10^4 Langmuir of pure hydrogen gas. When an expected valency of 5 is assumed, the calculated shift is 3.2 eV. Our results agree well with the shift ($\simeq 2.8$ eV) observed by Brousseau—Lahaye et al. (1980) using low-energy electron energy-loss measurements.

Further plasmon shifts were not observed, which conforms with the known difficulty of forming chemically the metal trihydrides from the dihydrides.

Similar results were obtained for lanthanum and gadolinium. With these metals formation of contamination-free evaporated samples proved difficult; however, the trends observed were similar to those obtained for scandium and yttrium. The introduction of a localised $4f^7$ configuration in gadolinium does not appear to influence its hydriding behaviour. In both cases a hydrogen-derives valence band is formed by hydrogen 1s electrons forming a new band below the Fermi level.

Europium: which has a prematurely half-filled *4f* shell, is known to form only an ionic type hydride EuH_2. This metal was similarly exposed to

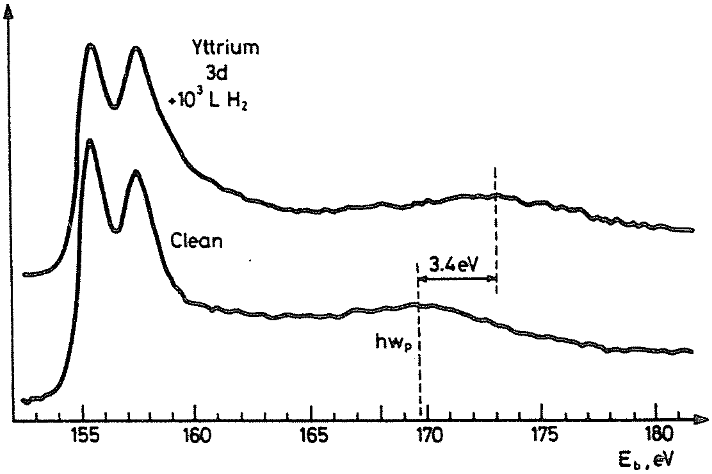

Fig. 3. 3d Core-level peaks of Y

hydrogen but no hydride formation could be found, which was either due to poor instrumental resolution or to there being no appreciable hydride formation under the experimental conditions prevailing.

In all cases only negligible core-level shifts ($\simeq 0.2$ to 0.4 eV) were observed on hydriding, which shows that little chemical electron bonding occurs.

Discussion

The hydrides of transition elements can be quite different on their chemical nature. An excellent summary and review of the topic was given by Gibb (1962). In this early work already was pointed out the question of stability of a hydrides, the tendency that its formation depends strongly on how many *d*-electrons exist in the metal. Metals having a lot of *d*-electrons (late-transition metals), have strong metallic bonds. There is a little reason to form stable hydrides (except Pd), but the early transition metals can gain energy by forming chemical bonds with H-atoms, therefore to react to hydride. In the surface region of the metals the situation can be derived from the bulk properties, hence our investigations are relevant to the bulk properties. The difficulties can be arrise only when the strength of chemisorptive bond is comparable to the hydridic one (Christmann (1988)). These effects are not important in the case of metals investigated by us.

Scandium, yttrium, lanthanum and gadolinium all form hydrides that can be classified as metallic. The dihydrides are characterized by high stability, which implies a low equilibrium hydrogen pressure so that at room temperature they are stable even in a vacuum (Gimzewski et al. (1977)). The structure of the hydrides remains cubic up to composition LnH_2.

For each metal a new valence band is formed as the hydrogen exposure is increased, which has a theoretical proof (Tammerman and Pindor (1982)). The hydrogen-derived valence band was found to be broad ($\simeq 4$ eV).

Theoretical predictions (Brousseau—Lahaye (1975); Christmann (1988); Kovalczyk (1976); Lamartine (1980)) and other experimental observation (Skala et al. (1982)) have indicated a new band below the Fermi level. This band can be doubled (Gupta (1981)) at the dyhidrides (the second band due to the interaction of the two H-atoms in the unit cell).

The position and the slope agree well with the theoretical predictions and other experimental results (Osterwalder (1985)), however these results are not enough deciding of our charge transfer problem. The analysis of the measured changes in the plasmon energy loss are more promising, because of the large sensitivity of the plasmon energy loss on to collective states in the vicinity of Fermi level.

The well-know plasmon frequency can be described by the classical expression (Dresselhaus et al. (1953), Pines (1955)).

$$\omega_p = \sqrt{\frac{4\pi e^2}{m}} \tag{1}$$

where n is the valence electron density per atom and m and e are the free-electron mass and charge respectively. The plasmon frequency and thus the energy are proportional to $n^{1/2}$. This expressions can be modified by the effective mass (m^*) (Dresselhaus (1953)) or the average mass (m^+) (Pines (1955)), depending on the real processes. At the pure metal in very early transition elements the free electron approximation ($m = m^*$) is good, because of the small amount of the d-electrons in the band. It can be clearly checked for example on the Sc metal, where the measured plasmon energy loss is 13 eV ± 0.3 eV, in good agreement with the calculations based on the free-electron model (12.96 eV). In the case of the saturated hydrides (pure di- and trihydrides) the band structure has two, — in many cases separated, — bands in valence-energy region. The measured plasmon energy loss corresponds to the conduction band. Hence the plasmon energy changes between pure metal and pure hydride gives information corresponding to the 2 or 3 added electronic states into the band (See Gibb (1962)). The plasmon energy loss measurements are sensitive for the changes during hydrogenation. Suppose that the logarithm of the explosure is proportional with the actual concentration of hydrogen in the measured surface layer and knowing the quadrate of the plasmon energy proportional with n/m^*; we expect that the logarithm of the exposure *vs.* E_p^2 will be linear. More precisely the deviation from the linearity is caused by

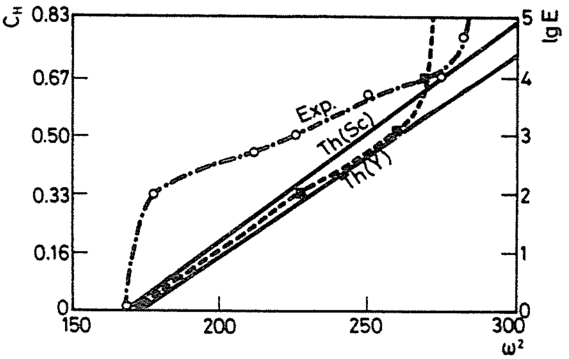

Fig. 4. The dependence of the plasmon energy by the hydrogen exposure
○ — Scandium, ■ — Yttrium, Th(Sc) and Th(Y) are the theoretically expected curves

the change of the effective mass of electrons in measured collective states. The dependence is given at Fig. 4. The deviation from the linearity is obvious, showing the changes of the m^* at the hydrogenation, indicated the processes in the conduction band. Consequently the careful evaluation of the data can give a measured primer information on the changes of the effective mass, therefore on the changes of the symmetry of the electronic wave-functions from the free 's-like' to the much localised '*d*-like' one. Hence we can directly measure the hybridisation occurring at the hydrogenation process. In the first steps of the hydrogenation is given a small amount of hydrogen into the material.

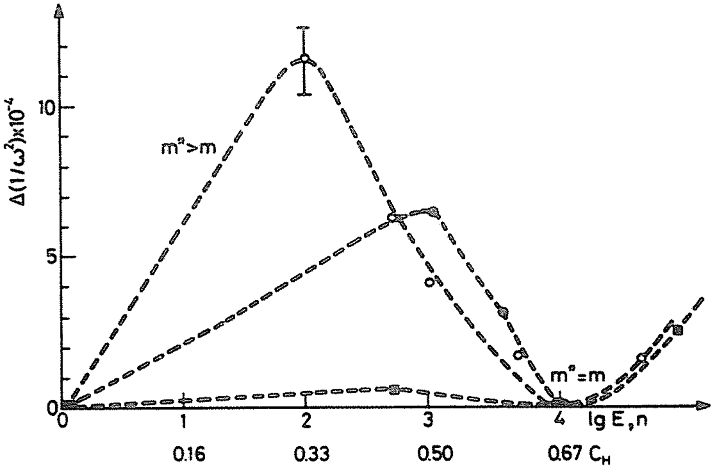

Fig. 5. The comorisan of our result with data obtained for Ti (Lamartine et al. (1980))
○ — Scandium, ■ — Yttrium, + — Titan
For the magnification of the effect the shift in ω^{-2} have been shown versus lg E (or C_H)

The hydrogen is solved, which means that the *d*-type holes in the electronic band of the transition metal are filled generally by the electrons transfered from the hydrogen (Gupta and Burger (1980)).

The effective mass of the transferred electrons occupying the *d*-holes are more then the same in the free case. (For example the decreasing of the bulk susceptibility (Schlapbach et al. (1983) by the hydridizing of Ni suggests the same picture. (The charge transfer in this case goes from the hydrogen ion to the metal.

This picture corresponds nicely with the measured data Ti—H system (Lamartine et al. (1980)) interpreted as being caused by the transfer of electrons from the hydrogen into the empty energy bands of titanium by the growing hydrogen-concentration in the system. The data measured by (Lamartine et al. (1980)) are shown for comparison with our measurements on the Fig. 5. The axis of concentration is fitted to the dihydrid concentration. From these data we can conclude that in the small and medium concentrations of hydrogen (below the dihydrid concentration) the charge transfer goes from the hydrogen to the metal.

At the further solution of hydrogen atoms into the material with increasing of the number of hydrogen atoms will open a new localised band at more deeper in energy emphasizing the *s*-behaviour of the electrons in hydrogen. It means, that the electronic density in the original band of the metal will be decreased, and the electrons at the vicinity of E_F playing role in the plasmon energy loss, become more and more *s*-like, hence the effective mass will be decrease.

It means that at the large concentrations (near to the dihydride one) of the hydrogen the system will be characterised by the TM—H_2 (TM is the transition metal) compound, with the well localised new bands below the Fermi level. The density of states at E_F will be lowered at the strong new band below the E_F generated by the hydride compound, and followingly the states at the E_F will be again more free electron like according with the theoretical (Gupta (1981)) and other experimental (Osterwalder (1985)) evidences. Therefore in this situation the charge transfer occurs from the metal to the hydrogen atoms (opposit as was before) supported by observations of (Osterwalder (1985)).

The measured plasmon energy loss reflects to the general number of electrons in the conduction band. The plasmon shift of 3.8 eV in the case of Sc metal is consistent with addition of two electrons from H 1s states to the conduction band, arising the effective valence up to 5.

The elements Ti, Zr and Hf have tetragonal distortion in their stoichiometric compound with H; for which explanation in terms of the Jahn—Teller effect is supposed that at the molecular cluster of TM—H_2 having spatially degenerate ground state, and the energy will be lowered by a distortion which lowers the symmetry of the cluster as well. The internal stresses introducing to the system by hydrogenation can cause the same effect, lowering the total electronic energy by the redistribution of the electronic states in the conduction band. A new bonding peak appears in the density of electronic states below the Fermi level.

The turn in direction of the charge transfer can be happened at the filling of Brillouin zone (Jones zone) creating a critical number of touching points of Fermi-surface with the zone boundary (Szász and Fabian (1988)). This conclude to the phase transition from the dominate metal—metal bonding region to the metal—hydride compound region, removing electrons from the top of the metallic band. The results seems to indicate the presence of the larger density of electronic states near the Fermi level at the introducing hydrogen in, which is lowered by the redistribution of states to lower energies by distortions of the lattice.

This picture is agreed with the conclusion of the other investigations (Ducastelle et al. (1970) and Nagel and Goretzki (1975)), in the case of the system Ti—H, where in the cubic phase (contained of H concentration ratio to the Ti smaller than 1.8), the density of states at the Fermi energy (N/E_F) (is increasing while the phase transition (at H/Ti$\simeq$1.8) is accompanied by lowering of N/E_F). This was true in the Ti—V—H ternary system as well. Thus a metallihydride is forming with the hydrogen 1s electrons entering a low-lying metallic band. We attribute this band to the formation of a new, hydride-derived valence band with two electrons donated from hydrogen 1s states; a proposal which is supported by the APW calculations by Switendick (1970), and by the results reported by both Eastman (1972) and Brousseau—Lahaye et al. (1975).

The plasmon shifts observed on hydriding of these two metals (Tables IIIc and d) also show that an effective valency of 5 is achieved. With gadolinium the observed plasmon shift does not agree closely with the theoretical value, which is attributed to the breakdown of the classical expression for the plasmon energy-loss in the case of this heavier element, and also to the difficulty of determining an exact position for the plasmon satellite peak in the metal *3d* spectrum. From the measurements on E_n we can conclude that europium does not react like the other metals investigated; this is not unexpected in view of the ionic nature of its bulk hydride.

Many questions are connected with the stability and possible phase transition at increasing of the hydrogen.

The conclusion of Temmerman and Pindor (1982), and the unsatisfactory agreement of the experimental and theoretical curves for YH_3 (Fujimori and Schlapbach (1984)) suggest us that the electronic structure (the filling of the *d*-band first of all) have an important role in the stability. Used the Pettifor's calculation (Pettifor (1970)) we can suppose that the number of the d-electrons in the alloy is essential in the point of view of structural stability.

According to the Pettifor's calculation, at $n_d = 4$ the band structure energy is turned to the preferable structure at approx. $n_d = 4.2$. This direct application of calculations for this hydride formation is not exact, but indicates same informations, corresponding with XPS experiments of Fujimori and Schlapbach (1984). The change an XPS spectra of Y—H system happen at $YH_{2.1}$, which is well agreed to the stability criteria, and can explain the unsatisfactory fitting the calculation given on the unchanged phase.

The redistribution of the electronic states at the hydriding process causes the lowering of the total electronic energy, which is one of the stabilising factor of the new phase. For the stability was proposed an interpretation (Switendick (1978)) with the Fermi level at the minimum of the density of electronic states, very similarly to the theory of Nagel and Tauc (1975) for the amorphous alloys. The effect of the hydrogen on stability is clear at many cases of the amorphous metals (Szász and Fabian (1988)) and on the other hand metastable structures depend on in many cases the electronic structure (Szász and Fabian (1988)); Eastman (1972); Brousseau—Lahaye et al. (1975); Fujimori and Schlapbach (1984); Pettifor (1970); Nagel and Tauc (1975); Szász et al. (1988); Voisin and Pasturel (1987). The catalytic effects in the hydrogenation (Schlapbach et al. (1979)) depends on first at all the special hydrogen-bonding in the surface area (Szász et al. (1988)). The excitonic-like hydrogen bonding (Szász and Fabian (1989)) can help the decomposition of molecules observed by L. Schlapbach et al. (1979). At the saturation of the content, an intensive interaction can be happened between the hydrogen ions as observed in metallic glasses (Schroeder and Köster (1983)).

Conclusion

The binary dihydrides of scandium, yttrium, lanthanum and gadolinium are easily formed by exposing the clean metal films to hydrogen gas at 10^{-4} torr pressure. The plasmon satellite shifts on hydriding in dilute cases, supporting the alloy theory of hydride formation for Sc, Y, La and Gd, with the hydrogen atoms donating electrons to metallic states, increasing the effective mass of electrons at E_F.

In each case a new valence band is formed as the hydrogen exposure is increased. The hydrogen-derived valence band for each of the metals was found to be broad ($\simeq 3.5$ eV wide), and symmetrical; its formation is due to the presence of two hydrogen atom states in the metal unit cell. In the stabilisation of different-phases the electron-state changes have a crucial role.

The addition of a third hydrogen atom causes a band-gap to form, and the third hydrogen atom to become bound. The hydride would thus gradually lose its metallic properties between the dihydride and trihydride compositions. Europium metal is a good example. The free atom does not have d-valence electrons and the hydride (EuH_2) is essentially ionic, indicating the presence of a band gap and that the hydrogen 1s electrons are bounded.

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