

**ELECTRON SPECTROSCOPIC STUDIES OF SOME HYDROGEN
IMPLANTED METALS**

Thesis submitted to the

Faculty of Science

University of Poona

for the degree of

COMPUTERISED

DOCTOR OF PHILOSOPHY

in

PHYSICS



by

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June, 1986

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C E R T I F I C A T E

This is to certify that this thesis entitled "Electron Spectroscopic Studies of some Hydrogen Implanted Metals", describes the original research work done by Mr. Sanjai Sinha, under my supervision, for the Degree of Doctor of Philosophy in Physics of the University of Poona. Such material which have been obtained from other sources have been duly acknowledged in this thesis.

N.C.L.,
Pune 8.


Dr. A.P.B. SINHA,
Research Guide

Here's to 'HYDROGEN'

(Isotopes: ^1H , ^2H , ^3H ; electronic configuration $1s^1$; Energy: 13.6 eV)

the fuel of the 'future',
the 'life-support' of the stars !

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MOTIVATION

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R.P. Singh
Documentation Officer

29th July 1986

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Dear Sir,

This is to certify that the NCL Library has received a copy of the Ph.D. thesis entitled "Electron Spectroscopic Studies of some - Hydrogen Implanted Metals" of Mr. Sanjai Sinha, Physical Chemistry Division, NCL, Poona-8.

Yours faithfully,


(R.P. Singh)

MOTIVATION

Research on metal/hydrogen systems has attracted attention for reasons motivated from both a basic as well as applied point of view.

Hydrogen, the first element in the periodic table, has the simplest electronic structure possible: a single electron in a 1s orbital. Intuitively, therefore one would expect binary systems of hydrogen with metals to be simple and well understood. However, it is this unique electronic structure which makes the behaviour of hydrogen in metals more complex. Three models were advocated to explain the nature of the chemical bond in metallic hydrides. The protonic model, which assumes that the hydrogen atom enters the system as a proton, giving up its electron to the metal host to fill the d-band holes. The anionic model, assumes that the hydride ion H^- is formed, while the covalent-bond model assumes that the metal and hydrogen form covalent bonds. However, theoretical studies and recent electron spectroscopic studies have now established that these models are oversimplifications, and the electronic structure and bonding in these materials have only recently begun to be better understood.

Applications of metal/hydrogen systems extend into many areas e.g.,

- 1) Purification of hydrogen, hydrogen filters.
- 2) Hydrogen embrittlement, powder metallurgy.

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- 3) Metal hydrides applied as moderators, reflector, shielding or control materials in nuclear reactors.
- 4) Isotope separation using isotope-dependent properties of metal hydrides.
- 5) The fusion reactor, e.g., interaction of H with the plasma containing wall, permeation of H. Extraction of tritium in lithium.
- 6) Hydrogen technology, water splitting, methane-water splitting.
- 7) Heat storage using metal hydrides.
- 8) Metal-hydride heat pumps for home heating, especially for use of solar heat.

This thesis presents the results of a systematic study by Electron Spectroscopy (XPS, UPS) of some binary metal/hydrogen systems prepared by a non-equilibrium method, namely in-situ, low-energy implantation of molecular hydrogen ions into the metals of interest. The method has the advantage that no contamination is present on the metal surface, which would otherwise mask the effects of hydrogen, and the H/metal ratio can be tuned over a wide range since the equilibrium solubility of the host metal can be overcome.

CHAPTER - 1

1.1 PREPARATION

Metal hydrides are usually synthesized by charging the metal from a reservoir of hydrogen gas or liquid electrolyte containing protons [1,2]. The basic reactions being



In the electrochemical charging method, the metal sample acts as the cathode in the electrolyte. Concentrated orthophosphoric acid (H_3PO_4) or sulphuric acid (H_2SO_4) are used as an electrolyte upto temperatures of at least 500°K. Below room temperature, alcoholic solutions of HCl and H_2SO_4 are used. This electrochemical method has various advantages - simple experimental setup, easy extension to higher concentrations and lower temperatures, and low contamination. In principle, the adjustment of the hydrogen concentration can be accomplished by fixing the electrochemical potential of the sample in relation to the electrolyte. In practice, side reactions occur and the basic phenomenon involved in the process are not well understood. For instance, the reaction $2\text{H}_{\text{ad}} \rightarrow \text{H}_2$ (gas) uses up most of the electric current flowing in the cell. Therefore, the efficiency of charging is often limited to a few percent and depends on sample shape and current density. The normally used cell voltages of 100 mV to 1 V are much higher than the equilibrium voltages for the hydrides. In this case concentrated hydrides are formed rapidly near the surface. They act as diffusion barriers and cause stresses on the surface. Furthermore,

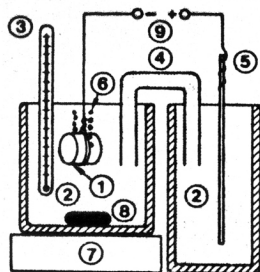


Fig. 1.1 Schematic drawing of arrangement for electrochemical doping of samples with hydrogen: 1 sample polarized as cathode, 2 electrolyte, 3 thermometer, 4 current bridge between hot cathodic (left) and cold anodic (right) compartment, 5 cathode, 6 hydrogen gas bubbles formed by H-H recombination at anode surface during current flow (unwanted but unavoidable side reaction), 7 heater and motor for magnetic stirrer, 8, 9 electric connections to power supply, e.g., potentiostat

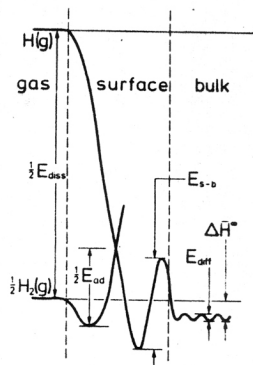


Fig. 1.2 Schematic potential energy diagram of a molecule H_2 and an atom H between gas phase and bulk of niobium. E_{diss} is the dissociation energy of the molecule (2.2 eV/atom H) in the gas phase; E_{ad} , the activation energy of dissociation at the surface; E_{s-b} , the activation energy of transfer of atom from surface into bulk; ΔH^∞ , the enthalpy of exothermic dissolution (-0.3 eV/half molecule for Nb); E_{diff} is the classical diffusion activation energy (0.1 eV/atom for Nb)

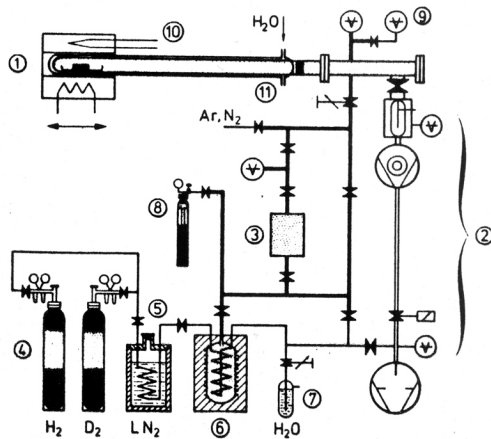


Fig. 1.3 Apparatus for hydriding with hydrogen gas: 1 removable furnace positioned over the sample, 2 pump unit with cold baffle: turbomolecular pump and backing pump, 3 calibrated volume, 4 containers for pressurized gas, 5 cold trap to remove H_2O , 6 palladium-silver permeation cell to purify hydrogen from pressure containers, 7 hydrogen exhaust, 8 container with metal hydride from which very pure hydrogen is released, 9 precision pressure gauges, 10 thermocouple, 11 jacket for rapid cooling with water

electrochemical charging is accompanied by chemical dissolution of the metal, especially when sulphuric acid is used. Fig. 1.1 shows a drawing for an electrochemical cell.

In the gas charging method, the charging rate is determined by energy barriers on the surface as schematically indicated in Fig. 1.2 and by diffusion in the bulk. The metal surfaces are usually poisoned by impurities which modify and enhance the energy barriers shown. An important part of the charging process consists of cleaning the surfaces or modifying them in a way to increase or decrease the surface penetration rate. Gas charging is based on the pressure-concentration (H/M)-temperature curves otherwise known as the solubility curves. Fig. 1.3 shows a modern gas charging apparatus. One variant of this method is to have a high pressure stage fitted to the preparation chamber of an electron spectrometer, and heat and cool the sample under a pressurized hydrogen atmosphere.

Another method is to use energetic proton beams, to force hydrogen into metals which have very low equilibrium solubilities for hydrogen. This method has been used at liquid helium temperatures to prepare dilute and concentrated solid solutions for superconducting experiments [2]. There are some problems with this technique which concern site location of hydrogen and lattice defects. We use this method for preparing binary metal/hydrogen systems. This is discussed in detail in Chapter-3.

1.2 STRUCTURE

Hydrogen atoms prefer one type of interstitial site over all others in a given lattice, however, the physics of site preference has not yet been clarified satisfactorily, apparently owing to the small energy differences involved. The energy difference between various site occupancies is typically of the order of several tens of millielectronvolts, which is comparable with the energy of lattice relaxation and the energy eigenvalue of a hydrogen atom.

Several different techniques have been utilized to determine the lattice location of hydrogen atoms [1,3]. They include neutron diffraction, ion channelling, inelastic neutron scattering. X-ray diffraction is generally not suitable for locating the light hydrogen atoms in the presence of heavy metal atoms. Since X-rays interact with the orbital electrons of an atom, the X-ray scattering power of an atom depends on the number of orbital electrons, Z of that atom, and hence increase regularly with atomic number, e.g. the X-ray scattering amplitude of hydrogen is only about 2% of lanthanum. Since the intensity of scattered radiation is a function of the square of the scattering amplitude, the contribution of the hydrogen atoms in the hydride structure to the X-ray pattern may be as low as 1/3000 that of the lanthanum atoms. Also, the ratio of the amplitude of the actual scattered radiation to that of a single electron called the atomic scattering factor f , is equal to Z , when the Bragg angle, θ , is zero. As θ increases, the atomic scattering factor decreases as a function of $\sin\theta$. Hence, the ratio of metal to

hydrogen scattering amplitudes becomes lower as θ increases, the net result is that the intensity suffers more. Therefore, lattice site location of hydrogen atoms in a hydride by normal X-ray techniques is not a viable method.

Neutron diffraction yields the most direct information on the lattice site location. The de Broglie wavelength λ of thermal (~ 0.1 eV) neutrons is about $1 \text{ \AA}$, the same order of magnitude of interplanar spacings, and hence can be used for crystal structure determination. Since neutrons are scattered primarily by the nucleus, and since the size of the nucleus is considerably smaller than the neutron wavelength, there is essentially no variation of the scattering amplitude with scattering angle. Another advantage is the fact that the scattering amplitude does not vary in any simple manner with Z . Values of the scattering power, or coherent scattering cross-section for neutrons, which is a function of the square of the scattering amplitude, are shown in Table 1.1 for some metals which form hydrides.

Table - 1.1
Scattering powers of some metals for neutrons

Metal	Scattering Power	Metal	Scattering Power
H	1.82	V	0.03
D	5.4	Zr	4.9
Li	0.47	Pd	4.4
Na	1.55	Ba	3.4
Mg	3.60	La	8.7
K	1.5	Ce	2.7
Ca	3.0	Th	12.8
Ti	1.45	U	9.0

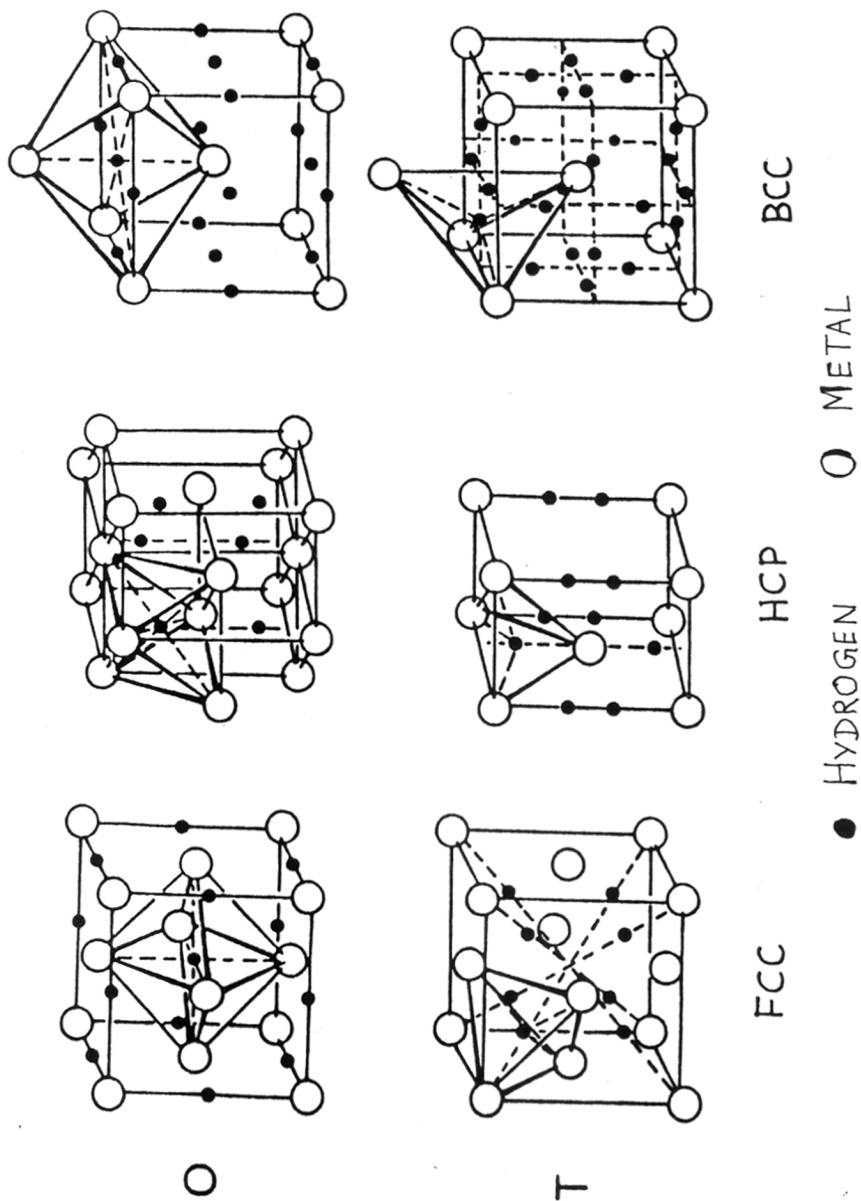


Fig. 1.4

It can be seen that the scattering power of hydrogen is actually greater than those of some heavier elements. Considering the case of lanthanum hydride again, the ratio of scattering power of lanthanum to hydrogen is about 5:1 for neutron diffraction, rather than approximately 3000:1 as in the case of X-rays. Fig. 1.4 shows the tetrahedral (T) and octahedral (O) sites in (a) f.c.c., (b) h.c.p. and (c) b.c.c. lattices, occupied by hydrogen atoms in binary hydrides.

F.c.c. structure

The alkali metal hydrides all have the NaCl-type structure of two interpenetrating f.c.c. lattices i.e. H occupies the O sites and in this respect are similar to the alkali halides. The O site occupancy has been established for H and D in Pd and Ni. A number of f.c.c. hydrides with composition $x = H/M < 1$, including $FeH_{0.13}$, NiH_x ($x < 1.25$) and $RhH_{0.65}$ have been prepared by electrolytic charging or high pressure synthesis. The change in slope of the lattice parameter with composition suggests that H atoms in NiH_x and PdH_x begin to occupy T sites rather than O sites as the concentration x exceeds 0.8. At still higher concentrations ($x > 1.5$) an overwhelming number of metals form hydrides of fluorite (f.c.t) structure in which H occupies T sites. No hydrides are formed with $x > 2$, with d-band metals, indicating that the filling of both T and O sites is not allowed under normal conditions of pressure p and temperature T .

H.c.p. structure

Among the hexagonal hydrides of chromium, manganese, iron,

cobalt, molybdenum ($x = H/M < 1$) prepared by high pressure synthesis, O site occupancy has been established for chromium hydrides in ND experiments.

T site occupancy in solid solutions has been found by ND for H in titanium and zirconium, and dual occupancy for H in yttrium. However for large x ($x < 2$) in titanium, zirconium and hafnium the hydrides have the f.c.c. structure, with hydrogen occupying the T sites. At $x \sim 2$, a f.c.c. to f.c.t. crystal-structure distortion is observed with hydrogen occupying the O_z sites.

B.c.c. structure

It has been firmly established that hydrogen and deuterium atoms occupy exclusively T sites in all phases of Nb-H and Ta-H systems, whereas in the V-H system most of the hydrogen and deuterium atoms enter T sites in the b.c.c. phase and O_z sites in the b.c.t. phases.

Relationship between metal and hydride structure

Metallic hydrides are frequently referred to as interstitial solid solutions. This would imply that there is no change in the metal structure on forming the hydride phase. Table 1.2 gives the structure of the metals and the corresponding metal sub-lattice structure in the hydride phase. It can be seen that in most cases the metal sub-lattice in the hydride phase is different from that of the metallic phase. Thus, the metallic hydrides are apparently definite chemical compounds having their own characteristic structures. Only in the case of V, Nb and Ta

does there appear to be any justification for referring to the hydrides as solid solutions. In this sense, palladium and nickel hydrides also may be considered solid solutions.

Table - 1.2
Structure of metals and corresponding hydrides

Metal	Metal structure	Hydride	Metal sublattice in hydride
Ti, Zr, Hf	hcp	TiH ₂ , ZrH ₂ , HfH ₂	fcc, fct
V	bcc	VH, VH ₂	bct and fcc
Nb	bcc	NbH NbH ₂	bcc and bco fcc
Ta	bcc	TaH	bct and bco
Cr	bcc	CrH, CrH ₂	hexagonal and fcc
Ni	fcc	NiH	fcc
Pd	fcc	PdH	fcc
La, Pr, Nd, Sc	hcp	LaH ₂ , PrH ₂ , NdH ₂ , ScH ₂	fcc
Ce	fcc	CeH ₂	fcc
Sm	rhombohedral	SmH ₂ , SmH ₃	fcc and hexagonal
Gd-Tm, Lu, Y	hcp	dihydrides	fcc
Eu	bcc	EuH ₂	orthorhombic
Yb	fcc	YbH ₂	orthorhombic
Li, Na, K, Rb, Cs	bcc	LiH, NaH, KH, RbH, CsH	fcc
Ca, Sr	fcc	CaH ₂ , SrH ₂	orthorhombic
Ba	bcc	BaH ₂	orthorhombic

Table 1.2 also shows the saline hydrides. The alkali and alkaline earth metals contract upon hydriding while the transition metals generally expand. This is sometimes taken to indicate a fundamental difference in bonding between saline and metallic hydrides. However, even if we assume the protonic or anionic model of bonding in metallic hydrides, the difference in volume change would still occur, since it is a consequence of the relative packing of the metal atoms in each structure, and also of the relative sizes of metal atom and ion radii. The b.c.c. structure of the alkali metals is a rather open one. On hydriding, the more efficiently packed f.c.c. structure is formed. For example, there are 2.5×10^{22} Na atoms/cm³ in the metal, and 3.4×10^{22} Na atoms/cm³ in the hydride. In contrast, most of the transition metals already have the efficient close-packed structure (h.c.p. or f.c.c.) before hydriding. Therefore, the addition of hydrogen to form the hydride will cause expansion.

With respect to structures and densities of hydrides, an interesting and technologically important property of hydrides is the high density of atoms as compared to other materials [1,4]. The number of hydrogen atoms/cm³ in some metal hydrides is actually greater than in solid hydrogen. This is shown in Table 1.3. The high hydrogen densities in the metal hydrides have led to their use as neutron moderators and shielding materials in nuclear reactors. Because of the high hydrogen densities, they are useful also for storing large quantities of hydrogen in small volumes.

Table - 1.3Hydrogen densities in some hydrogen containing compounds

Compound	# of H atoms/cm ³ x 10 ²²
Liquid H ₂ (20°K)	4.2
Solid H ₂ (4.2°K)	5.3
Water	6.7
LiH	5.9
TiH ₂	9.2
ZrH ₂	7.3
VH _{0.8}	5.1
GdH ₂	5.4
GdH ₃	6.4
YH ₂	5.7
UH ₃	8.2

1.3 THE ATOMIC CELL MODEL FOR ALLOYS

Recently it has been demonstrated that a cellular atomic model can account quantitatively for the enthalpy of formation of metallic alloys, both in the solid and in the liquid state. This has also been applied to metallic hydrides [5,6].

The starting point is that the Wigner-Seitz concept of atomic cells, as introduced in theoretical descriptions of pure

metal properties [7], is still meaningful for alloys. In the atomic cell model for pure metals it is important that atomic cells are electrostatically neutral and that the electronic charge distribution within the atomic cell has a horizontal derivative at the boundry between two neighbouring cells. In applying the atomic cell model to alloys, it is assumed that the energy change in bringing a metallic atom from pure metal to an alloy is related to a change of these two boundry conditions.

The heat of solution of (liquid) metal A into (liquid) metal B is

$$\Delta H_{AinB}^{-0} = -V_A^{2/3} P (\Delta \phi^*)^2 / (n_{ws}^{-1/3})_{av} + V_A^{2/3} Q (\Delta n_{ws}^{1/2}) \dots (1.3)$$

The first term accounts for the fact that charge neutrality is no longer required in an alloy. A redistribution of charge will lead to a lowering of the energy of the system; charge transfer can be characterized by a difference in an electronegativity parameter for the two constituent metals. Here the electronegativity parameter is represented by the metallic work function. The energy contribution is written as expected for the energy of an electrostatic dipole layer. It is proportional to the area of the interface between dissimilar atoms (and hence proportional to $V_A^{2/3}$ in the heat of solution of a mole of A atoms, V_A being the molar volume of A) and to the square of the difference in work function, $\Delta \phi^*$. It is inversely proportional to the average electrostatic shielding length (which, in turn, is proportional to the average value of $n_{ws}^{-1/3}$, where n_{ws} is the

electron density at the boundry of a pure metal atomic cell). P is an empirical constant, having the same value for widely different metal combinations. Table 1.4 gives ϕ^* , n_{ws} and $V_M^{2/3}$ for some transition metals and hydrogen.

Table - 1.4

Atomic model parameters for transition metals
and metallic hydrogen

M	ϕ^* (V)	n_{ws} (density unit) (1 $n_{ws} \simeq 4 \times 10^{22}$ e/cm ³)	$V_M^{2/3}$ (cm ²)
3d	Sc	3.25	2.05
	Ti	3.65	3.18
	V	4.25	4.41
	Cr	4.65	5.18
	Mn	4.45	4.17
	Fe	4.93	5.55
	Co	5.10	5.36
	Ni	5.20	5.36
4d	Y	3.20	1.77
	Zr	3.40	2.69
	Nb	4.00	4.25
	Mo	4.65	5.55
	Tc	5.30	5.93
	Ru	5.40	6.13
	Rh	5.40	5.45
	Pd	5.45	4.66
5d	La	3.17	1.4
	Hf	3.55	2.92
	Ta	4.05	4.33
	W	4.80	5.93
	Re	5.40	6.43
	Os	5.40	6.33
	Ir	5.55	6.13
	Pt	5.65	5.64
	H	5.20	3.37

The second term reflects the fact that for two metals A and B the value of n_{ws} will be different. This change of boundary conditions when a cell of A is transferred from pure A to a matrix of B metal leads to an energy change which is proportional to the contact interface area ($V_A^{2/3}$) and the square of the difference in $n_{ws}^{1/2}$ for the two metals. Again Q is a constant for widely different alloy systems. Equation 3 can be rewritten as

$$\Delta H_{AinB}^{-C} = [V_A^{2/3}/(n_{ws}^{-1/3})_{av}] [-P(\Delta\phi^*)^2 + Q_0(\Delta n_{ws}^{1/3})^2] \dots (1.4)$$

which, since the first factor tends to show little variation in practical alloy systems, in a relatively easier expression to handle [5,6].

Energy changes in the atomic model are derived as if they are interfacial energies for blocks of metal in contact. The connection with interfacial energies is reflected in the treatment of the variation of the integral heat of formation with alloy composition and the difference between liquid and solid alloys. For a binary alloy system the maximum enthalpy effect (if taken per mole of A atoms) is obtained for alloys rich in the partner metal, so that A atomic cells are embedded in a B matrix. For more concentrated alloys the enthalpy effect (per mole of A) is reduced by a factor f_A^B , which reflects the degree to which A atoms are in contact with dissimilar neighbours:

$$\Delta H_{alloy}^{int} = C_A f_B^A \Delta H_{AinB}^{-C} \dots (1.5)$$

Here ΔH_{alloy}^{int} is the integral enthalpy effect per mole of

atoms in the alloy, C_A is the atomic concentration of metal A and $\Delta \bar{H}_{AinB}^0$ is the enthalpy of solution of A in B or alternatively the heat of formation of a compound very rich in B. For a series of ordered alloys in a binary system, values of f_B^A have been obtained empirically [8] from experimental data on systems in which $V_A \simeq V_B$ and in which ΔH^{int} is known at a number of ordered compositions. The value of f_B^A for ordered phases is increased relative to the values expected for statistically disordered solid solutions. At the equiatomic composition the difference amounts to a factor of 1.5.

If A and B are of different size, the concentration dependence of ΔH becomes asymmetrical. Heats of solution are proportional to the surface area of the solute atoms, the heat of solution of A in B differs from that of B in A by a factor of $(V_A/V_B)^{2/3}$ [5,6].

The minimum in the ΔH against concentration curve in a binary system lies near the concentration at which the total area of A atoms equals that of B atoms.

Volume effects upon alloying

Within the atomic cell model, volume effects upon the formation of alloys or hydrides are due to a transfer of electronic charge between neighbouring atomic cells. The number of electrons transferred per atom of metal A in a binary alloy, ΔZ_A , is related to the negative term in the heat of formation as follows :

$$\Delta H_{\text{alloy}}^{\text{int}} (\text{neg}) \sim - c_A \Delta Z_A \phi^* \quad \dots (1.6)$$

The energy lowering is proportional to the number of electrons transferred and to the average chemical potential difference over which the electrons are transferred during formation of the dipole layer. As a consequence, combining eqns. 1.6 and 1.5 with the first term in eq. 1.4 we have

$$\Delta Z_A \sim f_B^A \frac{V_A^{2/3}}{(n_{ws}^{-1/3})_{av}} \Delta \phi^* \quad \dots (1.7)$$

The volume effect upon charge transfer from the outer regions of atomic cells A to outer regions of atomic cells B is determined by both ΔZ_A and the difference in the values of n_{ws}^{-1} for the two metals. Hence the volume effect per mole of A atoms is given by

$$\Delta V_m (\text{per mole A}) \sim \Delta Z_A \Delta (n_{ws}^{-1}) \quad \dots (1.8)$$

or combining eqns. 1.7 and 1.6,

$$\Delta V_m (\text{per mol A}) \sim f_B^A \frac{V_A^{2/3}}{(n_{ws}^{-1/3})_{av}} [\Delta \phi^* \Delta (n_{ws}^{-1})] \quad \dots (1.9)$$

The above discussion is perfectly relevant to considerations about the apparent volume of hydrogen in metals. If there is no charge transfer, the apparent molar volume of hydrogen in alloys would be that of metallic hydrogen ($V_m = 1.7 \text{ cm}^3$). In most binary hydrides volume contractions are fairly small. From Table

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1.4, the outer electron density of H metal is near that of Ti. It is only in more electropositive metals with smaller n_{ws} values that the volume contraction upon hydrogenation can be appreciable.

Stability of binary hydrides

Recently Bouten and Miedema [9] have given an empirical account of the enthalpies of formation of transition-metal binary hydrides. These results are discussed because the notion that hydrogen in alloys is a metal for which pure metallic hydrogen is the proper reference state has drastic consequences that apply to binary and ternary hydrides.

The empirical treatment of formation enthalpies of binary hydrides differs from that of binary transition-metal alloys in that a constant, R , is added to the term in brackets in eq. 1.4 :

$$\Delta H(\Delta H_m)(m \text{ small}) \sim [-P(\Delta \phi^*)^2 + Q(\Delta n_{ws}^{1/3})^2 - R] \dots \quad (1.10)$$

The constant R represents a hybridisation energy that is assumed to be generated at the common interface between hydrogen and transition-metal atomic cells. The additional term is introduced as a constant, i.e., for all transition-metal partners R has been given the same value.

A similar hybridization term has been successfully introduced in the empirical account of the heat of formation of alloys consisting of a transition metal and a polyvalent non-transition metal. Although there is no theoretical justification

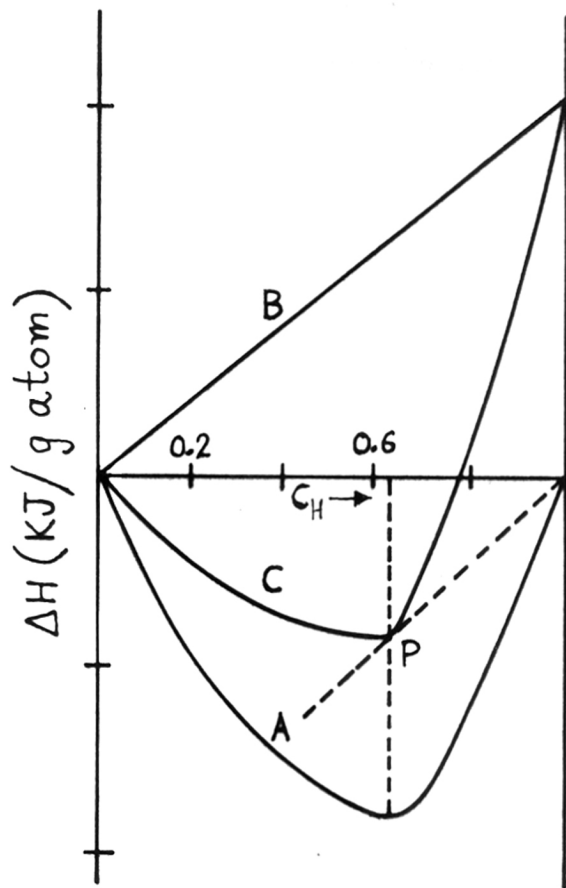


Fig. 1.5

for introducing R as a constant, there is theoretical evidence that strong hybridisation effects exist in transition-metal hydrides [10,11].

The difference between metal-hydrogen and ordinary binary metal systems :

The peculiar character of metal/hydrogen systems is illustrated in Fig. 1.5. If hydrogen were a normal metal, heats of formation of ordered metal-hydrogen compounds would fall on a smooth curve (curve A) as a function of atomic hydrogen concentration, C_H . This would allow for hydrides to be stable at very large C_H values. In Fig.1.5 curve A is not symmetrical around the equiatomic concentration because hydrogen atoms ($V_m = 1.7 \text{ cm}^3$) are much smaller than TM atoms (e.g. Ti($V_m = 10.6 \text{ cm}^3$)). A special problem with hydrides is that the reference state in experimental determinations of formation enthalpies is gaseous H_2 and not metallic H. The large enthalpy differences between these two forms of H add to the smooth curve a term

$$\Delta H_{\text{trans}} = C_H \Delta H (1/2 H_2 \rightarrow H_{\text{metal}}) \quad \dots \quad (1.11)$$

A value of this transformation enthalpy has been derived [9] from the dissociation energy of gaseous H_2 , the theoretical value of the cohesive energy of metallic hydrogen and an average value for the zero-point energy of H atoms in alloys ($\theta_E \sim 1500 \text{ K}$). The result is $\Delta H(1/2 H_2 \rightarrow H_{\text{metal}}) = 100 \text{ KJ/g atom H}$.

In Fig. 1.5 this term is represented by curve B. The result is curve C, from which one finds the point P to the right of which hydrides are unstable at $T = 0$.

For low hydrogen concentration not only curve B but also curve A is linear in C_H , because in H-poor alloys, H atoms will be fully surrounded by metal atom neighbours. If C_H is gradually increased in a series of ordered hydrides, curves A and C start to deviate from the initial linear dependence at that concentration at which H atoms are no longer completely surrounded by A atom neighbours. This is the case when hydrogen atoms start to touch each other. Above point P there are so many H-H contacts that A-H contacts cannot compensate for them. This means that in a M matrix a critical volume fraction of H atoms is exceeded. This volume fraction depends slightly on the maximum stability in the binary hydride system. Therefore there will exist an approximately constant H-H interseparation. The distances r_{H-H} given in Table 1.5 refer to H-H separations for H atoms distributed in an imaginary simple cubic H sublattice.

In the empirical model the difference between hydride-forming and non-hydride forming transition metals is, in fact, not a fundamental one. It is a matter of the relative magnitudes of the alloying energy of hydrogen metal and the large positive transformation energy $H_2 \rightarrow H_{\text{metal}}$.

Table - 1.5

The critical at. conc. of H, C_H^{Max} and the corresponding interatomic distance between H atoms, $r_{\text{H-H}}$, at which hydrides are calculated to be stable at $T = 0^\circ\text{K}$, and $T = 300^\circ\text{K}$, $p = 1 \text{ atm}$.

M	C_H^{Max}		$r_{\text{H-H}} (\text{\AA})$	
	0°K	300°K	0°K	300°K
Sc	73	67	2.27	2.45
Ti	69	62	2.25	2.43
V	60	49	2.32	2.61
Y	75	70	2.32	2.53
Zr	73	67	2.29	2.46
Nb	67	50	2.31	2.60
La	75	71	2.43	2.58
Hf	72	66	2.29	2.46
Ta	65	55	2.36	2.63

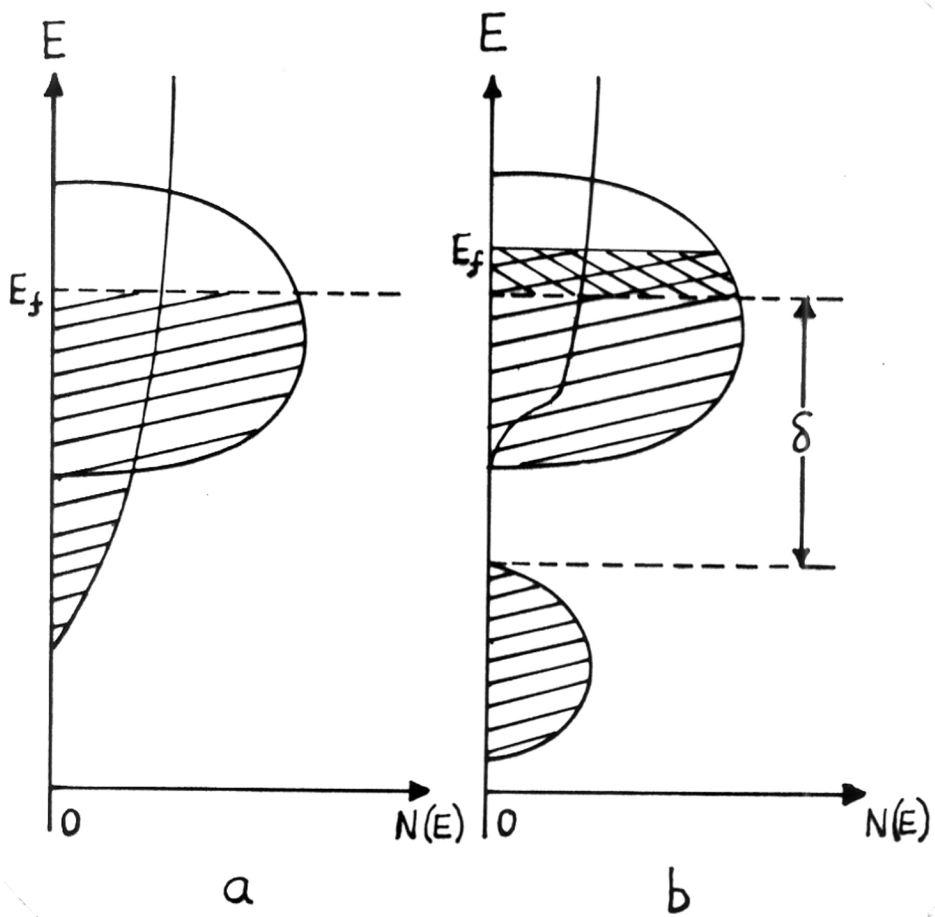


FIG. 1.6

1.4 ELECTRONIC BOND STRUCTURE MODEL

The electronic band structures of transition-metal mono and dihydrides have been extensively studied by Switendick [12]. The picture that resulted is depicted in Fig. 1.6.

The density of states against energy curve of a transition metal can be schematically represented as consisting of a narrow high density d-band and a broad low density energy band of s, p-type electrons. Upon formation of a hydride (mono) the density of states is drastically modified at the low energy side. As a consequence of the introduction of hydrogen a new set of levels is formed, comprising states that have predominant s symmetry around the position of the hydrogen site. Switendick has suggested that the position of the low-lying s-type band is of central importance to the stability of the hydride. These additional states have indeed been demonstrated in UPS and XPS experiments.

For low-concentration hydride phases it has been found that the position of the low-lying s-type band relative to the d band is fairly independent of the hydrogen concentration. In higher hydrides (large C_H) the low-lying level is displaced upwards. If one assumes that there is a connection between enthalpies of formation and the position of the additional level (value of δ in Fig. 1.6), a reduction of δ at relatively large C_H effectively becomes a repulsive interaction between neighbouring hydrogen atomic cells, leading to the concept of a minimum interseparation between H atoms that was first introduced by

Switendick. This minimum separation derived by Switendick equals $2.2 \text{ \AA}^0$, which is quite close to that derived from the empirical model (Table 1.2).

In another approach to band structure Gelatt et al. [11] used a renormalised atom approach. They concluded that in a binary hydride the two-electron states in the metal-hydrogen bonding level are derived from states of the pure metal. In this model the hydrogen can be considered to contribute in additional electron to the metal d-band (Fig. 1.6).

Gelatt et al. pointed out that, although the formation of the additional s-type energy level represents the main contribution to the cohesive energy of a hydride, it is not the only one. There is also a slight lowering of energy of the metal-like d bands and an energy effect connected with the additional electron in the d band.

From his self-consistent calculations Gelatt [13] concludes that neither the protonic or anion models make sense for metallic hydrides. If a given spherical volume is considered around the proton, the electronic charge within this volume appears to be similar for widely different metal-hydrogen systems. It appears that hydrogen in metallic hydrides is first of all a metal. Second, estimates of charge transfer do not make sense if the hydrogen atomic volume is taken to be the same in all metallic situations. Upon accepting or giving up charge ΔZ , a hydrogen cell is assumed to increase or decrease in molar volume by an amount proportional to $\Delta Z / (n_{ws})_H$.

1.5 XPS AND UPS STUDIES

Most of the electron spectroscopic studies of binary hydrides have centered around the IIIA metals namely Sc, Y, the IVA metals, Ti, Zr, Hf, the VA metals, V, Nb, Ta and probably the oldest and most well studied is the PdH system, amongst the transition metals. There are some band structure and density of states calculations for Cr, Mn, Ni and Pt hydrides however to our knowledge no experimental studies exist for these systems.

Fujimori et al. [14] have studied the YH_x system with X-ray photoemission spectroscopy. They identify, for core levels of $YH_{2.1}$ two components, attributed to well screened and poorly screened core-hole states. Taking into account these mechanisms in Y, $YH_{2.1}$, YH_3 , they observe no chemical shift of the core levels between YH_2 and YH_3 , whereas a large chemical shift is seen between Y and YH_2 indicating a Y to H charge transfer.

They also observe for $YH_{2.1}$ and YH_3 , hydrogen induced states at 6 eV. $YH_{2.1}$ shows emission at E_f with highly asymmetric core-level line shapes, with shoulders at the high B.E. side. For YH_3 emission at E_f is weak with symmetric core-levels, consistent with a semiconductor model.

Weaver et al. [15] have studied metal-hydrogen solid solutions of ScH_x , YH_x . They find a single well-defined hydrogen induced feature 5 eV below E_f . In yet another paper Weaver et al. [16] have studied ScH_2 , YH_2 , LuH_2 . They observe a series of bonding-bands from 2 eV to 10 eV below E_f . They also find a

strong *kw* dependence of these bands, and charge transfer to hydrogen sites from core level shifts.

Weaver et al. [17] have studied the electronic structure of TiH_x , ZrH_x and HfH_x using photoelectron spectroscopy and synchrotron radiation. These systems were prepared by the gas charging method. They obtained metal d-derived bands within 3 eV of E_f , and a bonding band centered at ~ 5.5 eV. They have also observed changes near E_f and ~ 7 eV in samples bridging the fcc-fct distortion in ZrH_x , $1.63 < x < 1.94$. These changes have been attributed to a Jahn-Teller effect. The binding energies are shifted towards higher energies indicating charge transfer to the hydrogen site.

Nefedov et al. [18] and Veal et al. [19] have studied the TiH_x , ZrH_x and ZrH_x systems respectively, with XPS. Both these studies show evidence for considerable charge transfer to the hydrogen site. The latter study also shows a strong hydrogen bonding band 7 eV below E_f .

Sasaki et al. [20] and Baba et al. [21] have studied the ZrH_x and TiH_x prepared by hydrogen implantation. They observe charge transfer to hydrogen sites. Sasaki et al. obtain a bonding band at 3.4 eV below E_f for ZrH_x , without any change in $N(E_f)$. Baba et al. observe a bonding band 3.5 eV below E_f for TiH_x , without any change in $N(E_f)$.

Peterman et al. [22] have done a band structure calculation, and photoemission study of the VH_x , NbH_x and TaH_x ($0.6 < x < 1.0$) using synchrotron radiation ($10 < kw < 100$ eV). Their systems

were prepared by the gas charging method. They observe two hydrogen-derived features at ~ 5.5 and 7.5 eV binding energies, and also that the metal d band is substantially modified by the hydrogen interaction, with a decrease in the density of states at the Fermi level $N(E_f)$ compared to the pure metal. However they do not observe any clear evidence for charge transfer. On the other hand, Nefedov et al. [18] have studied the core levels of VH_x ($0.8 < x < 1.93$) and NbH_x ($0.95 < x < 1.86$) with 1486.6 eV radiation and they observe substantial shifts towards high binding energies indicating charge transfer towards the hydrogen site.

Baba et al. [21] and Sasaki et al. [20] have studied the VH_x and NbH_x systems prepared by hydrogen implantation. They observe charge transfer to hydrogen sites but no changes in $N(E_f)$. Baba et al. observe a bonding band at 5 eV below E_f for VH_x and Sasaki et al. observe a bonding band 4.6 eV below E_f for NbH_x .

Eastman et al. [23] have done a UPS study of the PdH system prepared by evaporating Pd in a 5×10^{-6} torr H_2 onto a substrate at 350°C and subsequently exposed it at room temperature to 170 torr of H_2 for 30 mm. They observed hydrogen-induced states centered at 1 eV below the bottom of the Pd-derived d-bands. They however do not observe any changes in $N(E_f)$.

Schlapbach et al. [24] have done an XPS/UPS study on the PdH system prepared by exposure of Pd at 300°K to 15 bar hydrogen and then cooled to 100°K . They observe a d band shift away from E_f , and consequently a reduction in $N(E_f)$. They observe a hydrogen

induced band at a 8 eV below E_f but no emission at ~ 5 eV. They also observe a small charge transfer towards the H site.

Bennet et al. [25] have done an XPS study on the PdH system prepared in a similar manner. They observe new states with considerable d character 8 eV in the valence band, a slight narrowing of the valence-band spectrum, and a shift of E_f out of the d manifold of states. A core-line shift indicates a charge transfer to the H site, with a reduction of the asymmetry of the line.

1.6.1 Metal-Semiconductor Transitions

The effect of hybridisation and electron interaction on the electronic behaviour of d-electron systems is a subject engendering great activity and controversy, especially as far as the metal to insulator transitions are concerned. Some well documented cases are NiO and NiS [26,27].

A different metal to insulator or metal to semiconductor transition is found to occur in the hydrides of the light rare earth metals [28,29]. They form dihydrides and trihydrides and exhibit a temperature-dependent metal to semiconductor transition at $RH_x \simeq 2.75$. This transition is not accompanied by a structural transformation from the initial f.c.c. lattice of the host metal. Kulikov and Tugushev [30] have proposed an excitonic insulator model for these systems with two different types of electron-hole coupling. One type gives rise to a dielectric state whereas the second type gives rise to a semimetallic state.

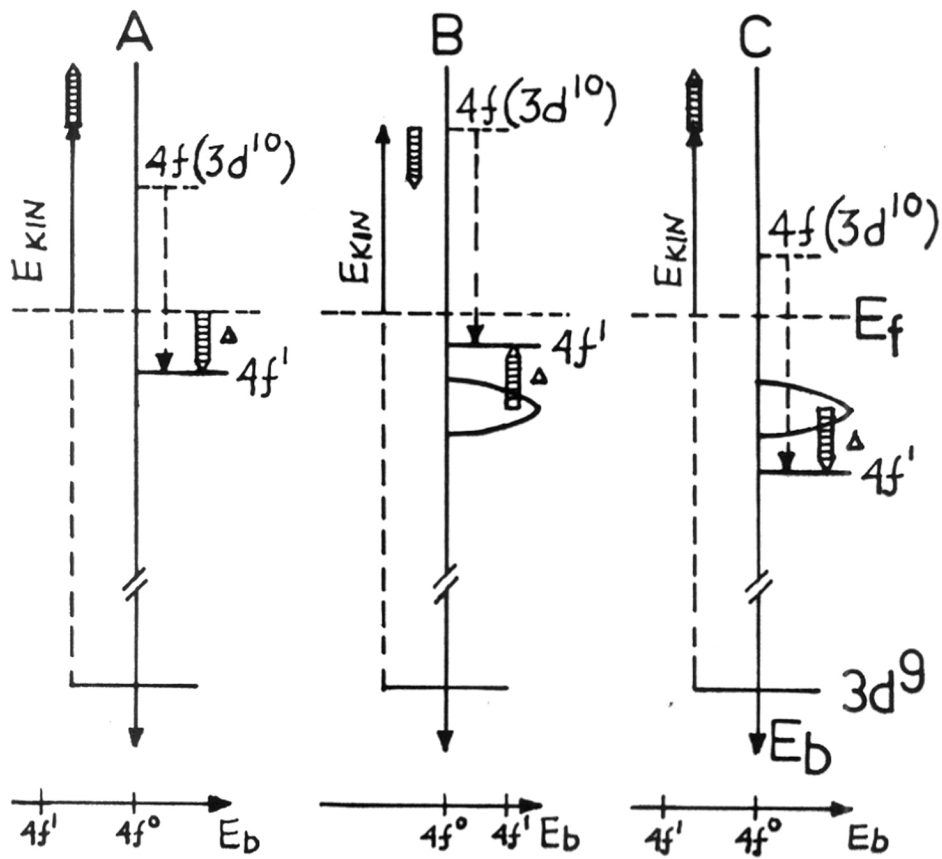


Fig.1.7

A similar behaviour has been observed in the hydride of the intermetallic alloy YFe_2 for very high hydrogen exposures [31].

1.6.2 Core-hole Screening

Photoemission experiments measure a final state which is lacking one electron with respect to the ground state. This core hole represents a strong perturbation in the case of well-localized shells and the surrounding electrons tend to screen this positive charge. The effect is particularly strong for the 3d core holes of light rare-earths as screening by 4f electrons is very efficient.

In LaH_3 , the 3d core hole spectra show, in addition to the main line ($3d^9 4f^0$ final state), intense satellites on the low binding energy side due to well screened $3d^9 4f^1$ final state [32]. This satellite structure has been attributed to the screening of the 3d core hole by a charge transfer "shake-down" process from the new hydrogen induced band to the 4f level pulled down "below" this band (Fig. 1.7).

In the dihydrides, the satellites are even more intense. However, the mechanism is slightly different. The satellites are attributed to a hybridization between the 4f screening states and the hydrogen induced band [29].

1.6.3 Changes in Valency and 4f-localization

The screening effects mentioned in the previous paragraph lead to three well-defined peaks in the core level spectra of intermediate systems according to the three possible final states

$3d^9 4f^2 c^2$, $3d^9 4f^1 c^3$ and $3d^9 4f^0 c^4$ (c denotes s, p and d conduction states). The relative positions of the peaks can provide information about the 4f-core-hole Coulomb interaction U_{fc} and the f-f correlation energy U_{ff} , whereas the intensity ratios give information of the coupling Δ of the 4f states to the conduction electrons and of n_f in the ground state.

These effects have been studied [33] in the compound $CeRu_2$ in which Ce is considered to be tetravalent and having a 4f count n_f of 0.8 electrons. This tetravalency interpreted as a depletion of 4f states is attributed to a combined effect of 4f delocalisation by 4f and conduction band hybridisation ($\Delta \simeq 120$ meV).

On hydriding to give $CeRu_2H_{x,x} \simeq 4$, the Ce 3d satellite peak disappears. The f count n_f increases to unity and Δ decreases to $\simeq 60$ meV, with Ce becoming trivalent.

1.6.4 Heavy Fermion Behaviour

The coefficient γ of the electronic specific heat for most metals and metallic alloys is $\sim 1\text{-}10$ mJ mole $^{-1}$ K $^{-2}$. Recently, however, superconducting compounds with $\gamma \geq 1$ J mol $^{-1}$ K $^{-2}$ in the normal state were discovered (UBe_{13} , $CeCu_6$, $CePb_3$, $CeCu_2Si_2$ etc.), and having an effective mass $m^* \sim 10^2 m_e$ and hence were called heavy fermion systems. This behaviour was attributed to a very narrow band at E_f caused by a weak hybridisation of 4f states with s-p bands.

Recently, it has been observed [34] that Ce hydrides, though magnetically ordered at low temperatures, also exhibit heavy fermion-like behaviour. The electronic specific heat coefficient γ of $\text{CeH}_{2.6}$ amount to $\sim 110 \text{ mJ mole}^{-1} \text{ K}^{-2}$ as compared to $\sim 10 \text{ mJ mole}^{-1} \text{ K}^{-2}$ for γ -Ce, and in photoemission spectra an intense peak growth at E_f is observed below 60°K .

1.7 SUPERCONDUCTIVITY IN METAL/HYDROGEN SYSTEMS

The exciting properties of metal/hydrogen systems, which led to their intense study, awoke interest in a new field of physics when superconductivity was discovered in Th_4H_{15} and PdH in 1970 and 1972 respectively [35]. Because of the high density of hydrogen in these systems, it was speculated that metallic hydrogen might be responsible for the superconductivity. The reason for this speculation being that metallic hydrogen was thought to be a superconductor with a very high transition temperature T_c of more than 100°K .

Superconductivity and Normal-state Parameters

According to the Bardeen, Cooper and Schrieffer (BCS) theory, the microscopic mechanism leading to the superconducting state is the attractive interaction between the conduction electrons via lattice vibrations. Their expression for T_c is

$$T_c = 1.14 \theta_D \exp [-1/N(E_f)V] \quad \dots \quad (1.12)$$

where θ_D is the Debye temperature, $N(E_f)$ is the electronic density of states at the Fermi level, and V an effective pairing potential considered a constant.

Subsequent theories (Eliashberg equations) take into account the details of the electron-phonon interaction. The central quantities in these theories are the functions $\alpha^2(\omega)F(\omega)$ and the Coulomb pseudopotential μ^* , where $\alpha^2(\omega)$ is an averaged electron-phonon coupling function, $F(\omega)$ the phonon density of states, and μ^* describes the repulsive electron-electron interaction.

From the exact, but complex, Eliashberg integral equations, McMillan has derived the useful T_c equation

$$T_c = \frac{\langle \omega \rangle}{1.2} \exp \left[\frac{-1.04 (1 + \lambda)}{\lambda - \mu^* - 0.62 \lambda \mu^*} \right] \quad \text{..... (1.13)}$$

This equation describes T_c quite accurately if the following definitions are used for the average phonon frequency $\langle \omega \rangle$ and the coupling constant λ :

$$\langle \omega \rangle = 2 \int \alpha^2(\omega) F(\omega) d\omega / \lambda \quad \text{..... (1.14)}$$

$$\lambda = 2 \int [\alpha^2(\omega) F(\omega) / \omega] d\omega \quad \text{..... (1.15)}$$

Since, for the majority of the superconductors $\alpha^2(\omega)F(\omega)$ is not known, $\langle \omega \rangle$ is approximated by θ_D and eqn. 1.15 is replaced by

$$\lambda = \frac{N(E_f) \langle J^2 \rangle}{M \langle \omega^2 \rangle} = \frac{n}{M \langle \omega^2 \rangle} \quad \text{..... (1.16)}$$

where $\langle J^2 \rangle$ is an average of the electron-phonon interaction over the Fermi surface, M is the ion mass, and $\langle \omega^2 \rangle$ is an averaged squared phonon frequency. It has been found that for some

classes of materials η varies much less than its factor $N(E_f)$ and $\langle J^2 \rangle$. Hence λ and therefore T_c are governed by the phonon factor $M \langle \omega^2 \rangle$. The dependence of T_c on $N(E_f)$ as given by eqn. 1.16, is in these cases, implicitly contained in $M \langle \omega^2 \rangle$ because the high density of states materials are elastically softer i.e. electron and phonon properties are interconnected.

Depending on the material, the influence of $N(E_f)$ or that of $F(\omega)$ is more obvious or dominant. Generally speaking, high T_c may result from a large $N(E_f)$ and contributions of soft phonon modes in $F(\omega)$ or more precisely, low-frequency contributions in $\omega^2 F(\omega)$.

A further possibility to enhance T_c consists of adding new vibrational modes, by dissolving light elements interstitially in a host lattice. If the ratio of the heavy mass to the light mass is large, the electron-phonon coupling constant λ can be decomposed into an acoustical and an optical part

$$\lambda = \lambda_{ac} + \lambda_{opt} \quad \dots \quad (1.17)$$

It is, however, not possible to restrict the contribution of the heavy mass to λ_{ac} and that of the light mass to λ_{opt} , for an interference term has to be taken into account. The electron-phonon coupling through optic phonons should always lead to an enhancement of T_c unless an intrinsically favourable λ_c is reduced by the addition of interstitials.

Th/H System [36]

The introduction of hydrogen in Th (itself a superconductor with $T_c = 1.37^\circ\text{K}$) enhanced the T_c to values varying from 7.5 - 9.0°K depending upon subtle differences in sample preparation, at a ratio $\text{H/Th} = 3.75$. This ratio gives a stoichiometric system Th_4H_{15} .

The heat capacity was measured from 1.4 to 20°K in both the normal and superconducting states. γ increases from 4.31 to 8.07 mJ/mole K^2 . The Debye temperatures are 163°K for Th and 211°K for Th_4H_{15} . The phonon densities of states was probed by incoherent neutron scattering and the optical PDOS exhibited two broad peaks centered around 150 and 180 meV overlapping with the acoustic spectrum and these phonons are assumed to be responsible for the high T_c of Th_4H_{15} . Cluster approximations show a significant contribution of the f band to the electronic density of states at E_f , which may account for the high γ value observed in the specific heat experiment. Owing to the steep rise of the f band near E_f , its position critically determines T_c .

Pd/H System [37-39]

Pd is not a superconductor due to harmful spin-fluctuations, however the PdH system has shown rather high T_c values for a ratio $\text{H/Pd} > 0.8$. A T_c of 9°K was achieved at $\text{H/Pd} \simeq 1$ and astonishingly high values of 17°K for $\text{H/Pd}_{55}\text{Cu}_{45} \simeq 0.7$, 15.6°K for $\text{H/Pd}_{70}\text{Ag}_{30} \simeq 0.8$ and 13.6°K for $\text{H/Pd}_{84}\text{Au}_{16} \simeq 0.9$. All these systems were prepared by implanting H at liquid He temperatures.

The appearance and enhancement of superconductivity is attributed to three reasons (i) reduction of χ to zero at $H/Pd \simeq 0.6$, or by addition of noble metals, (ii) changes in $N(E_f)$ and (iii) increase in the electron-phonon coupling due to softening of some optic phonon modes.

Al/H System [40]

Al is a superconductor with $T_c \sim 1.2^\circ K$. A high T_c of $6.75^\circ K$ has been achieved in this system after implanting H at liquid He temperatures, to a ratio $H/Al \simeq 2$. This high T_c value has been attributed to changes in the phonon spectrum i.e. change in the electron-phonon coupling constant and the electronic density of states at the Fermi level $N(E_f)$.

Zr/H System [41]

The implantation of H and D leads to an enhancement of T_c upto $3.14^\circ K$ and $4.65^\circ K$ with a saturation at high doses corresponding to the same ratio $H/Zr \simeq 0.13$. Unlike other Zr alloys, the superconducting properties cannot be simply explained by a shift in $N(E_f)$, to higher values due to the electrons of H filling the d-band of Zr.

This T_c enhancement is similar to the Pd/H system. The most striking difference between both systems is the different ratios, $H/Pd \simeq 1.0$ compared to $H/Zr \simeq 0.13$. But pure Zr is a superconductor in contrast to the strongest paramagnetic element Pd. This paramagnetism is believed to be the reason for the absence of superconductivity in Pd. Thus in Pd, a H concentration of

$H/Pd \simeq 0.7$ is needed just to diminish the harmful paramagnetism and create superconductivity above $0.2^{\circ}K$. So in a simple picture this leaves a H concentration of $H/Pd \simeq 0.3$ to further enhance T_c in PdH. This ratio is similar to that of the Zr-H system. As the E_f lies near minimum of the electron density of states a shift to higher or lower energies results in a more or less pronounced increase of $N(E_f)$. This should be helpful for superconductivity. In addition, electron-phonon coupling to the optic H phonon modes could further enhance T_c . Coupling to the optic modes has been shown from measurements of the temperature dependence of the resistance of Zr alloys with high H concentration.

Enhancements of T_c have also been reported in the simple metals Cd, In, Sn and Pb after implantation of H, at liquid helium temperatures.

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CHAPTER - 2

2.1.1 Historical Perspective

Photoelectron spectroscopy is presently one of the most important techniques for probing the electronic structure of atoms, molecules and condensed matter.

The basis for photoelectron spectroscopy is the 'photoelectric effect'. In his historic paper entitled 'On a heuristic point of view concerning the generation and conversion of light', Einstein in 1905, [1], explained the photoelectric effect in terms of the simple relationship:

$$E_{\text{kin,max}} = \hbar\omega - \phi \quad \text{.....} \quad (2.1)$$

i.e., the maximum kinetic energy E_{kin} of a photoemitted electron is equal to a quantized package of light energy $\hbar\omega$, related to the classical frequency ω , minus the work necessary to release the electron from the emitter, the work function ϕ .

Einstein's relationship (eqn. 2.1) remains to-date the most fundamental relationship upon which any interpretation of photoemission spectra is based, and forms the basis of the single- (independent) electron approximation which assumes that the total energy of the incident photon is absorbed by a single electron in the excitation process.

X-ray photoelectron spectroscopy has developed into a powerful method for probing atoms, molecules and solids under the stimulation of pioneering studies beginning in the early 1950s, notably by Siegbahn and co-workers at Uppsala University [2,3].

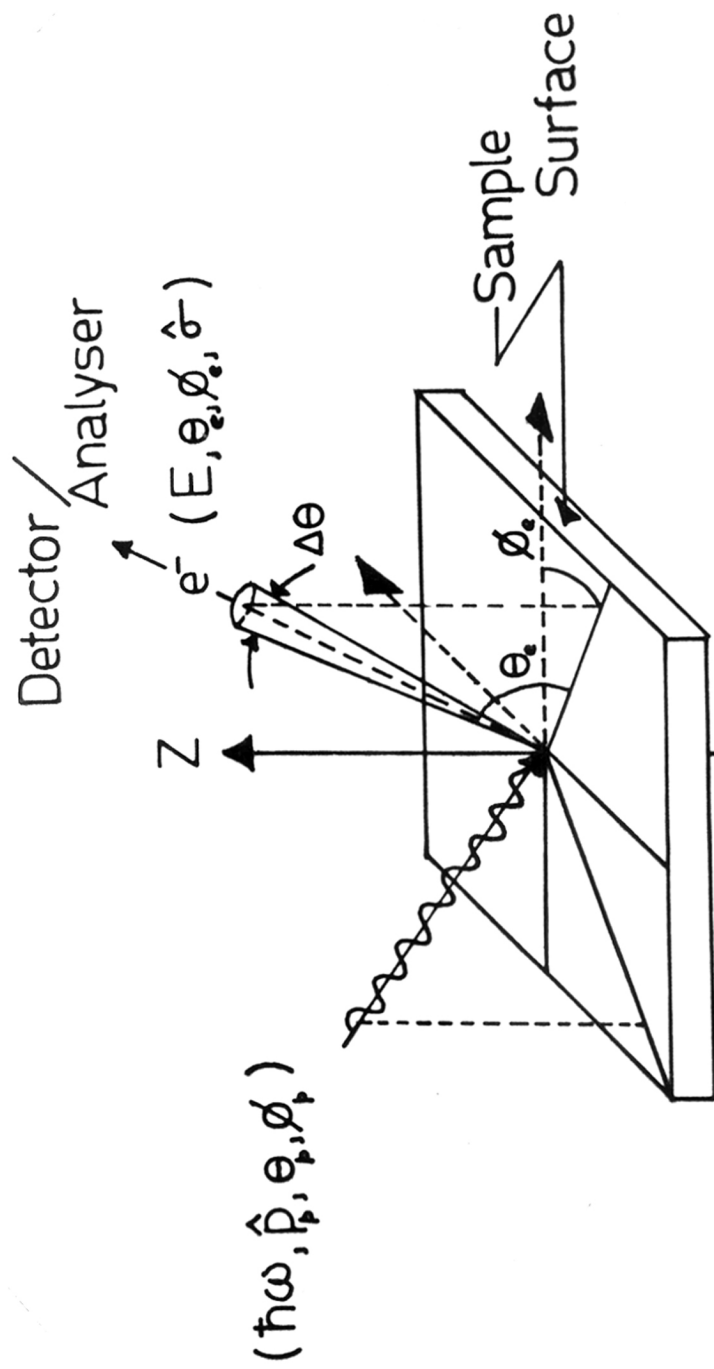


Fig. 2.1

Meanwhile, ultraviolet photoelectron spectroscopy (UPS) was developed separately by various groups due to the lack of suitable tunable photon sources spanning the ultraviolet and X-ray regimes. Prominent in the development of UPS were Apker et al. [4], Allen and Gobel [5] and Spicer and Simon [6], all of whom realised that the electronic structure of a solid could be probed in this way.

2.1.2 The Fundamental Experiment

The fundamental experiment in photoelectron spectroscopy (photoemission) involves illuminating the sample to be studied to a flux of nearly monoenergetic radiation with mean energy $\hbar\omega$ and then observing the energy distribution of the emitted electrons. This is depicted in Fig. 2.1.

The photoelectron current measured by an ideal spectrometer, i.e., one capable of resolving the energy E , angles θ_e (polar) and ϕ_e (azimuthal), and electron spin $\hat{\sigma}$, in a function F of the parameters of the impinging photon and the settings of the electron spectrometer:

$$I = F(E, \theta_e, \phi_e, \hat{\sigma}; \hbar\omega, \vec{p}_p, \theta_p, \phi_p) \dots \quad (2.2)$$

where θ_p and ϕ_p give the direction of the incoming photon, $\vec{p}_p$ its polarization, and ω its frequency [7]. Depending upon the information desired, and the available experimental equipment, a judicious selection of the parameters in eqn. 2.2, must be made. The energy distribution curve (EDC) technique measures I as a function of E with all other parameters fixed. If θ_e and ϕ_e are

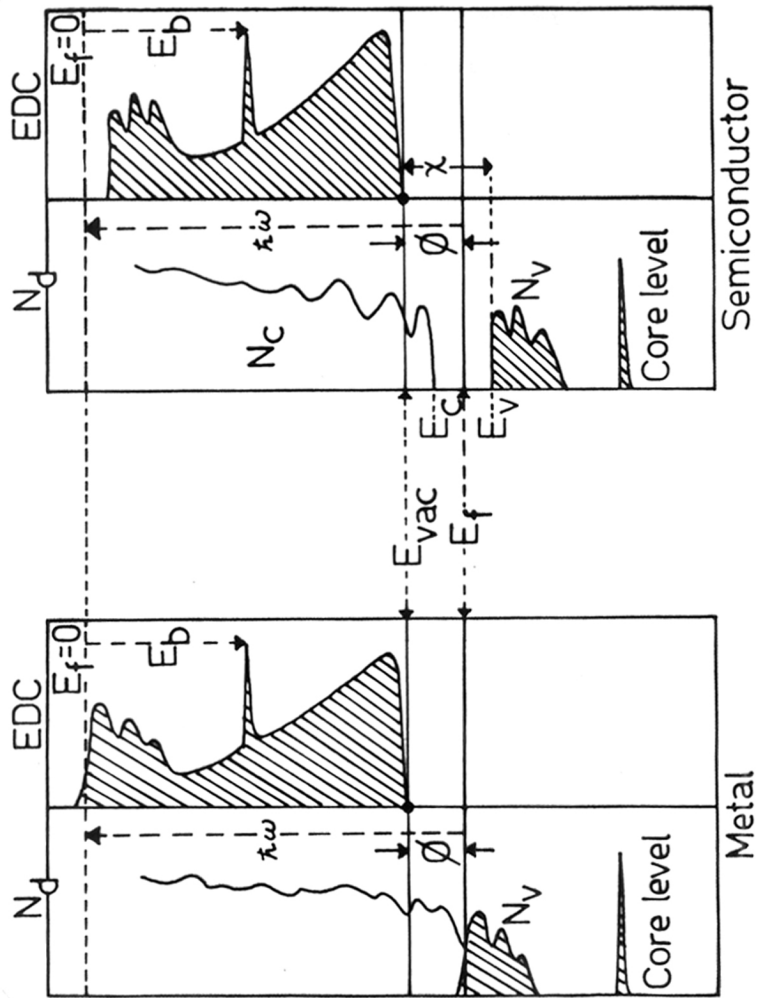


Fig. 2.2.2

resolved and used as variable parameters, one has the technique of angle-resolved photoemission. If $\vec{p}_p$ is varied, one observes the vectorial photoeffect. The technique of constant initial state spectroscopy (CIS) arising whenever $\hbar\omega - E$ is kept constant while sweeping $\hbar\omega$ and E . By analysing $\hat{\sigma}$, one obtains spin polarized photoemission.

Typical photoelectron spectra, or energy distribution curves (EDCs) for both a metal and a semiconductor (insulator) are shown in Fig. 2.2. It is assumed that the contact between sample and spectrometer is ohmic.

Let us assume that the core level in Fig. 2.2 is at a binding energy E_B' with respect to the vacuum level. If E_k' is the kinetic energy of the emitted electron corresponding to this level following excitation by a photon of energy $\hbar\omega$, then

$$\hbar\omega - E_k' = E_{\text{vacuum}} - E_i \quad \dots\dots (2.3)$$

where E_{vacuum} is the vacuum level and E_i is the initial-state energy of the system. Normally it is assumed that

$$E_{\text{vacuum}} - E_i = E_B' \quad \dots\dots (2.4)$$

hence

$$\hbar\omega - E_k' = E_B' \quad \dots\dots (2.5)$$

This procedure is commonly referred to as the one-electron approximation. It ignores the fact that after excitation of the photoelectron, the remaining electrons can relax towards the hole created. What is really measured is the difference in energy

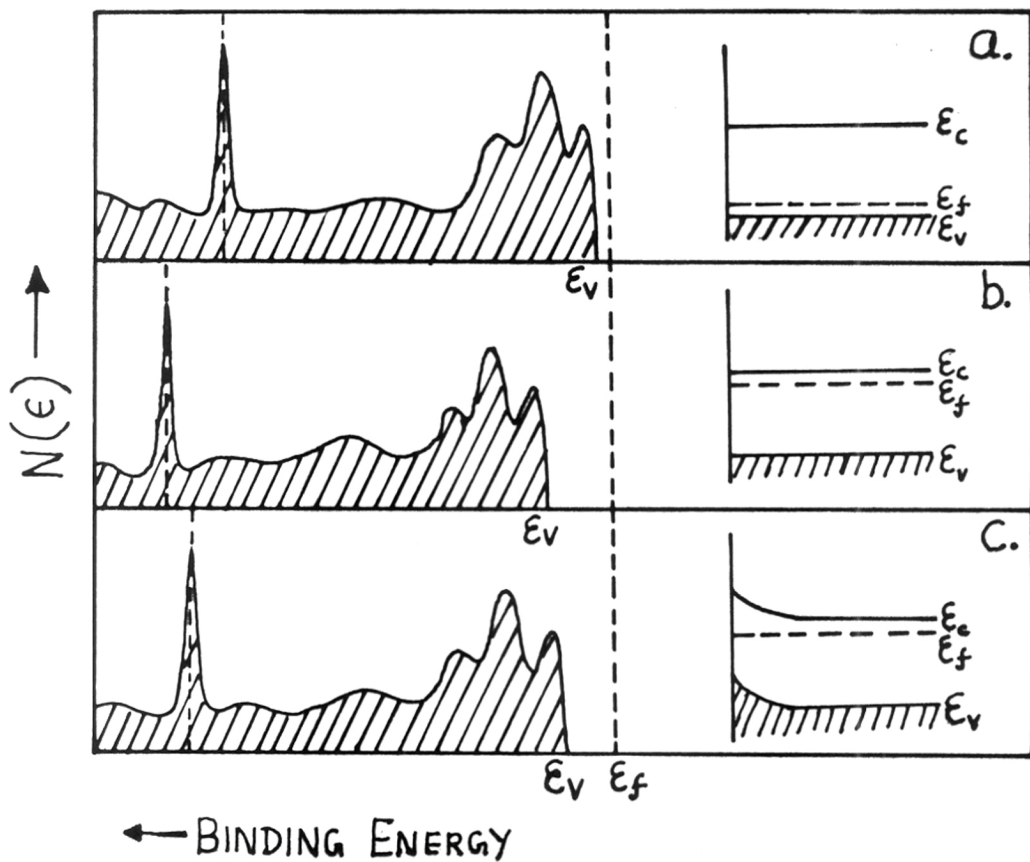


FIG. 2.3

between the initial state of the N-electron system and the final state with N-1 electrons, with the energy involved in the relaxation being carried away by the photoelectron. Strictly speaking, one can only derive binding energies using eqn. (2.5) provided that when one electron is removed from an N-electron system the energies associated with all orbitals are the same in the ion as in the neutral system. This well-known result is known as Koopmans' theorem [8].

In eqn. (2.5), the zero of energy is taken as the vacuum level. It is more customary to take the zero of energy as being the Fermi level E_f , in which case we have

$$\hbar\omega - E_k = E_B \quad \text{.....} \quad (2.6)$$

where both E_B and E_k , are measured with respect to E_f (and $E_B - E_k = \phi$, the work function). Most electron spectrometers measure E_k rather than E_k' , hence for the case of a clean metal where E_f is well defined, E_B may easily be found.

In case of semiconductors (insulators) there exist serious problems with respect to the above procedure for measuring E_B and E_k with respect to E_f . Fig. 2.3 depicts some situations arising in non-metallic solids.

In Figs. 2.3a and 2.3b, the Fermi level E_f is pinned at the acceptor and donor levels respectively, and hence the binding energy of the core level, measured with respect to E_f is drastically different in each case. This effect has been observed in many systems [9]. For non-metallic solids,

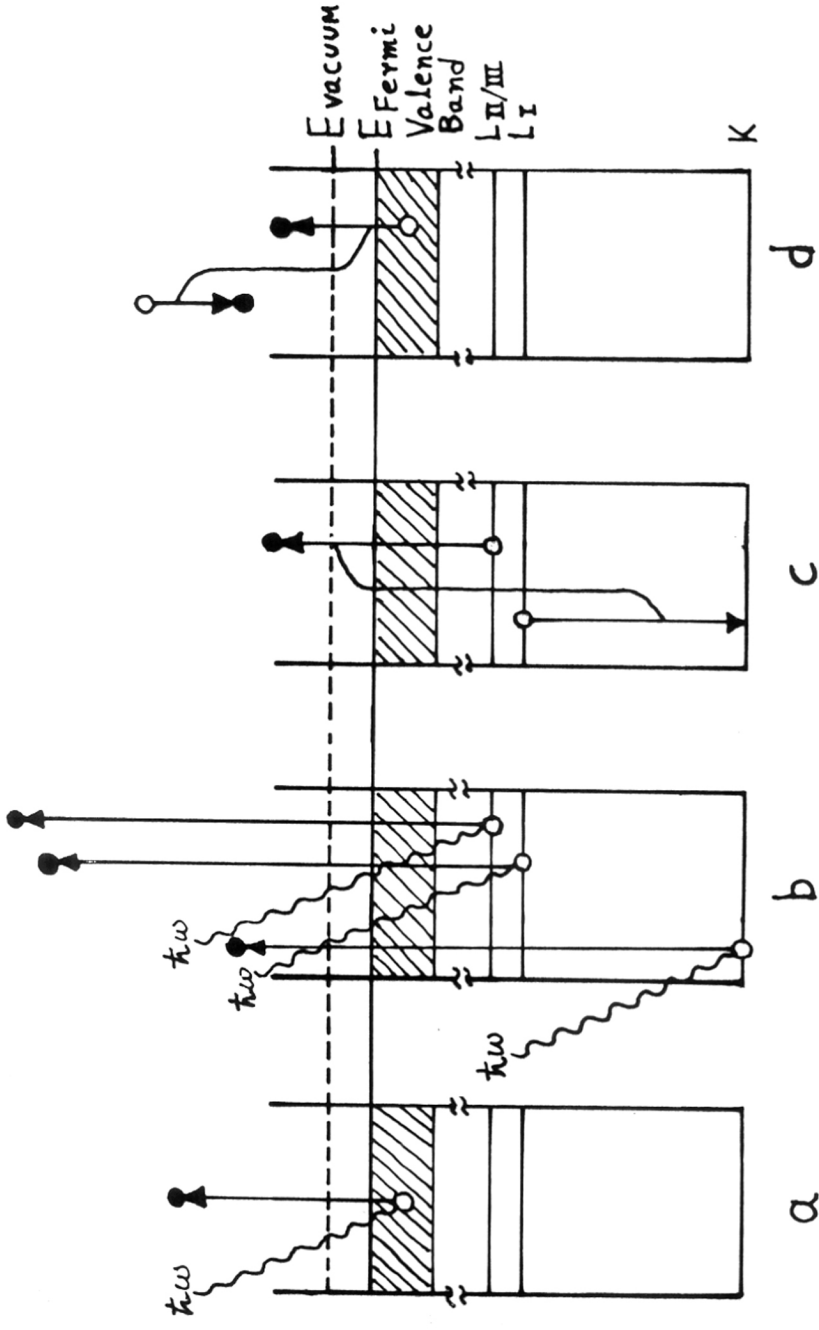


Fig.2.4

therefore, a better procedure is to establish the binding energy of occupied energy levels with respect to the upper edge of E_v . This effect has been used to map the position of E_f in the mobility gap of a-Si:H based films, as a function of doping, and the statistical shift due to temperature [7,10,11].

Another effect appearing in non-metallic solids is the band bending and/or Fermi level pinning due to intrinsic surface states (due to dangling bonds) or extrinsic surface states (adsorption of monolayers of atoms on the semiconductor surface) inside the band gap. This is depicted in Fig. 2.3c. These shifts again provide an excellent means of following the Fermi level position, and also for investigating the mechanisms involved in Schottky barrier formation [9,12,13].

It is also clear from Fig. 2.2 that if the total width B of the energy distribution curve can be accurately established then it is possible to find the work function ϕ for a metallic sample; it is simply $(\hbar\omega - B)$. The situation is more complex for a non-metallic sample. In this case $(\hbar\omega - B)$ simply gives the separation of the valence band edge and the vacuum level i.e. the photothreshold, provided the bands are flat.

2.1.3 Basic Physical Processes

The various basic physical processes [14] which would contribute to an XPS energy distribution curve are depicted in Fig. 2.4.

Fig. 2.4a shows photoexcitation from the highly delocalized

valence band states and Fig.2.4b photoexcitation which may occur directly from a highly localized core level. The fact that the eigen-functions of the electronic states are either strongly localized on individual atoms or delocalized over many atomic centers provides for physical phenomenon which serve to distinguish between the UPS and XPS regimes.

After excitation and emission of a core electron, the remaining core hole state can be filled either by radiative de-excitation, producing a characteristic X-ray emission spectrum or by the non-radiative Auger process. Fig. 2.4c shows schematically a KLL Auger process.

Fig. 2.4d depicts the secondaries and losses associated with the photoexcitation process. These are explained later on in this chapter.

2.2.1 The Three-Step Model

The three-step model of photoemission was first proposed by Spicer [15]. In this model, photoemission is treated as a sequence of

- i) the optical excitation of an electron,
- ii) its transport through the solid which includes the possibility for inelastic scattering by other electrons, and finally,
- iii) the escape through the sample surface into the vacuum.

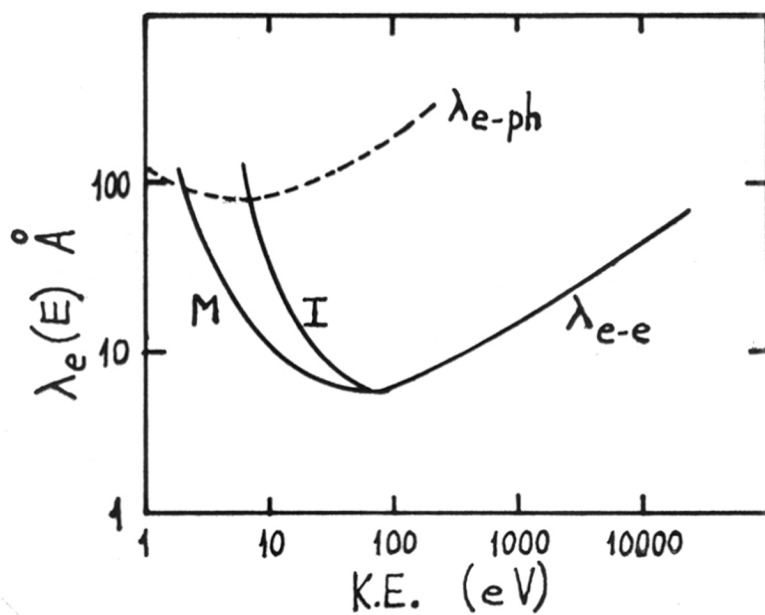


Fig. 2.5

The energy distribution curve (EDC) of the photoemitted electrons $I(E, \omega)$ is consequently a sum of a primary distribution of electrons $I_p(E, \omega)$ that have not suffered an inelastic collision and a background of secondary electrons $I_s(E, \omega)$ due to electrons that have undergone one or more inelastic collisions:

$$I(E, \omega) = I_p(E, \omega) + I_s(E, \omega) \quad \dots \quad (2.7)$$

The primary distribution is factorized according to the three-step model into a distribution of photoexcited electrons $J(E, \omega)$, a transmission function $T(E)$, and an escape function $D(E)$:

$$I_p(E, \omega) = J(E, \omega) \cdot T(E) \cdot D(E) \quad \dots \quad (2.8)$$

Under the assumption that the inelastic scattering probability can be characterized by an isotropic electron mean free path $\lambda_e(E)$, $T(E)$ is given by

$$T(E) = \frac{\lambda_e(E) / \lambda_{ph}(E)}{1 + \lambda_e(E) / \lambda_{ph}(E)} \quad \dots \quad (2.9)$$

$\lambda_{ph}(E)$ the photon penetration depth and exceeds a hundred Angstroms, and $\lambda_e(E)$ is the photoelectron mean free path.

The energy dependence of the escape depth of excited electrons [14] is depicted in Fig. 2.5, which gives a master curve which has to be considered as an average of measurements on many different materials. $\lambda_e(E)$ is limited over most of the energy range by electron-electron interactions (λ_{e-e}) for both insulators (I) and metals (M). For insulators, electron-phonon

events limit the escape depth. Collective losses may be excited above 10 eV and lead to escape depths of one or two atomic layers, the minimum of the curve. Cross-section variations increase the mean free path at energies of the order of Kiloelectron volts. The short mean free path of the electrons effectively limits the sampling depth in PES to ~ 4 to 20 atomic layers. It should be kept in mind, however, that the genuine surface electronic structure extends no more than 2 to 3 atomic layers into the bulk, hence the EDC or PES normally represent largely bulk properties. On the other hand, with the proper choice of E around the minimum in λ_e , PES can be turned into a sensitive probe of surface electronic structure.

The factor $D(E)$ takes into account the fact that the photoelectrons have to overcome a surface barrier before they emerge into the vacuum. This confines the emerging electrons to an escape cone with an opening angle 2θ given by

$$\cos\theta = \sqrt{B/E} \quad \text{.....} \quad (2.10)$$

where B , the barrier, is equal to the work function ϕ of the sample plus the Fermi energy E_f .

The gist of the three-step model is that $T(E)$ and $D(E)$ are slowly-varying functions of E so that the structure in the primary photocurrent $I_p(E, \omega)$ reflects the structure in $J(E, \omega)$.

2.2.2 Core-level Chemical Shifts

The discovery, during the early days of XPS, that non-equivalent atoms of the same element in a solid give core-level

peaks with measurably different BE's had a stimulating effect on the field. The BE difference was labelled the chemical shift. Non-equivalent atoms arise in several ways: difference in formal oxidation state, difference in lattice site etc. The physical basis of the chemical shift effect is illustrated by a relatively simple model used with success to interpret chemical shift data - the charge potential model [3], according which:

$$E_i = E_i^0 + kq_i + \sum_{j \neq i} \frac{q_j}{r_{ij}} \dots\dots (2.11)$$

where E_i is the BE of a particular core level on atom i , E_i^0 is an energy reference, q_i is the charge on atom i and the final term in the equation sums the potential at atom i due to 'point charges' on surrounding atoms j .

If the atom is considered to be an essentially hollow sphere on the surface of which the valence charge q_i resides, then the classical potential inside the sphere is the same at all points and equal to q_i/r_v , where r_v is the average valence orbital radius. A change in the valence electron charge (density) of Δq_i changes the potential inside the sphere by $\Delta q_i/r_v$. Thus the BE of all the core levels will change by this amount. Moreover, as r_v increases, the BE shift for a given Δq_i will decrease. If the summation term is dubbed V_i , then the shift in BE for a given core level of atom i in two different environments is

$$E_i^{(1)} - E_i^{(2)} = k(q_i^{(1)} - q_i^{(2)}) + (V_i^{(1)} - V_i^{(2)}) \dots\dots (2.12)$$

The first term ($k\Delta q_i$) clearly ensures that an increase in BE accompanies a decrease in valence electron density on atom i . The second term is not to be underestimated since it has the opposite sign to Δq_i . In molecular solids the atoms j are basically the atoms bonded to atom i , but in ionic solids the summation extends over the whole lattice; this is closely related to the Madelung energy of the solid and for this reason V is often referred to as a Madelung potential.

Eqns. 2.11 and 2.12 are oversimplified. A major simplification of the charge potential model is that it neglects relaxation effects, i.e. no account is taken of the polarizing effect of the core hole on the surrounding electrons, both intra-atomic (on atom i) and extra-atomic (on atoms j). This is one example of a final-state or many body effect which are discussed later in this chapter.

2.2.3 Spin-Orbit Splitting

The core-level structures in XPS spectra are a direct reflection of the electronic structure of atoms. These levels have variable intensities and widths and non-s levels are doublets.

The doublets arise through spin-orbit splittings. Two possible states, characterized by the quantum number j ($j = l \pm s$) arise when $l > 0$. The difference in energy of the two states, ΔE_j , reflects the 'parallel' or 'antiparallel' nature of the spin and orbital angular momentum vectors of the remaining electron. The magnitude of this energy separation is proportional to the

spin-orbit coupling constant ζ_{nl} which depends on the expectation value $\langle 1/r^3 \rangle$ for the particular orbital. The separation can be many electron volts. ΔE_j is therefore expected to increase as Z increases for a given subshell (constant n, l) or to increase as l decreases for constant n . The relative intensities of the doublet peaks are given by the ratio of their respective degeneracies $(2j+1)$. Table 2.1 gives the area ratios and designations (nl_j) of spin-orbit doublets.

Table - 2.1 : Spin-orbit splitting parameters

Subshell	j values	Area ratio
s	1/2	-
p	1/2, 3/2	1:2
d	3/2, 5/2	2:3
f	5/2, 7/2	3:4

The basic parameter which governs the relative intensities of core-level peaks is the atomic photo-emission cross-section σ . Values of σ have been calculated and tabulated by Scofield [16].

The peak width, defined as the full width at half-maximum (FWHM) ΔE , is a convolution of several contributions,

$$\Delta E = (\Delta E_n^2 + \Delta E_p^2 + \Delta E_a^2)^{1/2} \quad \dots\dots (2.13)$$

where ΔE_n is the natural or inherent width of the core level,

ΔE_p is the width of the photon source and ΔE_a the analyser resolution, all expressed as FWHM, and having a Gaussian line shape.

The inherent line width of a core level is a direct reflection of the uncertainty in the lifetime of the ion state remaining after photo-emission. Thus from the uncertainty principle we obtain the line width (in energy units).

$$\Gamma = \frac{h}{\tau} = \frac{4.1 \times 10^{-15}}{\tau} \text{ eV} \quad \dots (2.14)$$

with Planck's constant h expressed in eV-sec and the lifetime expressed in seconds.

2.3.1 Many-body or Final-State Effects

A single-electron theory of photoemission often provides not only an excellent starting point but also a quite adequate description of the energy-and angle-resolved photoemission spectrum from solids. However, there is a sizable class of photoemission events, usually typified by the breakdown of Koopman's theorem, in which the independent- (or non-interacting) electron theory provides a qualitatively inadequate description [14].

Consider, a specific example, the binding energy of an electron in a particular orbital of an N -electron system. Rigorously, the binding energy, defined as the energy required to bring the electron to rest infinitely far from the remaining $(N-1)$ electrons (and N positive charges), is the difference in

ATOM SOLIDS

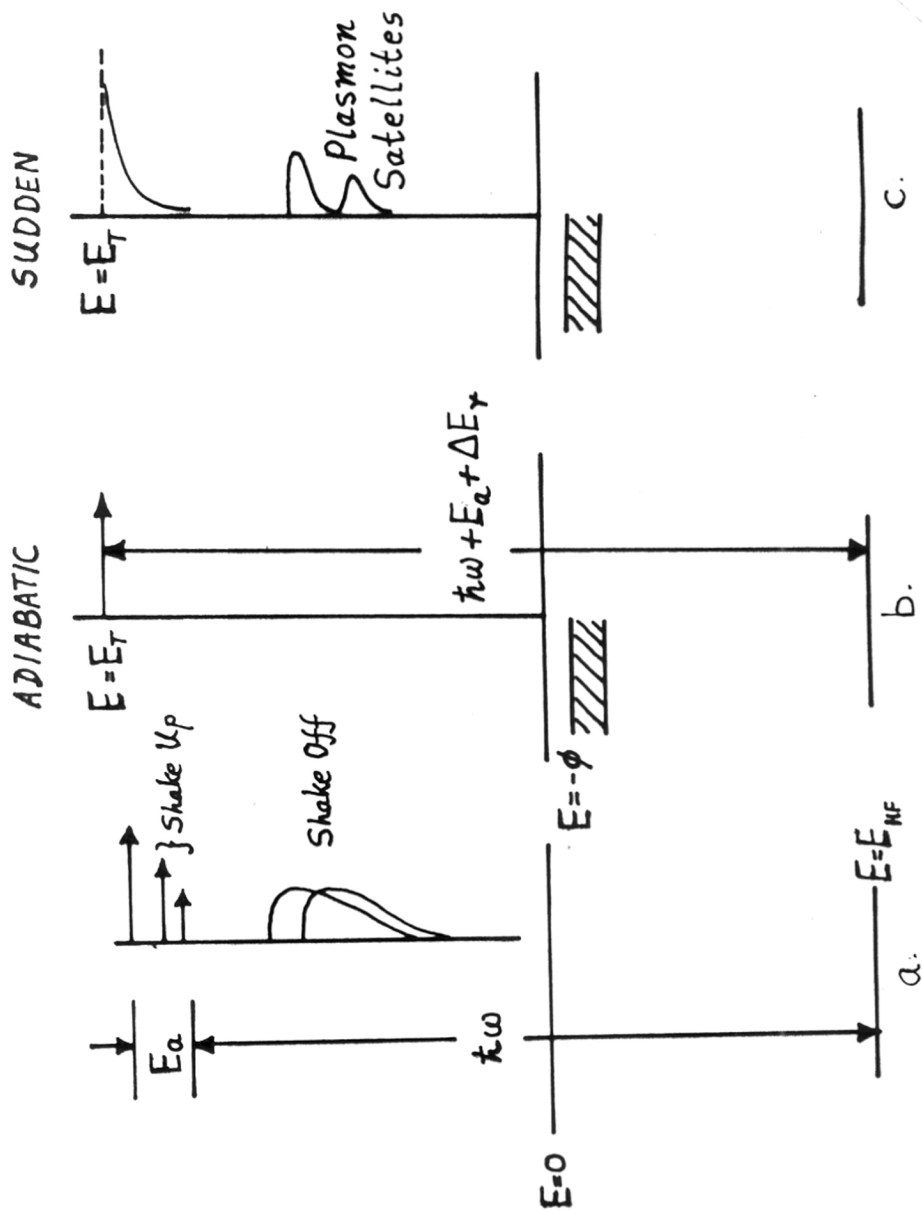


Fig. 2.6

total energies between the (N-1) and N-electron systems. If this energy is well approximated by the single-electron orbital energy, as it is for extended states, then Koopman's theorem is satisfied. However, if the removal of the electron significantly alters the effective potential seen by the remaining electrons, they readjust or relax into eigenstates of a new Hamiltonian and the observed 'binding energy' is smaller than the calculated orbital energy by an amount called the relaxation energy. Depending upon the time scale over which the effective potential is changed, yet another effect can occur. For slow adiabatic changes, the entire system is always in the ground state of the potential determined by the instantaneous charge density. More typical is the sudden limit in which the effective potential changes discontinuously in time at $t = 0$ (corresponding to immediate removal of the photoelectron).

An illustration of the many-body modification to photoelectron spectra of atoms and solids is shown in Fig. 2.6. Using photons of energy $\hbar\omega$, the frozen orbital atomic photoionization spectrum from a Hartree-Fock orbital E_{HF} is shifted upwards by the intra-atomic relaxation energy E_a as shown in Fig. 2.6a.

Moving on to the condensed phase, one notes that the source atom, upon photoionization, can now polarize the surrounding medium. In metals, the conduction band electrons move in to screen the hole, thus lowering their energy consequently an additional extra-atomic relaxation or screening energy shift ΔE_r further raises the adiabatic threshold energy above the atomic

result as shown in Fig. 2.6b. For metals treated within the free electron theory, the electronic excitation spectrum consists of a continuum of low energy electron hole pairs and a discrete collective plasmon mode. Low energy phonon modes are also present in real materials. Thus in the sudden limit, the photoelectron spectrum which includes 'shake-up' appears as in Fig. 6c. Table 2.2 puts the time scales in perspective, where related times, fundamental processes, observable consequences and energies are listed.

Table - 2.2

Time(s)	Process	Manifestation	Energy (eV)
$<10^{-17}$	Photon absorption	Plasmon satellites	1-10
10^{-16}	Screening response		
10^{-15}	Coster-Kronig and core-core-valence Auger	Hole switch-on line asymmetry	0-1.0
10^{-14}	Pair shake-up intra-molecular vibrations	Frank-Condon	0.1-1.0
10^{-13}	Phonons	Sidebands and broadening	< 0.1
10^{-12}	Core-valence-valence Auger	Hole delocalization	$< 10^{-2}$
Forever			

2.3.2 Multiplet Splitting

Multiplet splitting [17] (also referred to as exchange or electrostatic splitting) of core-level peaks occur when the system has unpaired electrons in the valence levels. For example, consider the case of the 3s electron in the Mn^{2+} ion. In the ground state the five 3d electrons are all unpaired and with parallel spins (denoted ^6S). If the spin of this electron is parallel to that of the 3d electrons (final state ^7S) then exchange interaction can occur, resulting in a lower energy than for the case of anti-parallel spin (final state ^5S). Thus the core level will be a doublet and the separation of the peaks is the exchange interaction energy

$$E = (2S + 1) K_{3s3d} \quad \text{.....} \quad (2.15)$$

where S is the total spin of the unpaired electrons in the valence levels ($5/2$ in this case) and K_{3s3d} is the 3s-3d exchange integral. The intensity ratio for the two peaks is given by

$$\frac{I(S + 1/2)}{I(S - 1/2)} = \frac{S + 1}{S} \quad \text{.....} \quad (2.16)$$

For the 3s in Mn^{2+} this ratio is $(5/2 + 1) / 5/2$ or 1.4 and $E \simeq 13$ eV. However, for the case of MnF_2 [18] the intensity ratio is $\simeq 1.8$ and separation $E \simeq 6.5$ eV. This discrepancy is due to relaxation and configuration interaction effects which complicate the simple model described.

Multiplet splitting for non-s levels is more complex because of the additional involvement of orbital-angular momentum coupling. Hence, in Mn^{2+} the 3p level is split into four levels. Multiplet splitting is strongest when both levels involved are in the same shell (as with 3s, 3p-3d), but the effects are still apparent in transition metal systems for 2p-3d interaction. This effect also causes broadening (with asymmetry) in both $2p_{1/2}$ and $2p_{3/2}$ peaks, leading to apparent variation in the separation of the peak maxima.

2.3.3 Shake-up Satellites

To the valence electrons associated with an atom the loss of a core electron appears as an increase in the nuclear charge. This major perturbation gives rise to substantial reorganization of the valence electrons (relaxation) which may involve excitation of one of them to a higher unfilled level (shake-up). The energy required for this transition is not available to the primary photo-electron and thus the two-electron process leads to discrete structure on the low KE side of the photo-electron peak (shake-up satellites).

Very strong satellites are observed for certain transition metal and rare earth compounds which have unpaired electrons in 3d or 4f shells respectively. The satellite intensity is usually much higher than would be expected for atomic-like shake-up. One explanation is that in the final state there is significant ligand-metal charge transfer compared with the initial state.

2.3.4 Shake-off Satellites

In a process similar to 'shake-up' valence electrons can be completely ionized, i.e. excited to an unbound continuum state. This process, referred to as 'shake-off', leaves an ion with vacancies in both the core level and a valence level. Discrete shake-off satellites are however, rarely discerned in the solid state because: (a) the energy separation from the primary photo-electron peak is greater than for shake-up satellites, which means that the satellites tend to fall within the region of the broad inelastic tail, and (b) transitions from discrete levels to a continuum produce onsets of increased intensity (i.e. broad shoulders) rather than discrete peaks.

2.3.5 Asymmetric Metal Core Levels

In a solid metal there exists a distribution of unfilled N-electron levels above the Fermi level E_f , which are available for shake-up-type events following core electron emission. In this case, instead of discrete satellites to low KE of the primary peak, the expectation is for the core level itself to be accompanied by a low KE tail. The higher the density of states at the Fermi level $N(E_f)$, the more likely is this effect to be observed.

2.3.6 Plasmon Loss Features

Any electron of sufficient energy passing through a solid can excite one or other modes of collective oscillation of the sea of conduction electrons. These oscillations have frequencies

characteristic of the material of the solid, and therefore need characteristic energies of excitation. An electron that has given up an amount of energy equal to one of these characteristic energies, in the course of excitation, is said to have suffered a plasmon loss. Within the solid the loss is said to be that of a 'bulk' plasmon, and if the fundamental characteristic frequency of the bulk plasmon is ω_b , then the plasmon energy loss is clearly $\hbar\omega_b$. Since electrons that have suffered a plasmon loss in energy can themselves suffer further losses of this kind in a sequential fashion, then a series of losses, all equally spaced by $\hbar\omega_b$ but of decreasing intensity, will occur.

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CHAPTER - 3

3.1 ELECTRON SPECTROMETER

Our system is a Vacuum Generators Scientific ESCA 3, MK-II, high resolution spectrometer [1]. The basic unit consists of two chambers.

One accommodates the analyser, detector and is fitted with a variety of sources for electron excitation. These are, a twin X-ray anode ($\text{AlK}_{\alpha} = 1486.6 \text{ eV}$ and $\text{MgK}_{\alpha} = 1253.6 \text{ eV}$) source for XPS studies, a Helium resonance lamp providing 21.2 eV (HeI) and 40.8 eV (HeII) photons for UPS studies and a 5 KeV electron gun for electron induced AES studies.

The second chamber is used for preparation of the sample, i.e. for Ar^+ ion etching, and for dosing the sample with various gases. These two chambers are separated by a gate valve, which when open allows the sample to be transferred to the analyser chamber.

The two chambers are pumped with EO4 diffusion pumps, backed by EDM 6 rotary pumps. The fluid used in the diffusion pumps is a polyphenyl ether which has a vapour pressure of 5×10^{-11} torr at room temperature. Additional pumping is provided by CCT 100 liquid nitrogen traps fitted on the diffusion pumps and titanium sublimation pumps fitted separately to the two chambers. In addition a 5 litres/sec ion pump is used to pump the X-ray source. Typical base pressure in the two chambers after bakeout at 200°C for 24 hours is about 8×10^{-11} torr.

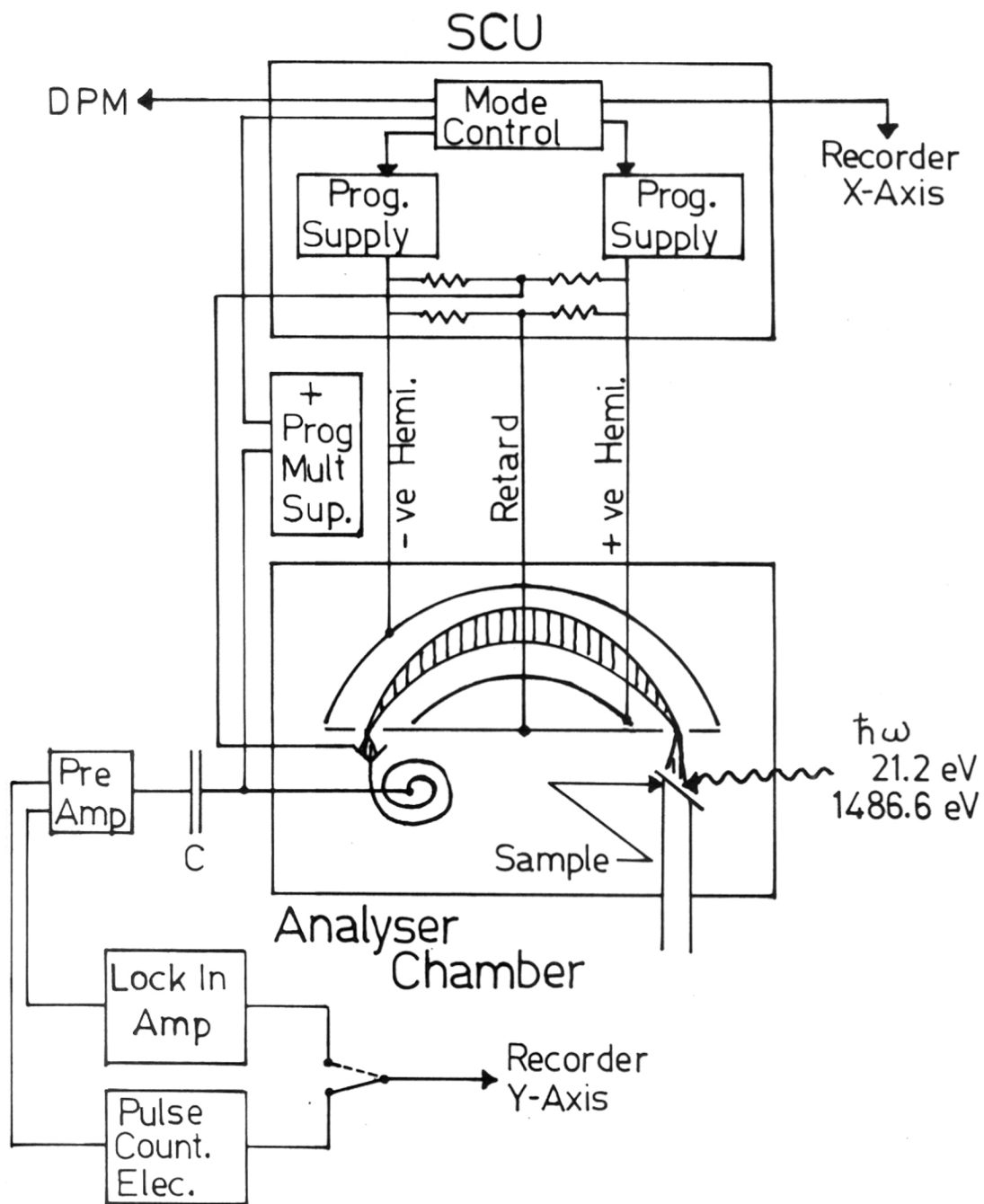


Fig.3.1

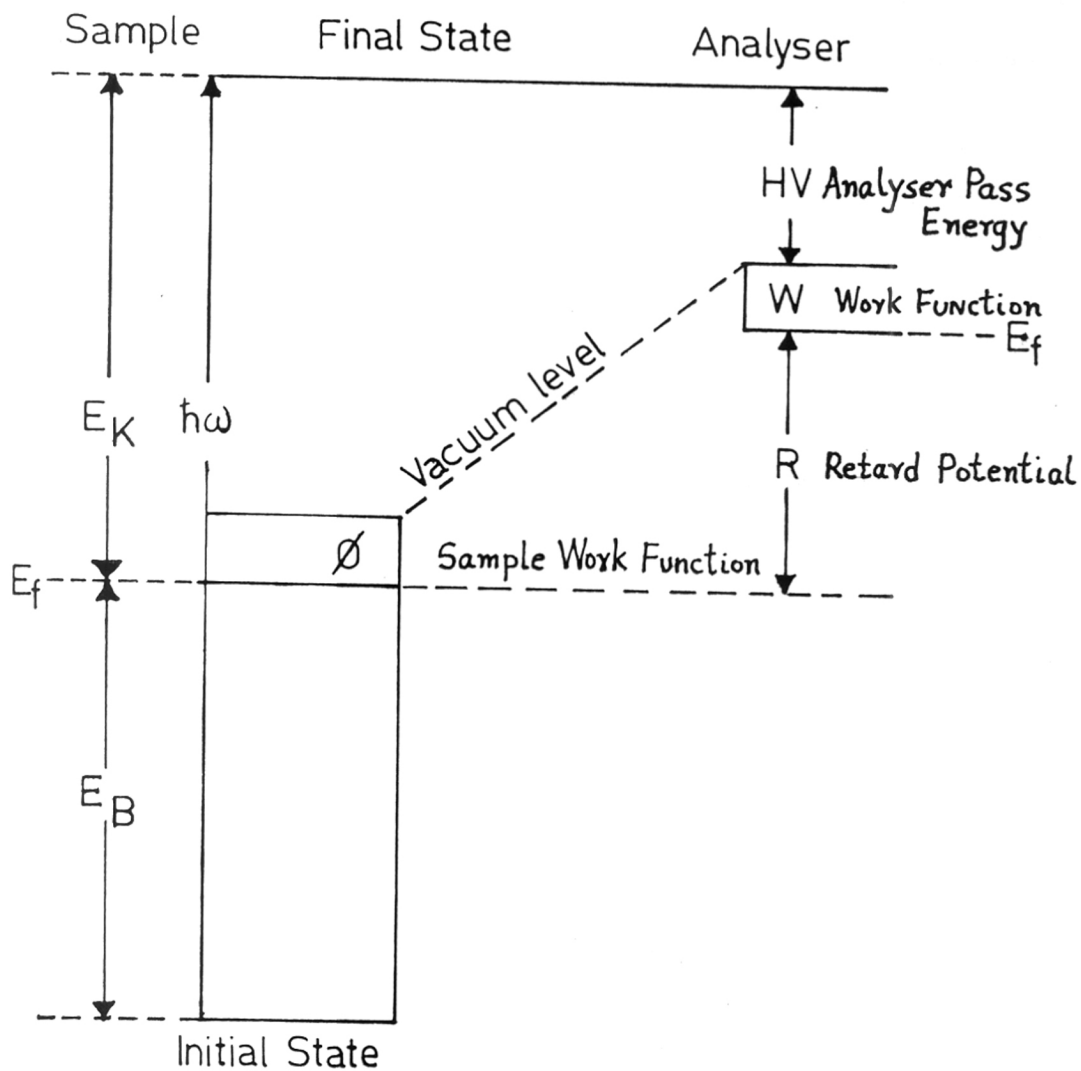


FIG.3.2

3.2 PRINCIPLE OF OPERATION OF ANALYSER

Fig. 3.1 shows a simplified schematic of the analyser and the controlling electronics [1].

The hemispherical (actually 150°) analyser acts as a narrow pass filter, letting through only electrons with an energy HV (eV) where V is the potential difference between the inner and outer hemispheres and H is a constant determined by the physical dimensions and is equal to 2.64 for our analyser.

Referring to Fig. 3.2, photoelectrons from the grounded sample are retarded in energy by an amount R eV immediately before entering the analyser. In effect the retarding potential ($-R$ volts) is the electrical center point of the analyser. Then if K eV is the kinetic energy with which an electron leaves the sample with respect to the Fermi level, we have

$$K = R + HV + W \quad \text{.....} \quad (3.1)$$

where W eV is the work function of the spectrometer.

Since source energy is known (1486.6 eV for AlK_{α} , 1253.6 eV for MgK_{α} and 21.2 eV for HeI) the binding energies of the photoelectrons are calculated from:

$$\text{Binding Energy} = \text{Source Energy} - \text{Kinetic Energy}$$

Resolution of Analyser

In an ideal state of affairs the analyser which acts as an energy filter, would let through only electrons with an energy

$e = HV$. In practice it lets through electrons having an energy range $e \pm de$ and it can be shown that

$$\frac{de}{e} \approx \frac{dr}{2r} + \alpha^2 \quad \dots (3.2)$$

where r = mean radius of hemispheres,

α = half angle of admission of electrons in radians,

dr = slit width.

Now de would be FWHM of a recorded peak assuming infinitely small source and core level line-width, and since for a given geometry de/e is constant, de will decrease linearly with e . Thus as we decrease analyser energy we decrease line-width and increase resolution; this is ultimately limited by source and core level line width. A typical operating analyser energy would be 50 eV, to give a FWHM for the Au $4f_{7/2}$ of about 1.5 eV. This line would be calibrated to appear at 84.0 eV.

Signal Detection

The electron current actually emerging from the exit slits is in the 10^{-16} to 10^{-13} amp range. To amplify this current a channel electron multiplier is used. This is a small, curved glass tube, the inside wall of which is coated with high-resistance material. If a potential is applied between the ends of the tube, the resistive surface acts as a continuous dynode.

An electron entering the low-potential end of the channel multiplier generates secondary electrons on collision with the wall of the tube. These are accelerated along the tube until

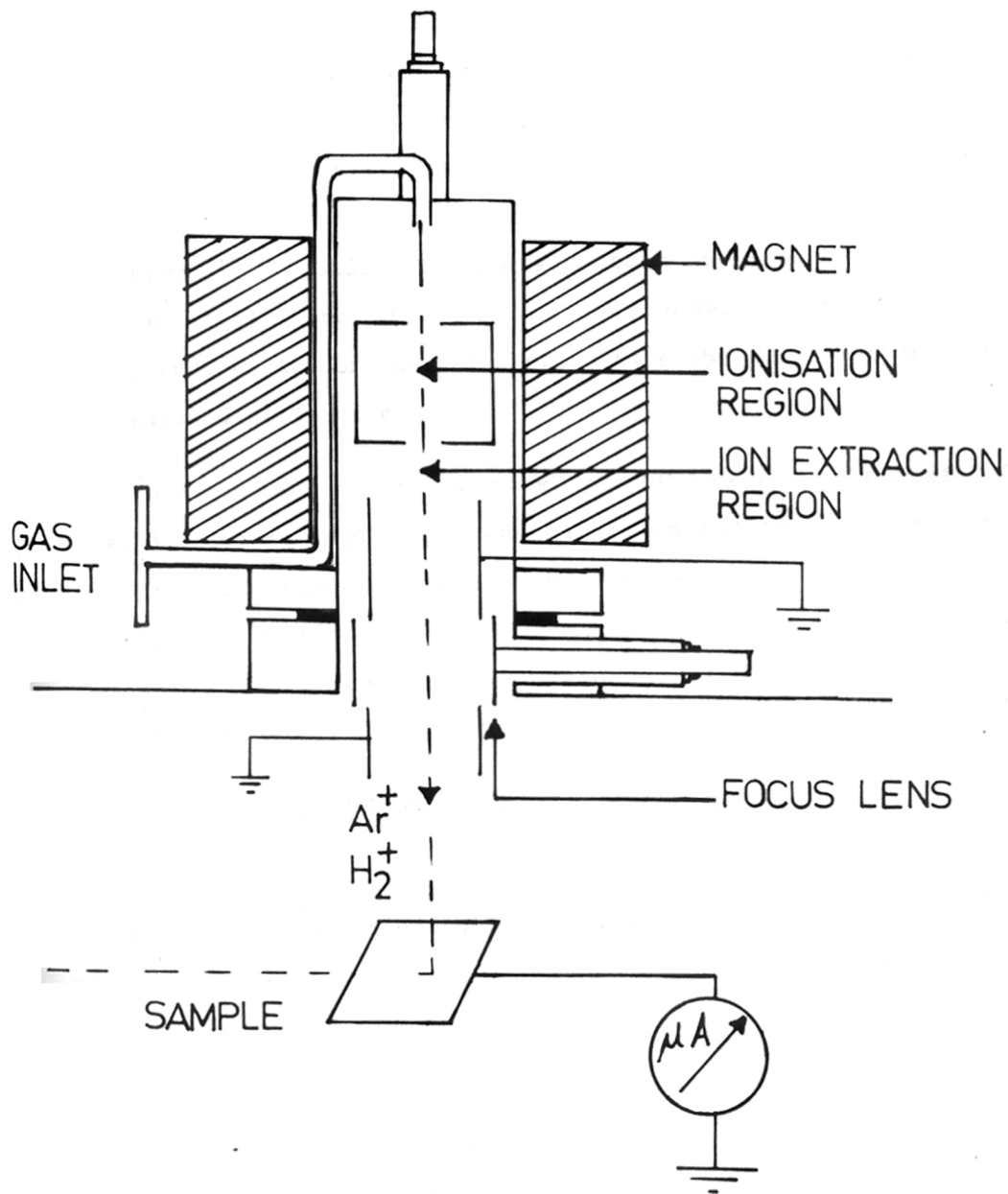


Fig. 3.3

they strike the wall again, where they further generate secondary electrons. This avalanching process produces a large number of electrons at the positive end of the tube. This multiplier thus responds to an input of one electron by producing an output pulse of charge. This pulse may contain about 10^8 electrons and its duration (FWHM) is about 10 nano-seconds. Because of the statistical nature of the pulse production the pulse heights have a Gaussian distribution.

These pulses are fed through the DC isolating capacitor C (Fig. 3.1) to an amplifier and then to an analyser (E control). This lets through only pulses which have an amplitude greater than E. These pulses are then converted to a NIM standard pulse of 5 volts amplitude, 500 nano-seconds duration and fed to the rate-meter which reads out counts (pulses) per second.

3.3 AG-2 ION GUN (DESCRIPTION AND OPERATION)

The model AG-2 (Fig. 3.3) is a 10 KeV ion gun, which we use for both sputter-etching with Ar^+ ions, and for ion implantation of H_2^+ ions [1].

The AG-2 is a cold cathode source ion gun with ion beam extraction, acceleration and focussing. The gun is mounted on a standard 2 3/4" OD copper gasket flange. The gas inlet pressure is regulated using an all metal bakable model MD-6 leak valve.

An electromagnet surrounds the ion source. Ion acceleration is variable over the range 0-10 KeV. Beam energy depends on the discharge conditions in which the ions have an initial energy in

the region of 1.5 KeV. Beam current depends on the accelerating electrode potential and on the gas pressure in the discharge.

The electronics necessary for the operation of the AG-2 sputter ion gun are included in the AGS-2 power supply which provides:

1. a self protected unstabilised discharge supply that is insulated for operation upto 15 KV with respect to earth.
2. a 10 KV high voltage supply (+ve w.r.t. earth) to control the energy of the ion beam,
3. a 10 KV high voltage supply (+ve w.r.t. earth) to control focussing of the ion beam onto the specimen.

The cold cathode discharge is sustained from a voltage doubler supply. The discharge supply is designed to provide 9 mA limited output current in the event of the output terminals being short circuited. The beam energy and focus supplies are separate, type 180 A programmable supplies which share a common 24 V DC supply separately fused. The type 180 A supplies are stabilised and protected against a short circuit of their output terminals.

In a typical etching experiment the sample is oriented such that the path of Ar^+ ions is at a grazing angle ($\sim 10^\circ$) to the sample surface. This was chosen so as to minimise surface damage and implantation of Ar^+ ions.

During hydrogen implantation the sample is oriented such that the path of H_2^+ ions is perpendicular to the sample surface.

3.4 WHY U.H.V. REQUIRED

The mean free path or inelastic scattering length in solids are $2-5 \text{ \AA}$ and $10-30 \text{ \AA}$ for 200 eV and 1000 eV photoelectrons respectively. The sampling depth decreases as $\sin \theta$, where θ is the electron take-off angle as measured with respect to the sample surface. Hence this makes the preparation and preservation of a clean sample surface the main experimental task in a photoemission experiment [2,3].

At an escape depth of $10 \text{ \AA}$ and assuming a lattice constant of $4 \text{ \AA}$, the first atomic layer contributes about 60% and 30% to the total spectrum for 200 eV and 1000 eV photoelectrons respectively. Electrons excited deeper in the solid may also escape, from the surface, but lose energy on their way to the surface and are detected in the background on the high binding energy side of the peaks or the low energy tail of the spectrum.

A foreign atom on the surface of the sample makes itself felt in two ways:

(i) at the limit of negligible interaction between adsorbate and substrate (physisorption), it adds its own photoemission lines to the spectrum of the substrate.

(ii) in the strong bonding limit (chemisorption), the interaction between adatom and substrate changes the energy levels of the substrate as well.

The most notorious contaminants are O_2 and CO, which add the O 1s line at 534 eV and C 1s line at 284 eV. The O 2p level

around 6 eV shows up most prominently in the UPS spectra. Its UPS strength/atom is over an order of magnitude stronger than the metal s and p valence levels with $n > 2$. Hence, a minimal amount of oxygen contamination suffices to obliterate UPS spectra of valence bands. The XPS ls lines of carbon and oxygen are intense enough to detect coverages of the above mentioned molecules of $1/10^{\text{th}}$ of a monolayer or less on almost all substrates.

Mean Free Path

The mean free path L is the average distance that a molecule moves before colliding with another. L is given by kinetic theory as

$$L = (1/2^{1/2}) (1/nd^2) \quad \dots \quad (3.3)$$

where d = molecular diameter which is dependent on the nature of the residual gas, and n = molecular concentration.

At 1 atmosphere the mean free path in air at 20°C is 6×10^{-6} cm, at 10^{-3} torr it is 5 cm, at 10^{-6} torr it is 51 metres and at 10^{-10} torr it is 350 miles.

Number of impacts with the sample surface

Kinetic theory gives an expression for the impact frequency as $\mathcal{N} = 35 \times 10^{22} \times p / (MT)^{1/2} \text{ s}^{-1} \text{ cm}^{-2}$ where p = pressure in torr, M = molecular weight of the residual gas and T = absolute temperature.

At 10^{-6} torr of oxygen and 20°C , $N = 3.62 \times 10^{14}$ and at 10^{-9} torr, $N = 3.62 \times 10^{11}$. Typical clean metal surfaces have approximately 10^{15} atoms/sq.cm. so that, if each oxygen molecule striking the surface sticks, the metal:oxygen atomic ratio at the surface would be 1:1 in $1/(0.32 \times 2) = 1.4$ sec. at 10^{-6} torr or 1400 sec. at 10^{-9} torr. Hence, a sample exposed to a gas at a pressure of 10^{-6} torr that has a sticking coefficient of 1, will accumulate a monolayer of that gas in 1 sec. Thus, pressures between 10^{-11} and 10^{-9} are mandatory for photoelectron spectroscopy and this requirement is twofold:

- (i) for conservation of a clean sample surface for time scales required to do the experiment and,
- (ii) for photoelectrons from the sample to reach the detector without being scattered, after passing through the analyser. This distance is normally in excess of 0.5 metres.

3.5 CLEANING PROCEDURES

Preparation of atomically clean, elemental surfaces are required prior to experimental studies of their physical and/or chemical properties. The preparation of a clean surface is more of an art rather than a science. There are a few commonly accepted procedures [2] these are divided into two groups:

- (i) cleaning procedures involving creation of a new surface,
- (ii) cleaning through removal of contaminated surfaces.

The procedures involved in group (i) are :

- (a) cleaving of a single crystal in-situ, along one of its low index lattice planes, to expose a new, highly ordered and smooth surface,
- (b) fracturing of a polycrystalline sample in-situ to expose a new surface,
- (c) in-situ sputtering or evaporation of sample onto the sample holder.

The procedures involved in group (ii) are :

- (a) flashing and/or annealing to high temperatures in-situ or in the presence of a reactive gas,
- (b) mechanically removing the surface layers by filing with a hard metal brush or scraping with a metal knife in-situ,
- (c) ion bombardment and annealing. This process is probably the most generally accepted method. Here, Ar gas is ionized by either a cold discharge or electron bombardment in an ion gun, and then accelerated through a lens system towards the sample which is grounded. This requires argon pressures of about 5×10^{-6} torr. Depending on the ion current and the sample material, monoatomic layers can be removed in seconds to minutes. However, ion bombardment leaves the surface slightly damaged, and therefore it becomes mandatory to anneal the sample to elevated temperatures.

Our method of cleaning samples follows the previous procedure. We track the surface cleanliness by monitoring the XPS 1s and UPS 2p levels of oxygen and carbon. Ion bombardment and annealing cycles are continued until these levels are not detected. Detailed cleaning procedures for individual metals are tabulated below (Table 3.1).

Table - 3.1

Metal	Outgassing in UHV		Ar ⁺ ion etching and annealing cycles			
	Temp. °C	Time Hrs.	Energy KeV	Current $\mu\text{A}/\text{cm}^2$	Annealing temp. °C	Total time Hrs.
Al	500	12	9	50	500	12
Ag	550	12	9	100	550	8
Au	550	12	9	100	550	8
Cd	-	-	9	50	-	6
Co	550	12	9	100	550	20
Cr	550	12	9	100	550	50
Cu	550	12	9	100	550	10
Ho	550	24	9	150	550	20
In	-	-	9	50	-	6
Fe	550	12	9	100	550	25
Pb	-	-	9	50	-	6
Mg	500	8	9	50	500	25
Mn	550	12	9	100	550	50
Ni	550	12	9	100	550	15
Nb	550	24	9	150	550	50
Pd	550	12	9	150	550	10
Pt	550	12	9	150	550	10
Ru	550	12	9	100	550	20
Ta	550	12	9	150	150	50
Sn	-	-	9	50	-	6
Ti	550	24	9	150	550	50
Yb	550	12	9	60	550	50
Zn	-	-	9	50	-	6
Zr	550	24	9	150	550	50

3.6.1 Ion-implantation

Ion implantation [4] is probably the oldest and foremost of radiation processing techniques used for controlled modification and tailoring of the chemical, mechanical, structural and electronic properties of surfaces of solids.

The advantages of ion-beams are: (i) ion beams are charged particles and hence their beams can be suitably controlled and focussed by electric and magnetic fields, (ii) ions carry the chemistry of the corresponding atom with themselves and as such make it easy to achieve alloying, compound formation and synthesis of solid solutions.

In addition to their use in modifying surfaces, ion-beams can also be used for characterization of surfaces. For example, (i) Rutherford Backscattering (RBS) can be used for probing the chemical composition and structure of surface layers, (ii) ion-beam crystallography can be used for study of phenomenon like chemisorption, surface restructuring etc. and (iii) ion channelling can be used for lattice location and characterization of defects and defect complexes etc.

When analysing the interaction of energetic ions with matter the following assumptions have to be made: (i) the solid target is amorphous, made from a single element and of uniform density, (ii) the energetic ions have a single initial energy and have parallel initial trajectories, and enter the target at the same point.

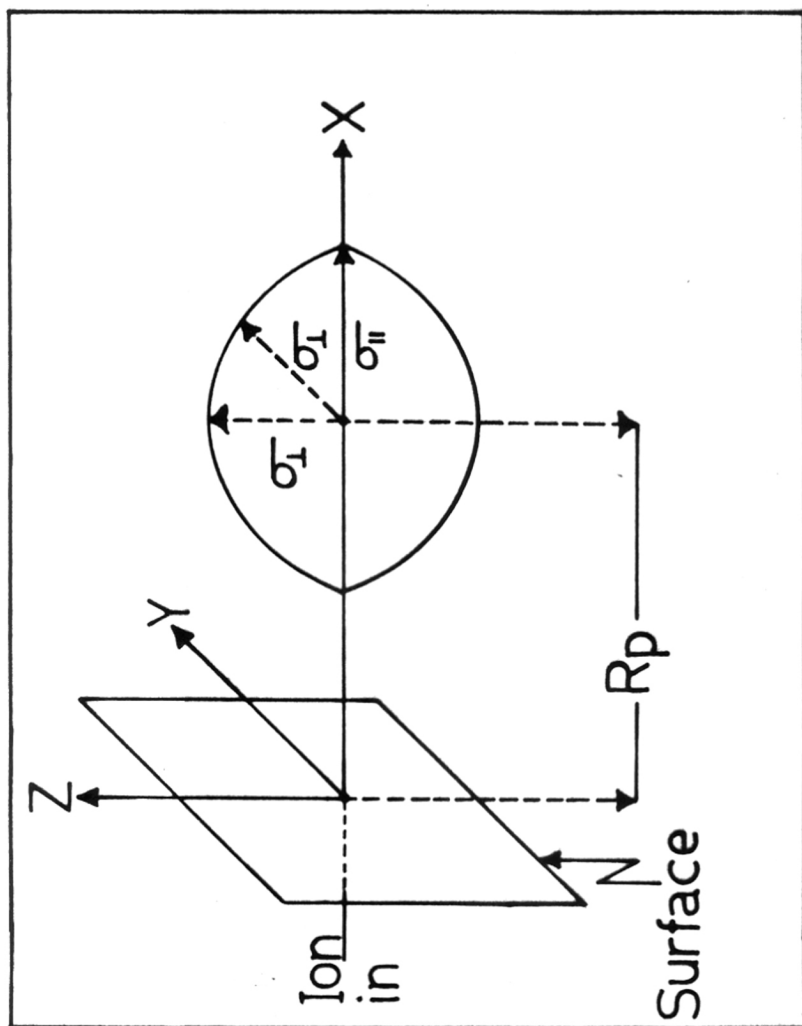


Fig. 3.4

The implanted distribution in the target is calculated using transport theory [4], and the final three-dimensional ion distribution is described as

$$f = \frac{\exp [-(x-R_p)^2/2 \sigma_{||}^2] \cdot \exp [-(Y^2 + Z^2)/2 \sigma_{\perp}^2]}{(8\pi^3 \sigma_{||}^2 \sigma_{\perp}^4)^{1/2}} \dots \quad (3.4)$$

This is shown schematically in Fig. 3.4, where the target surface is the Y-Z plane, with the ion-beam entering along the X-axis.

R_p = mean ion depth, is defined as the mean value of the final depth distribution. It may differ slightly from the position of the peak of the distribution.

$\sigma_{||}$ = Longitudinal straggling, is the square-root of the standard deviation of the final implanted depth distribution.

$\sigma_{\perp}$ = Lateral straggling, is the square-root of the standard deviation averaged perpendicular to the initial ion trajectory.

However, in a realistic situation (i) ion beams are wide with non-uniform lateral intensities, (ii) the distribution may change because of beam induced or thermal migration of the implanted ions. This is particularly true of implanted ions with high diffusivity (e.g. H, Li) or high solubilities in the target, (iii) physical targets may be polycrystalline and accidental alignment of the ion beam along a major axis may change the slowing down process. Normally, the final distribution is changed less than 10% for light ions and even less for heavier ions, (iv) surface roughness will directly increase longitudinal straggling.

3.6.2 Implantation of Hydrogen

In our case, the diameter of the ion beam was focussed to $\sim 1 \text{ cm}^2$ area. The ions were accelerated to an energy of 8 KeV, and were predominantly molecular hydrogen H_2^+ ions. Hitting the metal surface, every H_2^+ ion is split into two parts, each having an energy of 4 KeV. The attainable H concentration is only determined by the number of free interstitial sites. The advantage of the implantation method is its total independence of the equilibrium solubility of the host metal. All implantations were carried out at 300°K and terminated when the H/metal ratio reached unity.

Table 3.2 gives the straggling range σ_{11} , projected range R_p , and total path length L of 4 KeV hydrogen atoms implanted into various metals [4].

Table - 3.2

Metal		Mass density	Atom density	Range straggling	Projected range	Total path length
Atomic No.		gm/cc	$\rho: \#/\text{cc} \times 10^{22}$	$\sigma_{11}: \mu\text{M}$	$R_p: \mu\text{M}$	$L: \mu\text{M}$
Be	4	1.802	12.05	0.023	0.070	0.15
Mg	12	1.737	4.302	0.045	0.070	0.23
Al	13	2.698	6.023	0.027	0.030	0.16
Si	14	2.321	4.978	0.032	0.050	0.19
Ca	20	1.340	2.014	0.060	0.080	0.35
Sc	21	2.997	4.015	0.030	0.040	0.18
Ti	22	4.519	5.632	0.023	0.030	0.14
V	23	6.101	7.213	0.023	0.025	0.12
Cr	24	7.192	8.331	0.020	0.023	0.12
Mn	25	7.434	8.15	0.021	0.027	0.15

contd....

Metal		Mass density	Atom density	Range straggling	Projected range	Total path length
Atomic No.		gm/cc	$\rho \cdot \frac{\#}{cc} \times 10^{22}$	$\sigma_u : \mu M$	$R_p : \mu M$	$L : \mu M$
Fe	26	7.866	8.483	0.021	0.025	0.14
Co	27	8.796	8.99	0.021	0.025	0.15
Ni	28	8.895	9.126	0.020	0.021	0.12
Cu	29	8.949	8.483	0.020	0.021	0.12
Zn	30	7.11	6.55	0.022	0.025	0.15
Ga	31	5.908	5.104	0.025	0.025	0.15
Ge	32	5.338	4.429	0.027	0.027	0.17
Y	39	4.49	3.042	0.030	0.030	0.20
Zr	40	6.47	4.272	0.020	0.020	0.14
Nb	41	8.602	5.577	0.015	0.014	0.10
Mo	42	10.21	6.407	0.015	0.014	0.10
Ru	44	12.18	7.257	0.014	0.013	0.09
Pd	46	12.0	6.77	0.017	0.014	0.10
Ag	47	10.5	5.85	0.018	0.015	0.11
Cd	48	5.58	4.6	0.021	0.019	0.15
In	49	7.31	3.84	0.025	0.020	0.16
Sn	50	7.28	3.7	0.025	0.020	0.16
Sb	51	6.62	3.27	0.023	0.020	0.16
La	57	6.72	2.677	0.027	0.020	0.18
Ce	58	6.672	2.868	0.027	0.020	0.18
Pr	59	6.774	2.896	0.027	0.020	0.18
Nd	60	7.002	2.924	0.027	0.020	0.19
Sm	62	7.56	3.03	0.028	0.020	0.19
Eu	63	5.258	2.084	0.040	0.030	0.28
Gd	64	7.902	3.027	0.028	0.020	0.20
Tb	65	8.277	3.137	0.030	0.020	0.20
Dy	66	8.55	3.17	0.032	0.023	0.22
Ho	67	8.82	3.2	0.032	0.024	0.23
Er	68	9.09	3.27	0.032	0.024	0.23
Tm	69	9.33	3.33	0.033	0.024	0.23
Yb	70	6.98	2.43	0.050	0.034	0.32
Lu	71	9.83	3.38	0.033	0.024	0.23
Hf	72	13.1	4.43	0.023	0.018	0.18
Ta	73	16.6	5.53	0.020	0.015	0.15
W	74	19.3	6.32	0.020	0.014	0.13
Pt	78	21.4	6.62	0.018	0.014	0.10
Au	79	19.3	5.9	0.020	0.013	0.14
Tl	81	11.9	3.5	0.031	0.021	0.22
Pb	82	11.3	3.29	0.020	0.030	0.21
Bi	83	9.81	2.83	0.028	0.020	0.22

3.6.3 CALCULATION OF NUMBER OF HYDROGEN ATOMS IMPLANTED

The number of atoms implanted per unit area is given by

$$N = 10^{13} \cdot \frac{i t}{a} \quad \dots (3.5)$$

where i = current in microamps (μA),
 t = duration of implantation, and
 a = area of target (cm^2).

Case study : Cd

$$\begin{aligned} i &= 250 \mu A \\ t &= 120 \text{ min} \\ a &= 1 \text{ sq.cm.} \end{aligned}$$

$\therefore$ from equation 3.5,

$$\begin{aligned} N_H &= 10^{13} \times 250 \times 120 \times 60 \\ &= 1.8 \times 10^{19} \text{ atoms/sq.cm.} \end{aligned}$$

from Table 3.2

$$\begin{aligned} \rho_{Cd} &= 4.6 \times 10^{22} \text{ atoms/cc.} \\ \sigma_{II} &= 210 \text{ A}^\circ \\ R_p &= 190 \text{ A}^\circ \end{aligned}$$

Now we assume that the total number of hydrogen atoms N_H , are uniformly distributed over a volume

$$V = 1 \text{ sq.cm.} \times (2 \sigma_{II}) = 1 \text{ sq.cm.} \times 210 \text{ A}^\circ \times 2$$

Therefore, number of Cd atoms in volume V is

$$N_M = \frac{4.6 \times 10^{22}}{10^8} \times 420 \approx 1.9 \times 10^{19}$$

$$\text{Hence ratio } \frac{N_H}{N_M} = \frac{1.8 \times 10^{19}}{1.9 \times 10^{19}} \approx 1$$

3.7 LATTICE SITE LOCATION AND TRAPPING OF IMPLANTED HYDROGEN

Bugeat and Ligeon [5] have studied the lattice location and trapping of implanted hydrogen in some f.c.c. metals, using nuclear reaction analysis and ion channeling. Their parameters of interest were

- i) implantation energy (5-50 KeV)
- ii) implantation temperature
- iii) annealing temperature.

At low implantation energies (≤ 10 KeV) the energy of implanted H is predominantly lost through electronic excitation of the host metal atoms, and the number of displacements suffered by the host metal atoms is ≤ 1 , with the H atoms occupying octahedral sites.

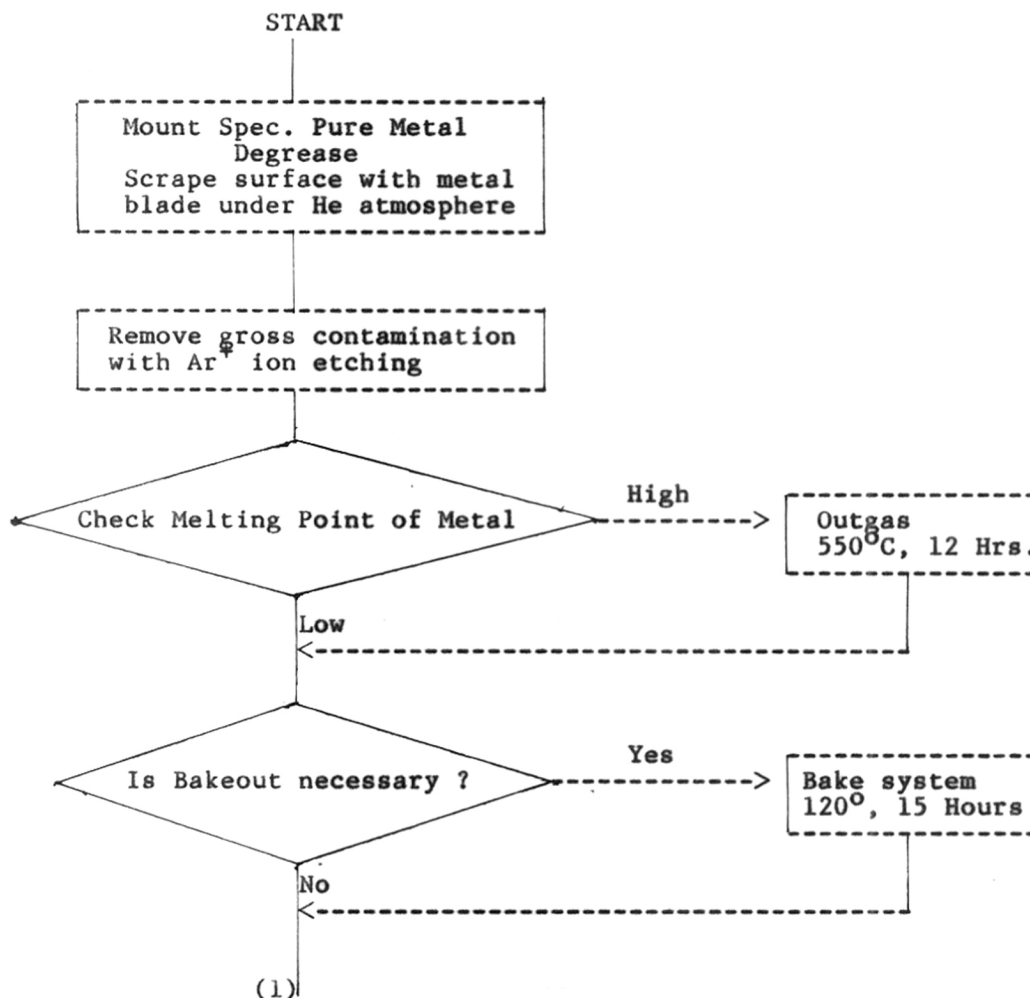
At low-temperatures (~ 4 K) and higher energies, some immobile vacancies, self-interstitials and hydrogen trapped at the wrong site due to influence of vacancies are also created. Hydrogen never occupies a substitutional site, due to a high potential wall surrounding the site. On annealing, at a temperature T_R ($\sim 300^\circ\text{K}$) migration of H and defects are observed and at a temperature T_{III} ($\sim 500^\circ\text{K}$) there is no trapping of H due to defects.

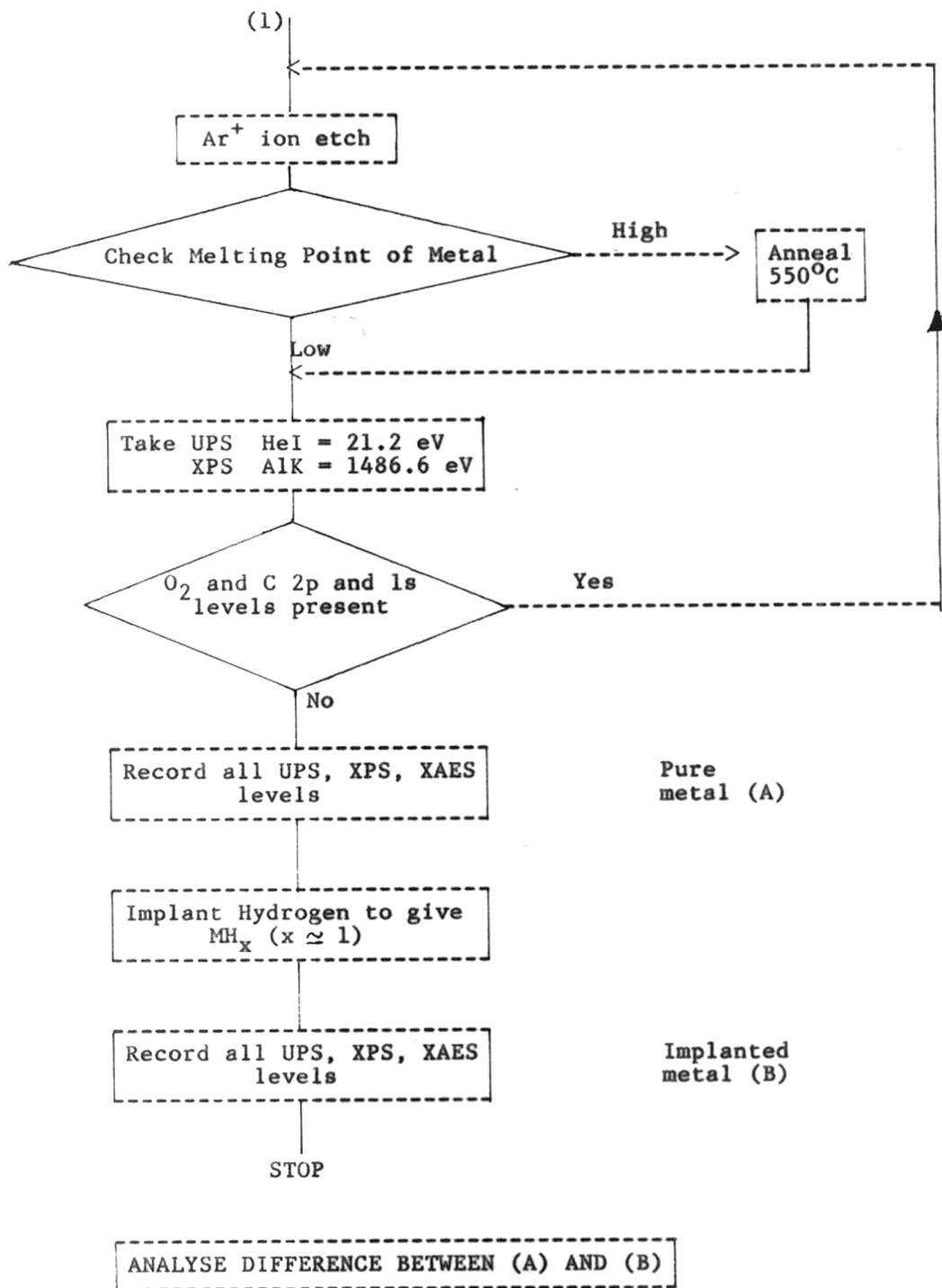
As the implantation temperature is increased, at a temperature T_R ($\sim 250^\circ\text{K}$), both the H implanted and defects are mobile, with the result that the defects created are automatically annealed out, and H occupying its site preference. Since our

implantation temperature is 300°K , we assume that defects, if any, are below the detection limit of our technique and we predominantly see the influence of H occupying its preferred site.

3.8 EXPERIMENTAL SEQUENCE

The flow chart below depicts a typical experiment.





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CHAPTER - 4

RESULTS AND DISCUSSIONS

The dissolution of hydrogen in a metal lattice and the formation of a metal hydride strongly disturbs electrons and phonons of the host metal, as reviewed in chapter 1. A study of the electronic properties of metal-hydrogen systems is therefore of fundamental value both to the understanding of the H-metal bond in the bulk, at the surface and to technologically important parameters such as heats of formation and thermal conductivity.

Until almost the mid 1970s, research on the electronic properties of metal hydrides were mainly susceptibility, resistivity, electronic specific heat and N.M.R. investigations. Hence the first band structure calculations had a major impact and stimulated experimental work on electron spectroscopic studies of the electronic and core-level structure of metallic hydrides.

In what follows we attempt to discuss the results of our exploratory work on some hitherto unknown and known binary metal-hydrogen systems (MH_x , $x \simeq 1$), synthesized by the non-equilibrium preparation method of ion implantation.

We have eliminated the MgH, AlH, ZnH, LaH and CeH systems, since we noticed the presence of oxygen, which has totally obscured the effects of H or has complicated the spectra. We also eliminate the AgH, AuH, HoH and the YbH systems since we do not observe any changes or the changes if any are too subtle to be noticed with the eye and would require computer analysis. Of

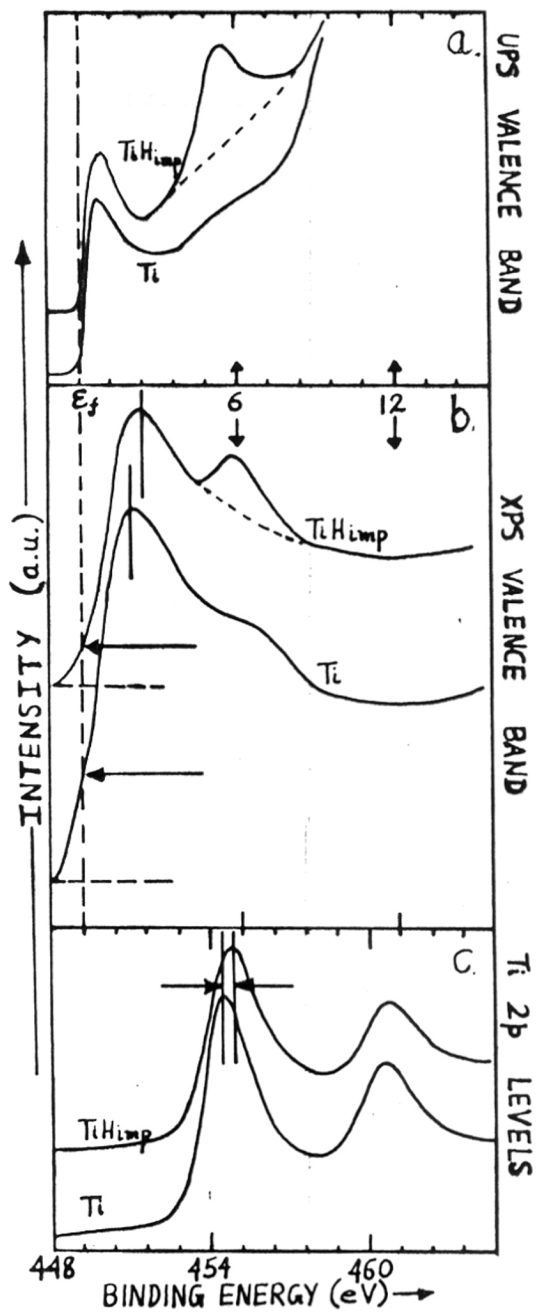


Fig. 4.1

the remaining systems, we give extremely condensed results, namely the valence band spectra and the spectra of the most intense core-level. We attempt to analyse these results on the basis of some band structure calculations and electron spectroscopic results available on systems prepared by conventional equilibrium methods. We also utilize the results of some classical measurements.

The TiH and ZrH Systems

Fig. 4.1a shows the UPS (21.2 eV) valence band of the TiH system. We notice a reduction in the d-band intensity and the appearance of a new structure at $\sim 5-6$ eV below E_f . This we attribute to the metal-H bonding band in agreement with available data [1]. Fig. 4.1b shows the XPS valence band. We again notice new structure at 6 eV, and in addition a shift of the d-manifold to higher energies with a reduction in $N(E_f)$. There is slight structure visible at ~ 6 eV for Ti also. We attribute this to adsorbed H_2 , since Ti readily reacts with H_2 , which is usually a principal residual gas in an U.H.V. system [2]. The structure observed at ~ 6 eV is in good agreement with the density of states calculation of Switendick [3]. However, this structure is attributed to s-like contribution to the total density of states. We attribute this band to states which are strongly hybridized, containing d as well as s character. The s-like states have negligible photoionization cross-section at 1486.6 eV, and would not show up in the XPS valence band spectra. Fig. 4.1c shows the 2p core-levels of Ti. We observe a shift of $\sim + 0.4$ eV for $2p_{3/2}$ level. This would imply an increase in the charge density

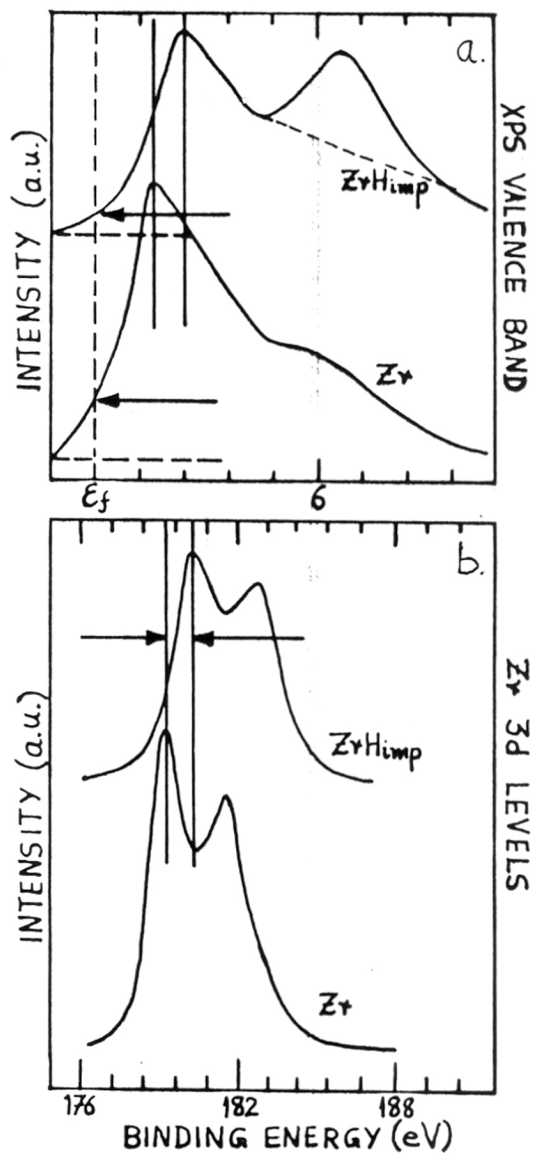


Fig.4.2

at the H site. This is in excellent agreement with available data on core -level shifts [4,5]. Baba et al. [5] have also studied the TiH system prepared by ion-implantation. However, they observe a bonding band at 3.5 eV against our 5.5 eV. They also do not observe any decrease in $N(E_f)$, which we observe.

Fig. 4.2a shows the XPS valence band spectra of the ZrH system. We observe a shift of the valence band peak by about +1 eV and a new structure between 6 and 7 eV. We also notice a fall in the intensity and decrease in $N(E_f)$. A structure at ~ 6 eV is also observable in the Zr spectra, which we attribute to adsorbed H_2 as in the case of Ti. The structure at ~ 7 eV in ZrH is in excellent agreement with the calculation of Gupta [6] and experimental results [1,7]. However in analogy to Ti, we feel that this band is due to states which are strongly hybridized, containing d as well as s character.

In Fig. 4.2b we show the 3d levels of Zr. We observe a shift of $\sim +1$ eV for the 3d level in ZrH. This would imply an increase in the charge density at the H site. This is again in agreement with available data [4,7,8]. Sasaki et al. [8] have also studied the ZrH system prepared by ion implantation. They observe a bonding band at ~ 4.5 eV as against our 7 eV and that in literature. They also do not observe any decrease in $N(E_f)$.

The $NbH_{0.5}$ and $TaH_{0.5}$ Systems

Both Nb and Ta were implanted to give a H/metal ratio of 0.5. Figs. 4.3a and Fig. 4.3b show the UPS and XPS valence band

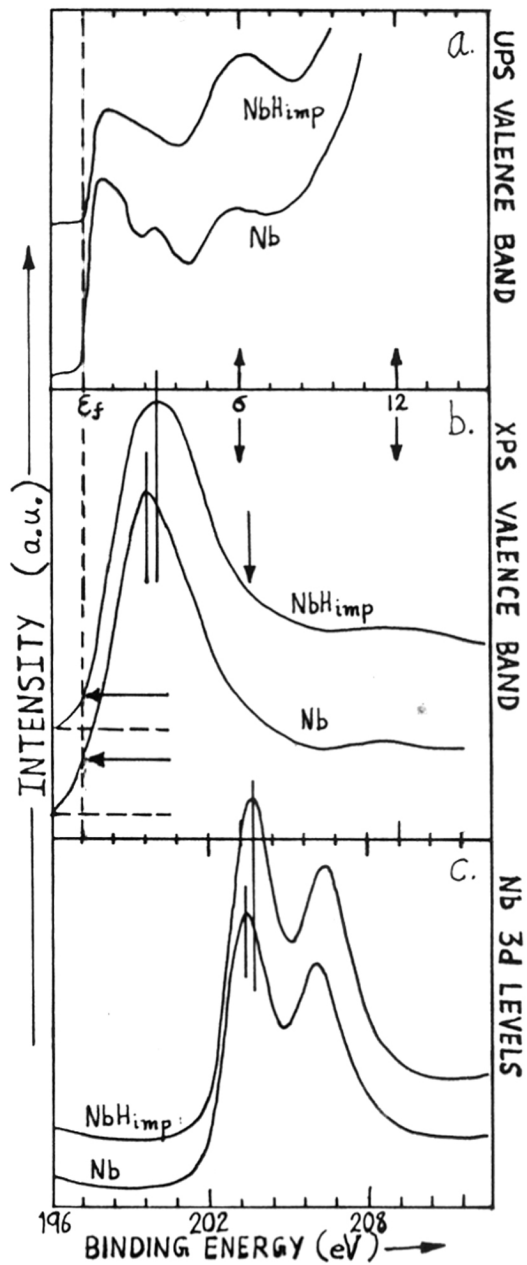


Fig.4.3

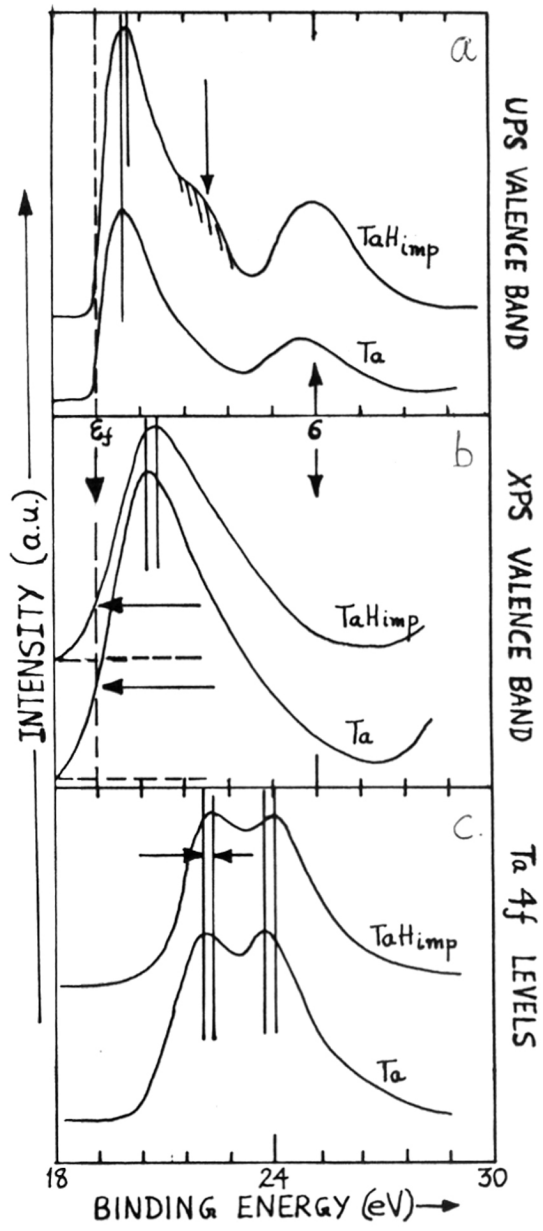


FIG. 4.4

spectra for the NbH system respectively. The structure at ~ 6 eV in the UPS spectra of Nb is attributed to adsorbed H_2 , in analogy to Ti and Zr. On implantation of H, the structure at ~ 6 eV is enhanced, and some new structure appears at ~ 3.0 eV. The structure at 6 eV is in good agreement band structure calculation [6,9,10]. The structure at about 3.0 eV has been predicted by Gupta [10]. The XPS valence band spectra shows a broadening with a reduction in $N(E_f)$. This reduction in $N(E_f)$ is in agreement with experimental data [9]. No intense structure is seen around 6 eV, which would imply that there is very little d contribution to the DOS in this region. This is again in agreement with calculation [9]. Fig. 4.3c shows the 3d core levels of Nb. A shift of $\sim +0.4$ eV is observed, implying an increase in the charge density at the H site. Sakaki et al. [8] have also studied the NbH system prepared by ion-bombardment. They observe a core level shift of $+0.8$ eV. However they observe structure at around 4.6 eV and no change in $N(E_f)$.

Figs. 4.4a,b,c show the corresponding situation for Ta. The behaviour parallels that of the NbH system. In the UPS spectra we find an increase in structure at 6 eV and a new structure at ~ 3.8 eV.

The XPS valence band again shows a broadening, however there is no indication of any emission at ~ 6 eV, indicating very low d-character. We observe a decrease in $N(E_f)$ and a slight shift of the valence band. We also notice a shift of the 4f levels by about $\sim +0.3$ eV. The structure at ~ 6 eV is in agreement with the results of Peterman et al. [9]. However, they observe an

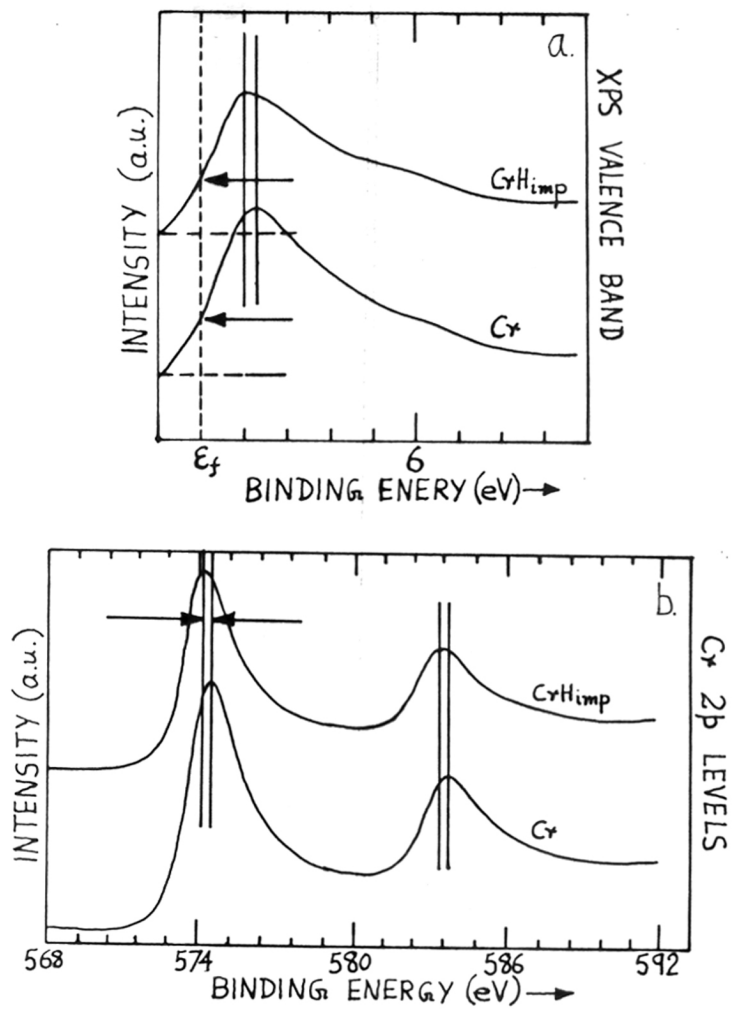


Fig. 4.5

addition structure at ~ 8 eV. In addition, they do not observe a 4f level shift contrary to our results.

The CrH and MnH Systems

Chromium and manganese exhibit extremely low solubilities for hydrogen. Recently, Snavely [11] has reported a hexagonal monohydride of CrH and a cubic dihydride CrH₂. Baranowski [12] has prepared the hexagonal form of CrH using high pressure synthesis and recently reported the synthesis of MnH [13].

The electronic specific heat coefficient γ for CrH_{0.97} has been measured to be 4.5 mJ/g mol K² as compared to a value of 1.4 mJ/g mol K² [14]. The magnetic susceptibility χ of CrH_{0.97} has a value of 220.9×10^{-6} emu/g mole compared to 181.8×10^{-6} emu/g mole for Cr. χ also exhibits considerable temperature and field dependence and rises to a value in excess of 265×10^{-6} emu/g mole below 10°K. These results imply an increase in $N(E_f)$.

Switendick [15] has done a band structure calculation (non self-consistent) for both CrH and MnH. He calculates an increase in $N(E_f)$ for both systems.

Fig. 4.5a shows the XPS valence band spectra for the CrH system. We notice a shift to about -0.3 eV for CrH and if we normalize intensities we find an increase in $N(E_f)$. Fig. 4.5b shows the Cr 2p levels. There is a shift of ~ 0.4 eV indicating a charge transfer from H atom to Cr site. The increase in $N(E_f)$ is in excellent agreement with experimental results.

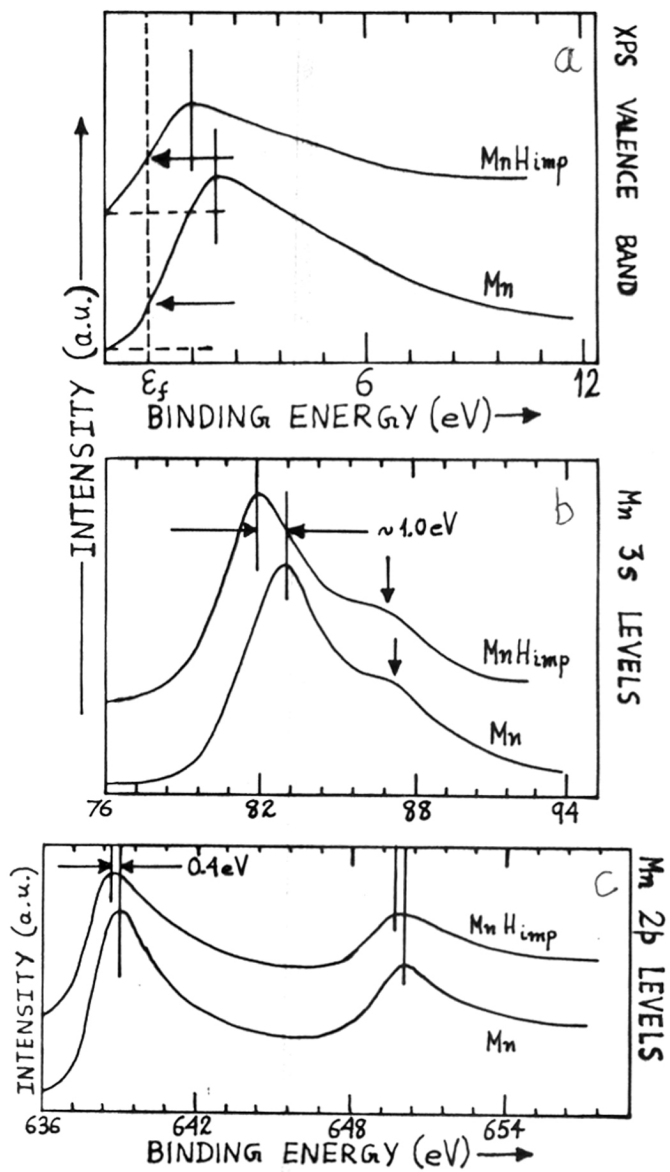


Fig. 4.6

Fig. 4.6a shows the XPS valence band of Mn. There is a shift of -0.5 eV of the peak maxima, and if we normalize the intensities we notice an increase in $N(E_f)$.

Fig. 4.6b shows the 3s multiplet split levels. There is a shift of -1.0 eV, with an increase in the separation of 0.8 eV.

Fig. 4.6c shows a shift of -0.4 eV of the $2p_{3/2}$ level in MnH, with a broadening and increase in asymmetry. These two effects are known to be a consequence of the increase in multiplet splitting.

These XPS spectra are probably the first reported for CrH and MnH.

The RuH, FeH and CoH Systems

Ru is a late-transition metal and is known [16] not to form a binary hydride by equilibrium methods. Fig. 4.7 shows the XPS valence band and the 4d levels of Ru in the pure and implanted metals. We find an increase in $N(E_f)$ after implantation, and a shift of the 4-d band. The 3-d core levels are also shifted by ~ -0.4 eV. To our knowledge this is the first XPS spectra of the RuH system.

XPS studies on the CeRu_2H_4 system [17] have shown that the 3-d levels of Ru, are broadened and shifted to higher binding energies. This has been attributed to the Ce 4f-induced lattice expansion with its related reduction of the spatial valence-electron density. The core level valence-electron Coulomb

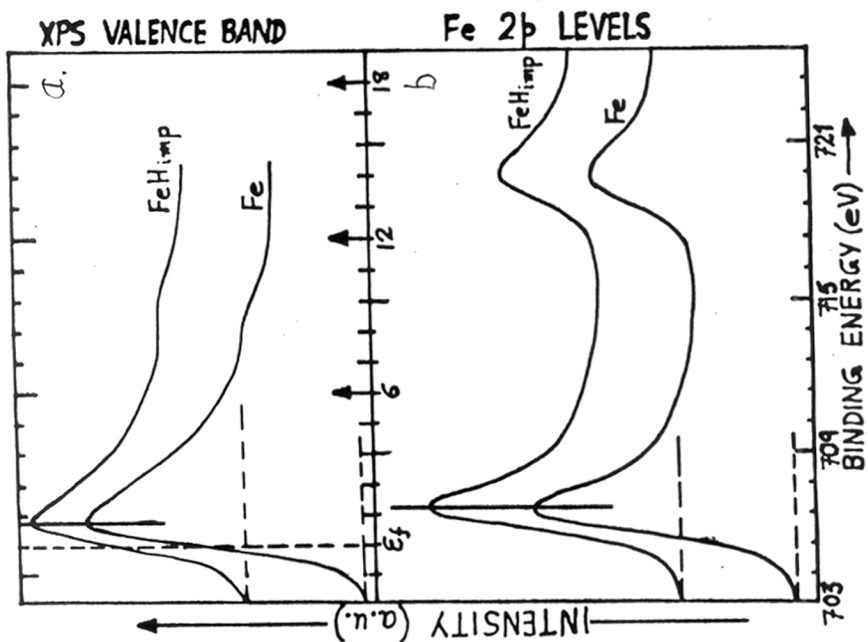


Fig. 4.8

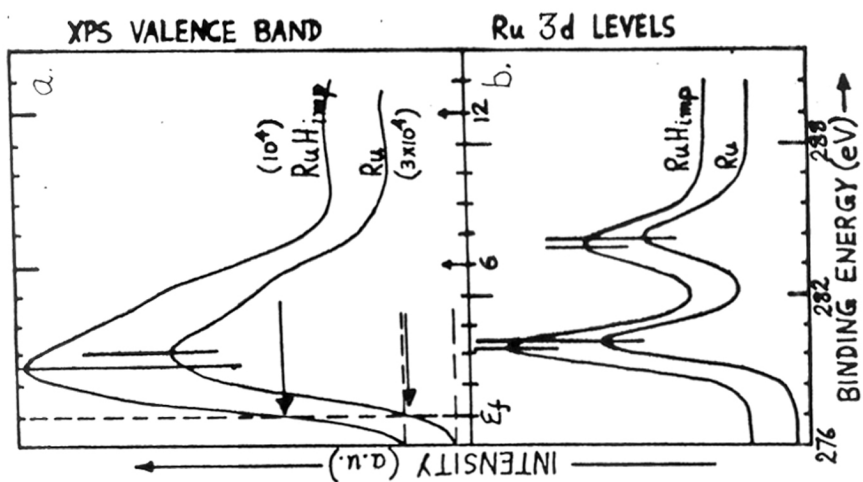


Fig. 4.7

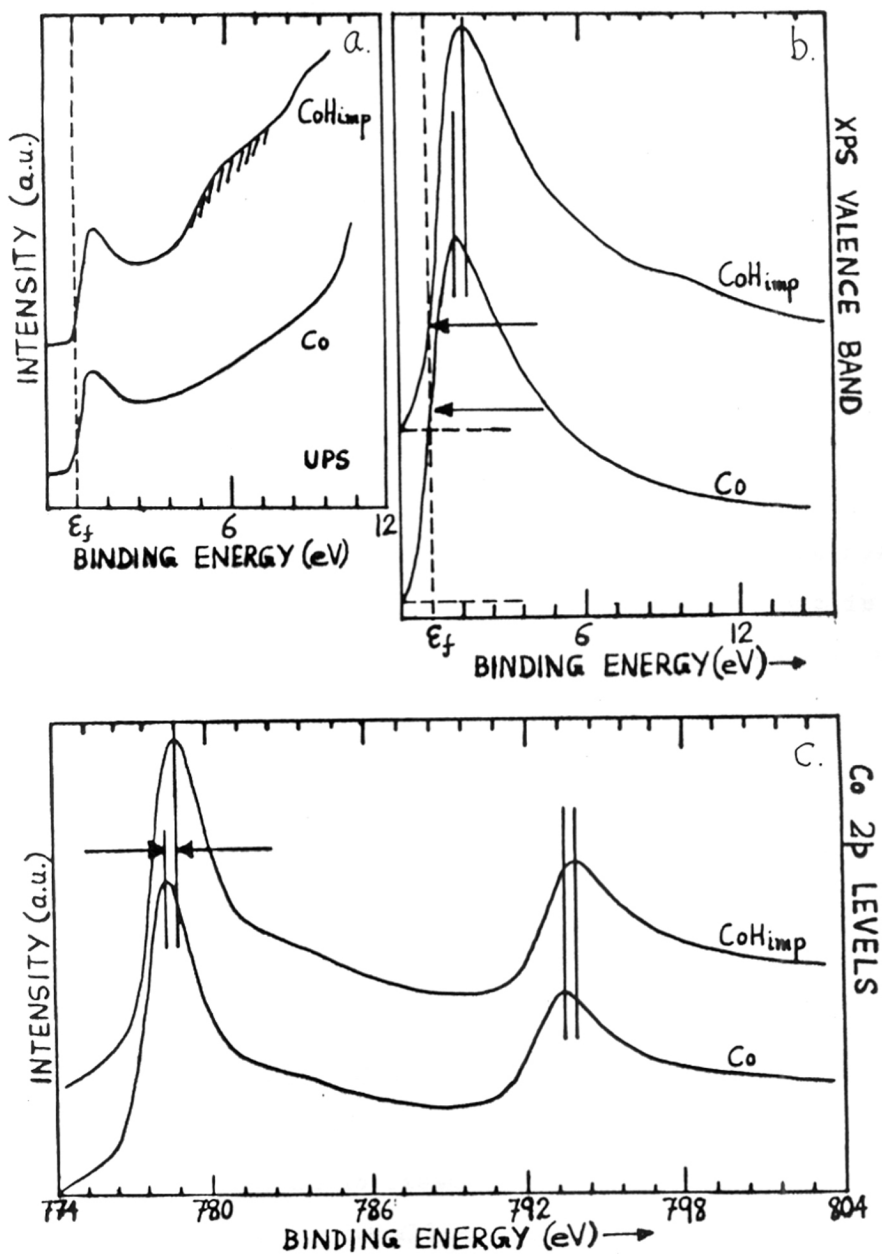


Fig. 4.9

repulsion is then reduced and hence the Ru 3d level is more deeply bound.

Figs. 4.8a,b show the corresponding situation for iron. We do not find any change or shift in the XPS valence band or 2p core level. We however do notice a fall in intensity. No such results are available for the Fe system.

However, in ternary hydrides of the type MFe_2H_x , ^{57}Fe Mossbauer spectroscopy has shown anomalous increases in the Fe magnetic moment [18]. There are no core-level studies available for these systems.

Figs. 4.9a,b and c show the situation for the CoH system. This system turns out to be a surprise. Its behaviour is very similar to that of Pd. The UPS spectra shows a new structure at ~ 6 eV. The XPS valence band shows a broadening in this region and a decrease in $N(E_f)$. The 2p core-level shows a shift of $\sim +0.5$ eV indicating an increase in the charge density at the H site. This is again possibly the first XPS spectra of the CoH system.

The NiH, PdH and PtH Systems

Nickel has a small solubility for H, and the NiH system has been prepared by the electrolysis method [19]. Some experimental results have been (i) an increase in the electronic specific heat capacity γ compared to metallic Ni, $\gamma_{NiH} \sim 2 \gamma_{Ni}$. This would imply an increase in $N(E_f)$ since γ is related to $N(E_f)$, (ii) a continuous decay of the ferromagnetism with increasing hydrogen

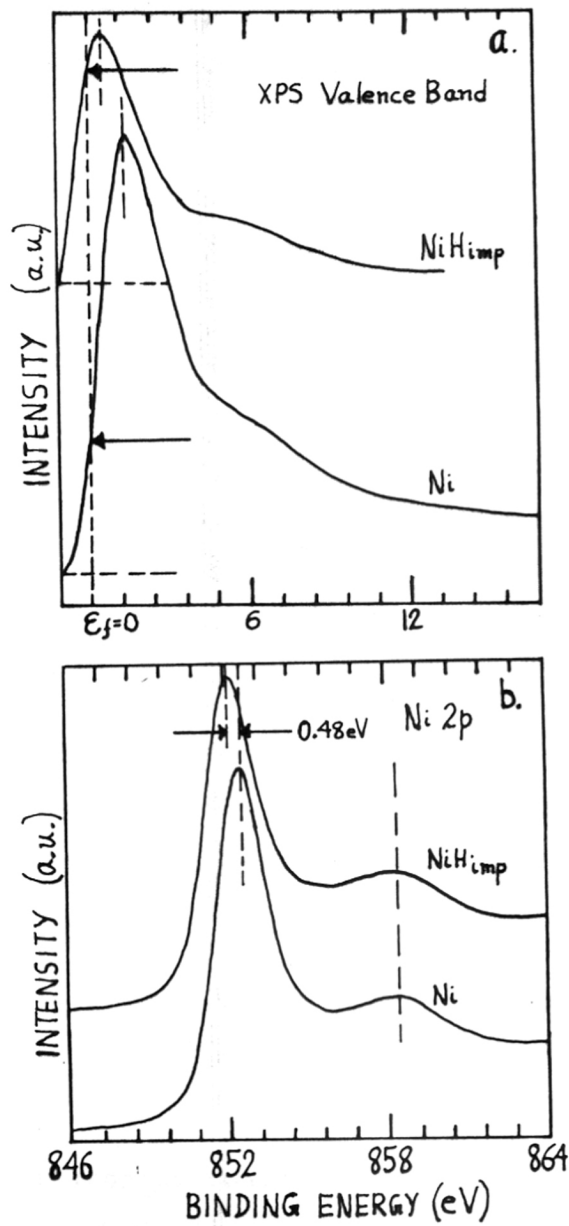


Fig. 4.10

concentration in the NiH system. This would imply filling of the Ni d-band.

A recent ab initio APW band-structure and density of states calculation for NiH by Gupta et al. [20], shows that the d-band holes are filled in the hydride. This feature is qualitatively similar to that found for PdH; however, E_f in NiH is much closer to the top of the d bands than in PdH. This has several important consequences: (i) NiH has a higher density of states at the Fermi level, $N(E_f)$, (ii) A larger metal d character and a smaller hydrogen s character at E_f , compared to PdH.

Fig. 4.10 shows what is possibly the first XPS spectra of the NiH system. In Fig. 4.10a are the XPS valence band spectra. It is quite obvious that there is a large increase in $N(E_f)$. This is in very strong agreement with specific heat measurement. Fig. 4.10b shows a Ni 2p core-level shift of -0.5 eV implying a charge transfer from the H site to the Ni site.

An increase in $N(E_f)$ would imply an increase in the Pauli contribution to χ . However, a drastic reduction in the Curie contribution to χ would possibly compensate this increase.

Since NiH is isoelectronic to PdH and whose magnetic behaviour is also similar, it could also be considered a strong candidate for a superconductor. However, no such behaviour has been observed for Ni films implanted at liquid He temperatures with H [21]. This behaviour has been attributed to (i) hardening of the optical phonons in NiH [22], (ii) the increase in the hydrogen s-contribution to $N(E_f)$ is insufficient.

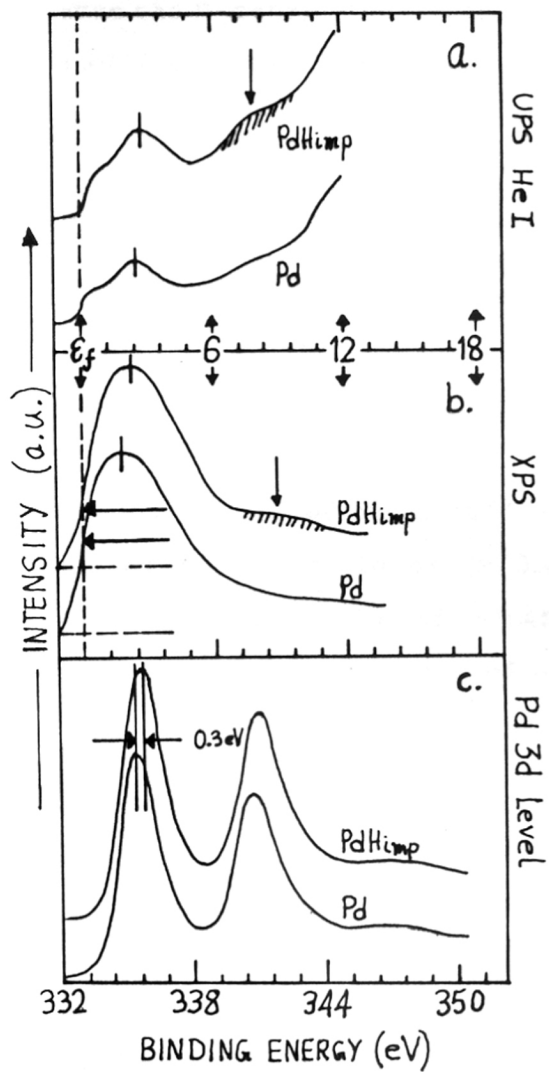


Fig. 4.11

We do not observe the H-metal bonding band at $\sim 6-7$ eV since the valence band satellite at this position would obscure it. We also observe an increase in separation of the 2p level and its satellite, however at present we do not have any explanation for this effect.

The PdH system is probably the oldest and most heavily studied system. Some important experimental results have been (i) discovery of superconductivity with a high T_c of 9 K for a H/Pd ratio of unity [23], (ii) decrease in the magnetic susceptibility from a high value of 600×10^{-6} emu/gm at. for Pd to essentially zero at a H/Pd ratio of $\simeq 0.6$ [24], (iii) A continuous decrease in χ from a value of ~ 9.48 mJ/mole K^2 for Pd to about 0.78 mJ/mole K^2 at a H/Pd ratio of 0.96 [25].

There have been numerous band structure calculations for this system [26-28]. From their examination we notice the following changes due to H incorporation: (i) The 'd-manifold' of Pd is modified and shifted relative to E_f and $N(E_f)$ decreases, (ii) A band is formed near the bottom of the Pd d-band corresponding to the bonding state between Pd and H. This is predicted to fall 5-6 eV or 7-8 eV below E_f , (iii) A small charge transfer should occur. However, charge transfer in both directions have been predicted [27,28].

Fig. 4.11a shows the HeI spectra for Pd and PdH. The d-band in PdH is shifted slightly relative to E_f and $N(E_f)$ decreases relative to Pd. A new emission at 8 eV is also seen in the PdH spectra.

Fig. 4.11b shows the XPS valence band spectra. A slight shift of the 'd-band' relative to E_f and decrease of $N(E_f)$ as compared to Pd are again seen. The emission at 8 eV is again seen, and would imply that it has considerable d-character.

Fig. 4.11c shows the 3d core levels for Pd and PdH. The shift is about + 0.3 eV higher than previously reported [29,30]. We do not observe any narrowing or change in the line shape as reported [30], probably due to the lower resolution used by us.

There is as yet no experimental evidence of a crystallographically distinct hydride of Pt, analogous either to those of Pd or Ni [31]. Relatedly, therefore, there is substantially less experimental information available for the Pt/H system in comparison with the Pd/H or Ni/H system. Even at about 25 K Bar of hydrogen pressure, there is no evidence by electrical resistivity measurements of the onset of hydride formation at 300°K [12].

Switendick [15,19] has discussed the relative stability of PdH and PtH. He argues that due to relativistic effects in the Pt metal band structure, levels that are initially high above E_f in a metal such as Pd- and that are lowered below E_f by hybridizing with H- are already below E_f in Pt metal. The system then gains less energy by H charging and hence monohydride formation is not favoured.

In contrast another recent band-structure calculation by Papaconstantopoulos [32], assuming PtH may be formed by ion implantation, has shown that as in PdH, the total density of

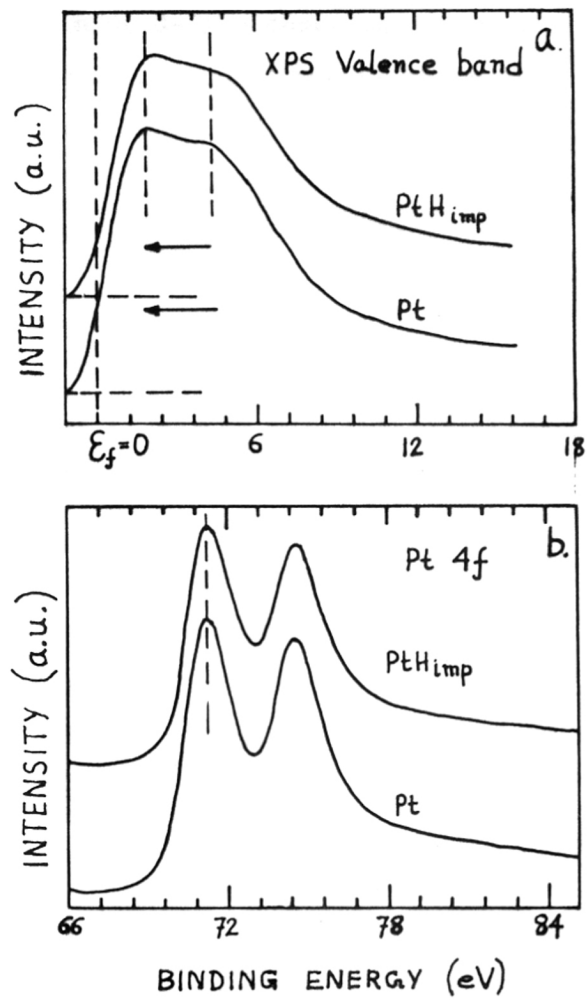


Fig.4.12

states and the dominant d-like contribution to the TDOS decreases at E_f compared to Pt. However, the s- and p- like DOS increase at E_f . Since the dependence of the superconducting transition temperature T_c on the H concentration is controlled mainly by the hydrogen s-like density of states at E_f , he calculates a T_c in excess of 10 K for PtH.

However, a search for superconductivity in PtH prepared by ion-implantation at liquid He temperatures has failed to show any evidence for the onset of superconductivity [21]. Fig. 4.12a shows the valence band of PtH and Pt. We notice a shift and broadening of the valence band of PtH compared to Pt. A consequence of the shift is that $N(E_f)$ decreases in PtH. This indicates filling of the 5d band of Pt analogous to that in PdH. Fig. 4.12b shows the Pt 4f levels which indicates there is no charge transfer between Pt and H atoms. These results are the first for PtH and support the calculations of Papaconstantoulos.

In the light of our results, the absence of superconductivity in PtH needs to be reexamined, through careful experimentation or an alternative explanation.

Correlation between Enthalpy of Formation and Core-level shifts for Transition-Metal Hydrides:

From empirical considerations a stable hydride has been given the following definition [33]. A stable hydride is one for which the equilibrium pressure lies below one atmosphere at $T=300^{\circ}\text{K}$. It has an enthalpy of formation more negative than -39 KJ/mol H_2 .

According to the atomic cell model (Chapter 1) of Miedema et al., developed for calculation of formation enthalpy, the energy changes involved in alloying (hydriding) are described by two terms: an exothermic contribution due to electronegativity differences and an endothermic contribution due to electron density mismatch at the cell boundaries. In applying it to hydrides an electronegatively and cell boundary electron density have to be assigned to metallic hydrogen.

In an independent approach Gelatt et al. [34] assumed that band structure contributions dominate the cohesive energy in hydrides and show that the enthalpy of formation is approximated by

$$\Delta E_1 \simeq E_b(MH) - E_b(H) = 2(\langle E_{LB}^{MH} \rangle - \langle E_{LB}^M \rangle) + n_d(\langle E_d^{MH} \rangle - \langle E_d^M \rangle) + E_F^M \dots 4.1$$

where $E_b(MH)$ and $E_b(H)$ are the one-electron band energies of the hydride and the pure metal respectively, $2(\langle E_{LB}^{MH} \rangle - \langle E_{LB}^M \rangle)$ is the shift in average energy of the lowest band containing two electrons, $n_d(\langle E_d^{MH} \rangle - \langle E_d^M \rangle)$ is the average shift in the d-band upon formation of the hydride multiplied by the number, n_d , of d-electrons contained in the occupied d-bands and E_F^M is the energy at which the added electrons enters the metal.

There is good agreement between enthalpy of formation derived by these two methods and those obtained from experiment. These are given in Table 4.1 in units of KJ/mole H_2 .

TABLE - 4.1

IIIA	IVA	VA	VIA	VIIA	VIIIA	IXA	XA
ScH ₂	TiH ₂	VH ₂	CrH	MnH	FeH	CoH _{0.5}	NiH _{0.5}
-200	-126	-54	-16	-9	+14	0	-6
YH ₂	ZrHr	NbH ₂	MoH	TcH	RuH	RhH _{0.5}	PdH _{0.5}
-225	-165	- 60	-12	(+36)	(+42)	(+25)	-40
LaH ₂	HfH ₂	TaH _{0.5}	WH	ReH	OsH	IrH	PtH
-210	-133	- 78	(+16)	(+52)	(+48)	(+42)	(+26)

Table 4.2 gives the shifts of the most intense core-levels, based on our work and available literature. These shifts are given in eV.

TABLE - 4.2

IIIA	IVA	VA	VIA	VIIA	VIIIA	IXA	XA
ScH ₂	TiH	VH	CrH	MnH	FeH	CoH	NiH
	+0.4 +0.6*	0.4*	-0.4	-0.4	0.0	+0.5	-0.5
YH ₂	ZrH	NbH _{0.5}	MoH	TcH	RuH	RhH _{0.5}	PdH
+0.8*	+1.0 +1.0*	+0.4 +0.7* +1.1*	-	-	-0.4 eV	-	+0.3
LaH ₂	HfH	TaH _{0.5}	WH	ReH	OsH	IrH	PtH
+1.0*		+0.4	-	-	-	-	0.0

* from literature.

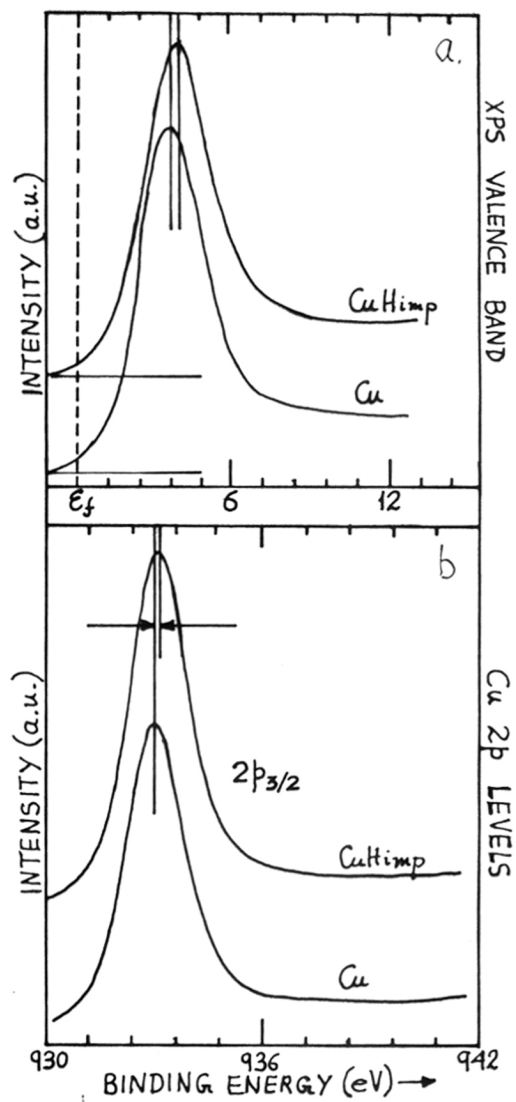


FIG. 4.13

From the above tables and from the definition of a stable hydride it is quite clear that for stable hydrides core-level shifts are always towards the high-binding energy side, and for unstable hydrides prepared by ion-implantation the core-level shifts are towards the low-binding energy side or is zero as in the case of Fe and Pt. Co seems to be an 'odd-ball'. Perhaps it is due to its HCP structure, whereas the calculations by Gelatt et al. are for an f.c.c. structure.

Another point to note is that we do not observe any hydrogen induced features in systems which do not obey the stability criterion.

The s-p metal/hydrogen systems

Hydrides based on s-p metals are unstable and can only be prepared by implantation or co-deposition techniques [35]. Of these In, Sn, Pb from the molecular hydrides Indane InH_3 , Stanane SnH_4 and Plumbane PbH_4 [36]. Implantation of H in Zn, Cd, In, Sn and Pb at liquid He temperatures has given relatively large increases in the superconducting transition temperature T_c [37].

Copper though in the 3d transition metal series has an electronic configuration $3d^{10}4s^1$ i.e. a full d-band and hence can be considered a simple metal. CuH is known to exist and has a wurtzite structure [38] and the bonding is believed to be covalent. Fig. 4.13 shows the XPS valence and 2p core levels in this system. We can discern a slight shift of ~ 0.2 eV to higher binding energy sides. This would imply that the bonding has a slight degree of ionicity.

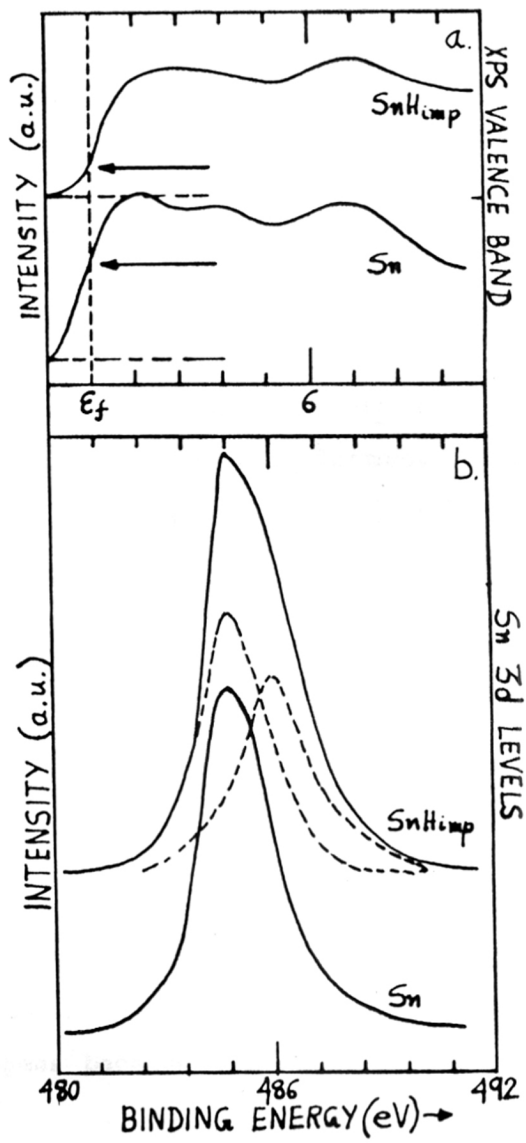


Fig. 4.14

We do not show the figure for the CdH system, since the valence band is obscured by the X-ray satellite of the 4d level of Cd. The 3d level however showed a shift of +0.4 eV implying an increase in the charge density at the H site. From this we could speculate a decrease in $N(E_f)$. There may be a possibility that the molecule CdH_2 may exist in analogy to the other s-p metals. We do not observe any shift in the core-levels or change in the valence band structure of In implanted with H. We attribute this to (i) formation of volatile InH_3 due to an active-ion beam (AIB) reaction with H_2 ions (ii) and/or spontaneous decomposition of the InH_3 formed. Indeed, In does form a highly unstable, volatile hydride [35] on bombardment with atomic H and has a life time of 2.8 to 215 msec.

Fig. 4.14a shows the XPS valence band of the SnH system. There is a change in line-shape and a shift to higher binding energies $N(E_f)$ decreases. Fig. 4.14b shows a broadening of the 3d level of Sn in SnH. A simple fit has been done. The separation of the metal and hydride component is of the order of +1 eV, indicating an increase in charge density at the H site. The existence of the pure metal peak would imply that some volatile SnH_4 (BP $-52^\circ C$) forms due to an AIB reaction with H_2 . We believe this happens because the implantation experiment was done for two samples of varying thickness. A hole was created in the very thin sample after H_2 bombardment, which would imply an AIB reaction.

We believe a solid phase hydride would form on implantation of H in Cd, In, Sn at temperatures less than $-200^\circ C$ or at liquid

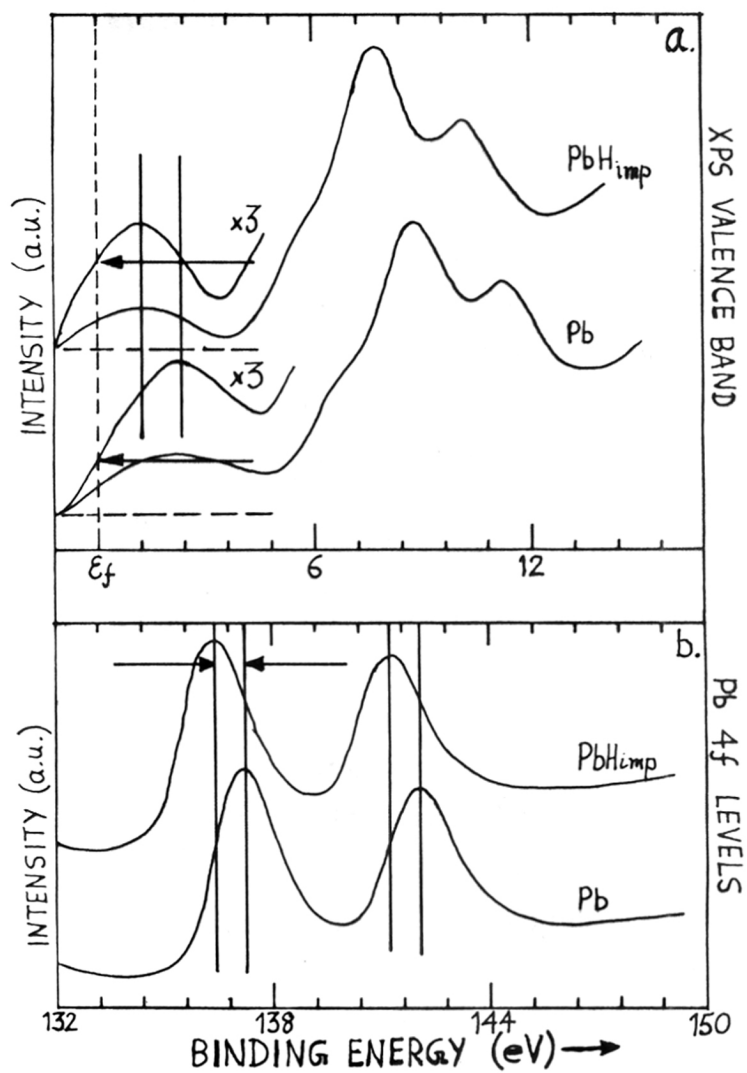


Fig.4.15

He temperatures, since the observed enhancement of T_c would require an increase in $N(E_f)$ for these simple metals.

In Fig. 4.15 are shown the corresponding situation for Pb. There is an increase in $N(E_f)$ for the PbH system. The Pb 4f level shows a shift of -1 eV in the implanted sample. This would imply charge transfer from the H atom to the Pb atom. The increase in $N(E_f)$ would be in good agreement with the enhancement of T_c for Pb implanted with H since Pb is a simple metal. We believe a solid hydride phase has formed.

To our knowledge no band structure and density of states calculations exist of the Cd, In, Sn, Pb systems.

Another important point to note is that the intensity of core-levels and valence bands in the implanted metals is always less than that in the corresponding metals. We attribute this to various reasons: (i) lattice dilation (known to be the case in TM-hydrides), implying lesser number of metal atoms seen in the probing volume, or (ii) change in transition probabilities.

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SUMMARY

Summary

In this section we point out the salient features of our study.

- i) We have shown that in-situ H implantation is a powerful preparation method of H/metal systems for electron spectroscopic studies.
- ii) H-induced states occur 4-10 eV below the Fermi level E_f , for systems whose heats of formation are more negative than -40 KJ/mol H_2 . These levels have varying amounts of d character. These results are in good agreement with band structure calculation. We also notice a decrease in the density of states at the Fermi level $N(E_f)$, compared to that of the metal.
- iii) No hydrogen-induced states are detected below the Fermi level E_f , for systems whose heats of formation are less negative than -40 KJ/mol H_2 or are positive. This implies that these states do not exist or have almost no d-character. The density of states at the Fermi level $N(E_f)$ increases compared to that of the metal.
- iv) The sign of the shift of the most intense core-levels in the hydrides correlates very well with the stability criterion for these hydrides. The shift is to high binding side for systems with heats of formation more negative than -40 KJ/mol H_2 . We observe shifts to the low binding energy side for systems whose heats of formation are less negative than -40 KJ/mol H_2 . However, Fe gives zero shift. This is because

the HCP form of FeH is stable only in the vicinity of liquid N_2 temperatures.

- v) The intensity of all levels in the implanted metals is less than the corresponding levels in the corresponding metals. We attribute this to three effects or a combination of these: a) lattice dilation, b) change in transition probabilities and c) a hydrogen overlayer on the surface.
- vi) The system CoH shows a similarity to the PdH system. This is contradictory to the behaviour which we would expect from its heat of formation.
- vii) There is evidence of active ion beam (AIB) reactions between In, Sn with H_2^+ ions. These systems are known to form volatile hydrides. Pb shows indication of a solid phase hydride.

Scope of future work:

We plan to extend this work to ternary metal hydrides where there is a paucity of electron spectroscopic studies. We would also like to study binary hydride systems at liquid N_2 temperatures, since some hydrides like FeH, WH, ReH and MoH are stable only at these temperatures. These studies would also be extended to rare-earth hydrides since these systems show some exotic effects.

ACKNOWLEDGEMENTS

The author expresses his deep sense of gratitude to his teacher and research guide, Dr. A.P.B. Sinha, Distinguished Scientist, National Chemical Laboratory, Pune for the inspiration and guidance, without which, this work would not have come into existence.

Thanks are also due to:

Dr. S. Badrinarayanan, who introduced me to 'the machine' and its intricacies.

Members of the Physical Chemistry Division, National Chemical Laboratory, for 'strong' and 'weak' interactions.

Dr. R.P. Agarwala, for making facilities available at Bhabha Atomic Research Centre.

The Indian National Science Academy, New Delhi, for awarding me a Senior Research Fellowship.

The Director, National Chemical Laboratory, for permission to carry out this work.

N.C.L.,
PUNE 411008,
June, 1986


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