TRANSITION METALS

I.1 Band Structure of Pure Transition Metals

As the atoms of a given element are brought close together, we find that the outer atomic s-electron wave functions join together forming a band of electrons. The band would have plane-wave character with some atomic symmetry near the ion sites. As the atoms are brought still closer together, the outermost d-electrons would also be expected to form a band. The d-band would be narrower than the sp-band since d-wave functions overlap less and so remain more tightly bounded by the atomic potential.

I.1.1 The Transition from Bound to Free Bands

We can form the electronic energy bands in solids into narrow tight-bound bands and nearly free electron bands as shown in Fig.1.1. The figure on the left shows the electronic states for a free-atom potential which is strong enough to bind all electrons that will later be free in the conduction band of the metal(on the right). When a number of such atoms are brought together to form a solid, this not only allows the atomic orbitals on neighbouring sites to interact and form a band but also the overlap of potentials lowers the barrier between neighbouring cells to such an extent that some of the supposed " atomic levels" now lie above the zero of muffin-tin potentials formed and are no longer bound states of the muffin-tin wells. As the bands arising

from distinct atomic levels begin to overlap one another in energy
such as 4s and 4p bands, they simply coalesce into a single nearly
free electron distribution, refered as sp-bands. Atomic d-levels,
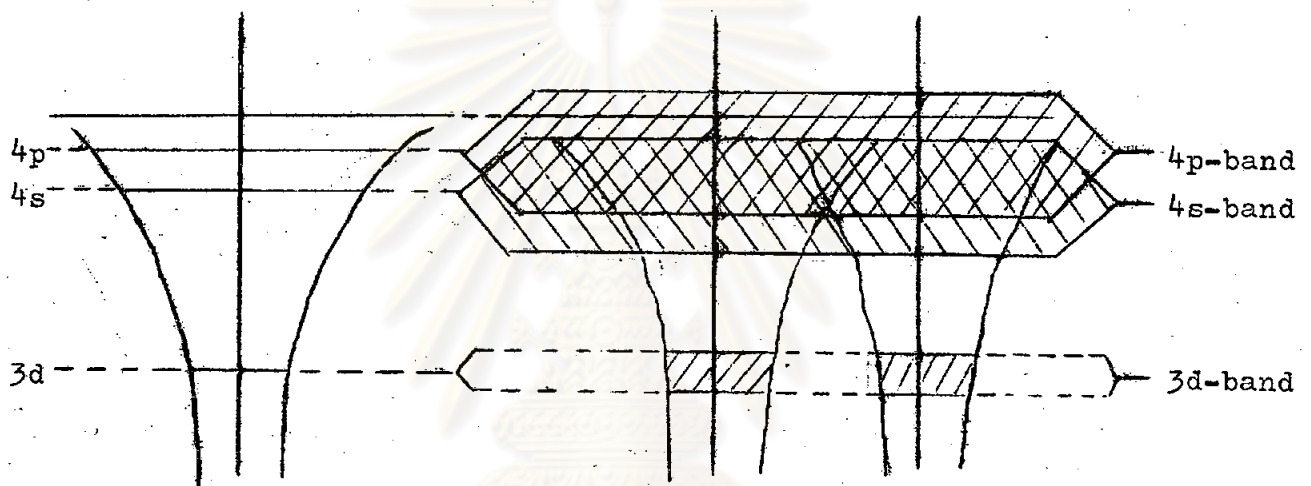however, from d-bands. These are shown in Fig.1.2.

Fig.1.1 Conventional LCAO description of the formation of
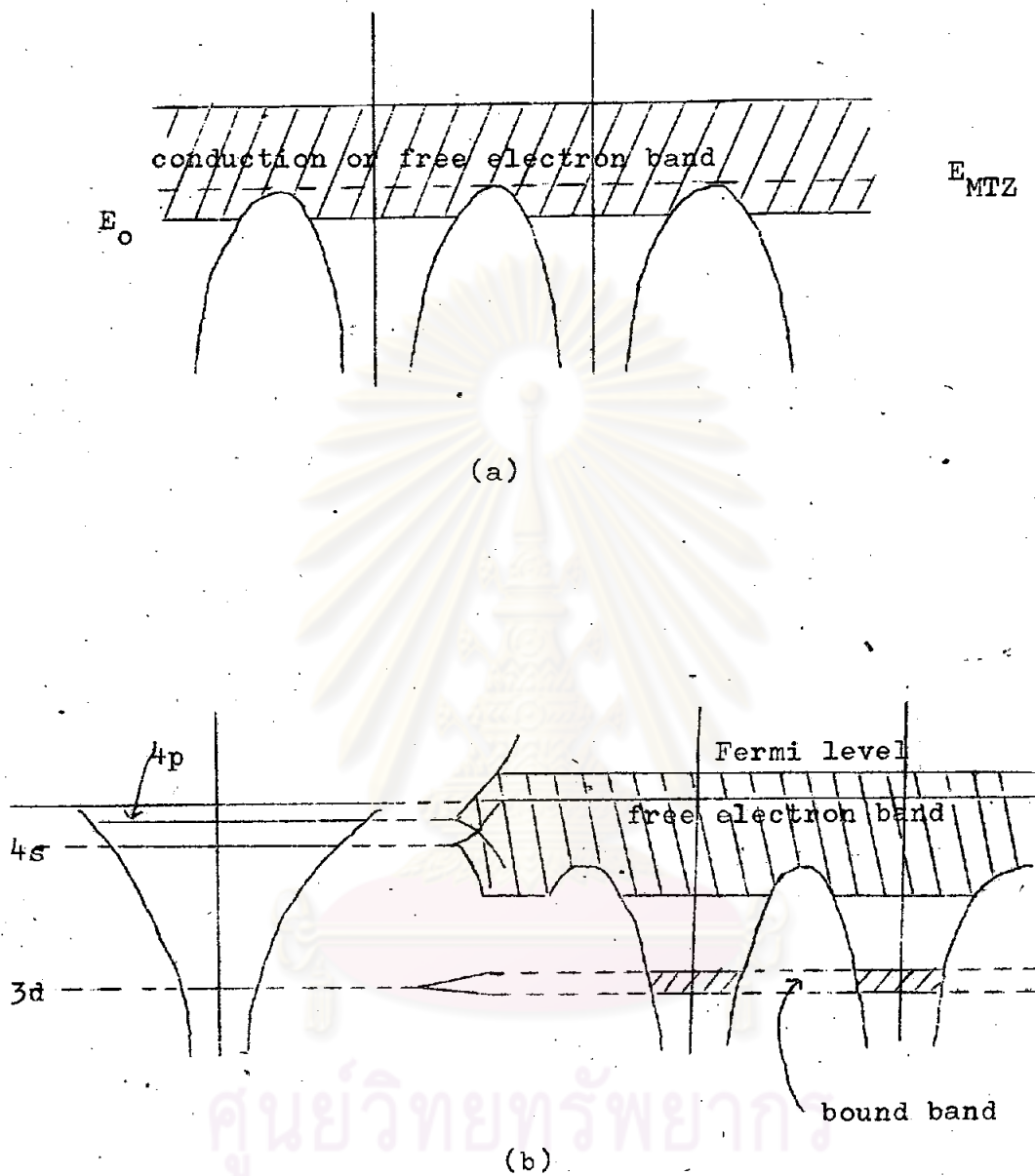metallic conduction bands.

(a)

(b)

Fig.1.2 (a) The bottom of free electron bands, E_o, lies a little
    below the assumed muffin-tin zero, E_{MTZ}.

(b) Conventional LCAO description of the formation of
    metallic conduction bands in terms of the muffin-
    tin potentials.

I.1.2 Resonance Bands

The pure and narrow d-bands are usually calculated by using the tight-binding method. It was noticed that the d-orbitals are so closely concentrated within the core of an atom that they produce only narrow bands by overlap with neighbours. In the transition elements these inner d-states are not all filled, but lie very close to the s or p " valence " states, which themselves combine to form an ordinary conduction band. The narrow d-band, with a density of states capable of holding up to 10 electrons per atom, lies within the s-p-band, and hybridizes with it where they cross(Fig.1.3)
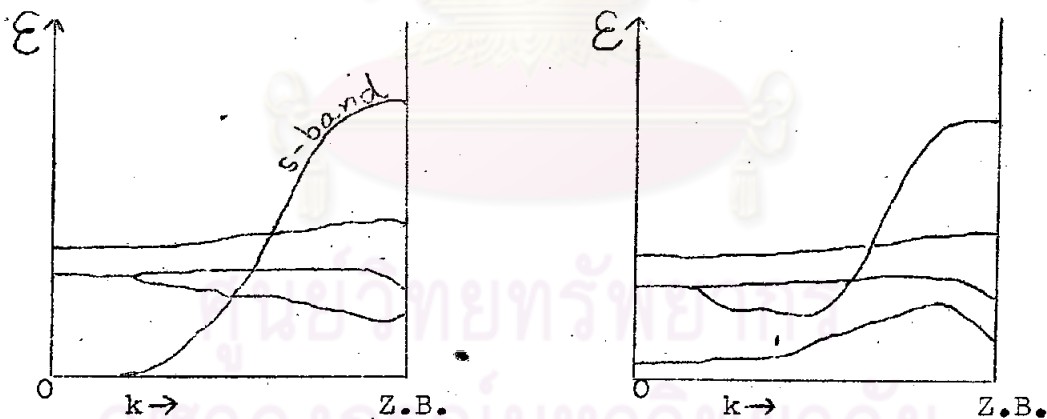

Fig.1.3 (a) d-bands crossing s-bands;

(b) s-d hybridization.

This complicated band structure is associated with a resonance at the former atomic d-level, and cannot be analysed into separate s-and d-bands. Nevertheless, we can say for example, that neither of the bands is full, so that the material is metallic, with conduction mainly by the s-electrons (Fig.1.4(a)). In the noble metals the d-states are in fact full, but they generate a resonance d-band within the ordinary N.F.E. band of the valence electrons, a few volts below the Fermi level (Fig.1.4(b)).
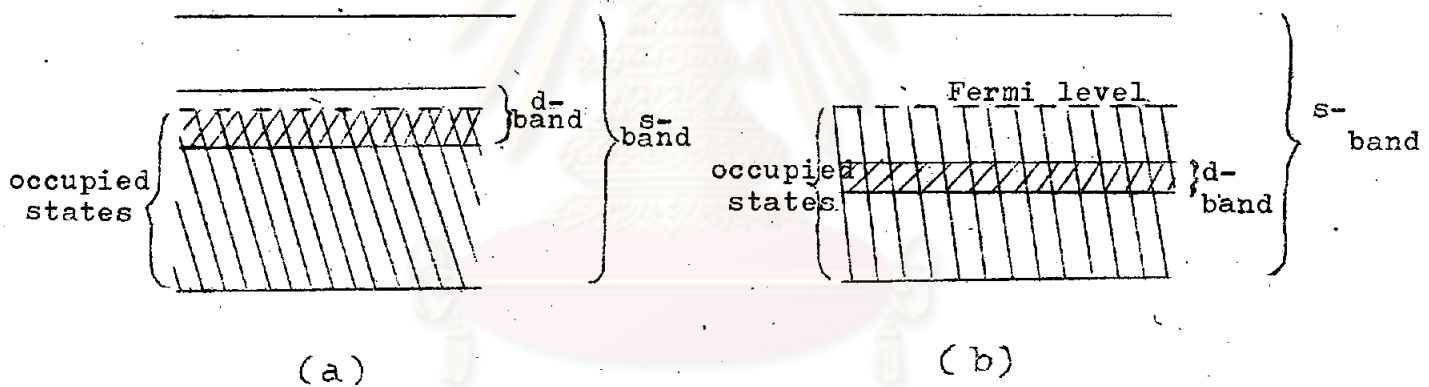

Fig.1.4 (a) Band structure of a transition metal

(b) Band structure of a noble metal

I.1.3 d-Band in Tight Binding

Except for important hybridization effects the d-bands closely resemble those obtained in the tight binding approximation whereas the conduction bands are similar to those of nearly free electron calculations. Consequently, the unhybridized d-bands can be represented in terms of linear combinations of atomic orbitals (LCAO) and the lowest conduction bands in terms of a "four-OPW approximation".

The principles of LCAO methods are:

(1) Write down the lattice potential as the sum of "atomic" potential V_i centered on the various lattice sites i

$$V = \sum_i V_i . \tag{1.1}$$

(2) Write down each electronic state in the solid as a linear combination of atomic (d) functions. For each site, i, there are 5 such atomic functions, denote $|im\rangle$, where the orbital moment m goes from 1 to 5; they are eigenfunctions of V_i, with energy E_0; their overlap integrals over two sites are neglected

$$|\psi(E)\rangle \simeq \sum_{i,m} a_{im} |im\rangle , \tag{1.2}$$

$$(T + V_i)|\psi_{im}\rangle = E_0 |\psi_{im}\rangle , \tag{1.3}$$

$$\langle im|jm'\rangle \simeq \delta_{ij}\delta_{mm'} , \tag{1.4}$$

and $$|a_{im}|^2 = 1 . \tag{1.5}$$

(3) From matrix elements $\langle im|V_\ell|jm'\rangle$, only the two-center integrals between first (or second) neighbours are retained.

The set of linear equations satisfied by the a_{im} coefficients is then of the type

$$(E_o + \alpha_{im} - E) a_{im} + \sum_{j \neq i, m'} \beta_{im}^{jm'} a_{jm'} = 0, \qquad (1.6)$$

with

$$\alpha_{im} = \langle im | \sum_{j \neq i} V_j | im \rangle, \qquad (1.7)$$

and

$$\beta_{im}^{jm'} = \langle im | V_j | jm' \rangle. \qquad (1.8)$$

The α integrals merely " shift " the energy of the atomic levels $\psi_{im}(E_O)$, while the β integrals mix them into molecular states extending over the whole solid. The β integrals also give rise to the width w of the band; they are akin to the bonding molecular integrals[1](Fig.1.5).
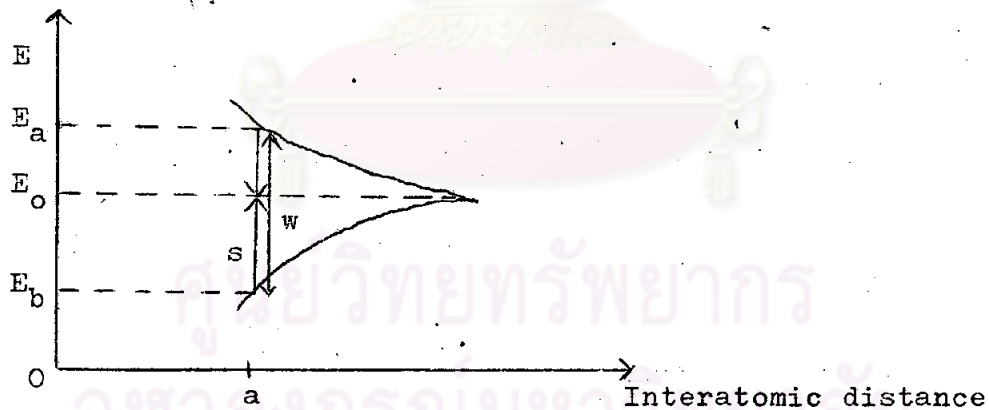

Fig.1.5. Energy shift(s)and width(w) of a narrow band.

I.1.4 Width of the d-Band

The shape of the d-band thus obtained depends on the values taken for the α and β integrals(1.7),(1.8). All computations in metals point to d-bands with a width w larger than their shift s,

as in Fig.1.5. Typical values are w=5-10 eV; s=1 to 2 eV. Such

widths are consistent with experimental data from x-ray spectra.[2]

    In the tight-binding scheme, the atomic selection rules

should hold to a good approximation. They predict a strong transi-

tion probability for absorption from or emission to inner p-shells.

For elements of the first transition series, transitions with 2p-

states give rise to strong bands, with widths definitely larger

than the Auger life time involved. Adding up the widths of the

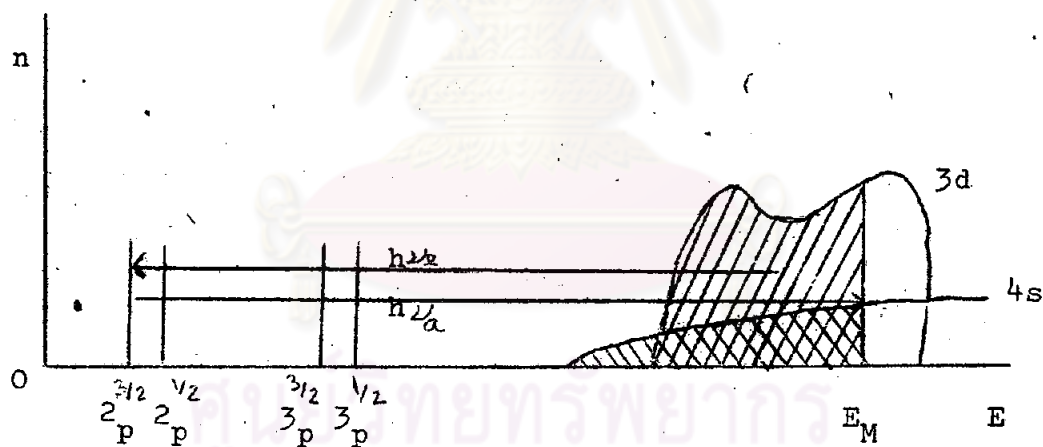absorption and emission bands(Fig.1.6),we obtain*d-band widths of

typically 5eV.

Fig.1.6 X-ray absorption and emission spectra

I.1.5 Density of States of the d-Band

    The density of states curve n(E) can be deduced from the

knowledge of the E(k) curves, since

$$n(E) \;=\; \int_{s(E)} \frac{dS}{|\nabla_k E|} \;,$$

where S(E) is the surface of energy E in the first Brillouin zone.
This has been done in tight binding with some accuracy only in the
cubic (b.c.c.,f.c.c.) phases.

Results in the tight-binding approximation are pictured in
Fig.1.7 and 1.8. Because the band width is large compared with
spin-orbit corrections,these do not change the main features of
n(E) (Fig.1.8a,b).

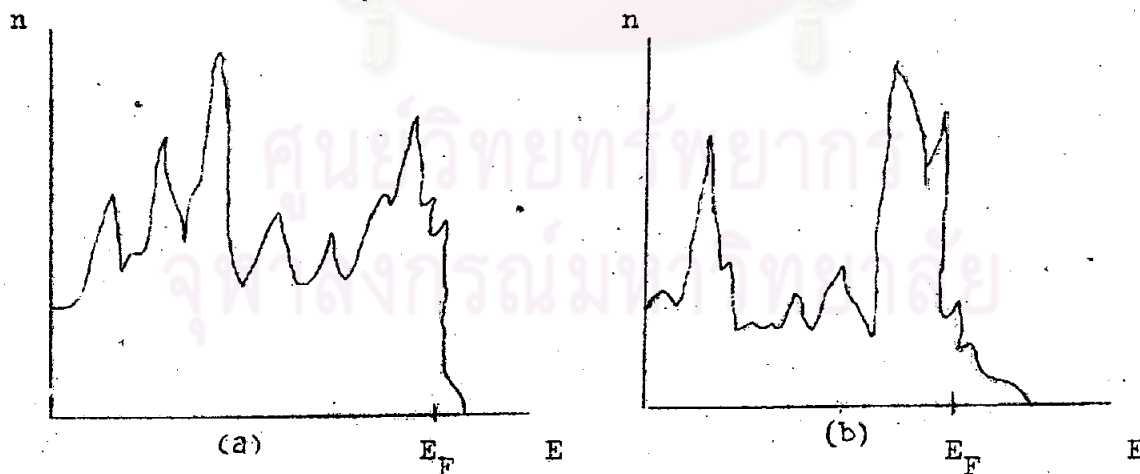Fig. 1.7 Density of states n(E) for the d-band in b.c.c. chromium.

Fig.1.8 Density of states n(E) for the d-band in f.c.c. metals:

(a) Pd; (b)Pt.

Even in these cases,the results can not be taken as very accurate,owing to uncertainties in the values of the α and β integrals and corrections for sd-mixing.

I.2 Transport Current in Transition Metals

In the classical theory of Lorentz the conductivity of a metal is

$$\sigma = \frac{ne^2 \tau}{m}, \tag{1.9}$$

where n is the number of electrons per unit volume, m the mass of an electron, τ half the time between collisions or"time of relaxation". In the quantum theory of conduction,this formula remains true with the following modifications;for m we must understand the "effective" mass of an electron in the crystal lattice,which will in general be greater than the actual mass m_o of a free electron. Secondly, τ must be calculated by the methods of quantum mechanics, so that $1/\tau$ is proportional (for $T > \Theta_D$)to:

(1) The mean square displacement,due to thermal motion,of the atoms from their mean positions. This is proportional to $T/_M \Theta_D^2$, where M is the mass of an atom, Θ_D the characteristic temperature.

(2) the density of states $N(E)$ at the surface of the Fermi distribution,i.e.,for the occupied states of highest energy.

According to the theory, the electrons in all states belonging to zones which are not fully occupied can contribute to the electric current;therefore the d as well as the s electrons must be classed as conducting electrons. The effective masses, however, will be very different;the conduction electrons of copper

and silver have been investigated by Fuchs[3] by the method of Wigner and Seitz; he finds that they behave approximately as free electrons. The same should be true for similar fields of Ni and Pd; we shall thus assume for the s-electrons

$$m_s \simeq m_o,$$

where m_o is the actual mass of a free electron. For the d-elec - trons, on the other hand, owing to the small overlap of one d-wave function with another, we must assume

$$m_d \gg m_o.$$

In other words, the d-electron takes longer to move from atom to atom under the influence of an applied field than does the s- electron.

The case where the Fermi distribution lies in two Brillouin zones has been discussed in detail by Mott[4] and a solution for $\mathcal{T}(k)$ obtained, subject to the following simplifying conditions:

1. The surface of the Fermi distribution lies in two zones,(a) and (b); zone (a) is nearly full and zone (b) nearly empty, the number of electrons in(b) being equal to the number of holes in(a).

2. The state of an electron in either zone being described by wave vectors k_a, k_b, the energies in the two zones are given by

$$E_a = E_o - \frac{\hbar^2 k_a^2}{2m} \quad , \quad E_b = \frac{\hbar^2 k_b^2}{2m}.$$

3. The transition probabilities $P(k_a k_a')$,$P(k_b k_b')$,$P(k_a k_b)$ are functions only of the angles between the initial and final wave vectors.

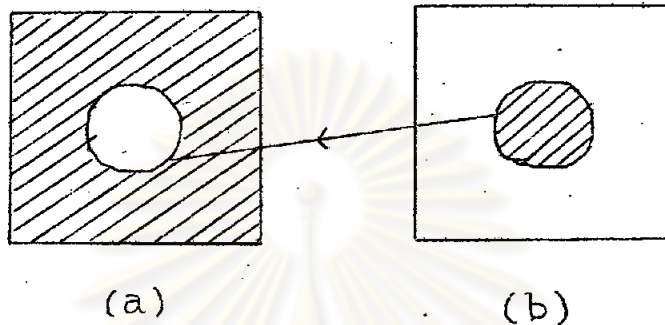The new feature of the problem is that transitions are allowed from one zone to another, as shown in Fig.1.9.

(a)   (b)

Fig.1.9 k-space of metal with two zones;occupied states are shaded.

With these assumptions it may be shown that $\mathcal{J}$ is independent of k in either zone; we may thus define two times of relaxation, $\mathcal{J}_a$, $\mathcal{J}_b$, one for each zone. Formula for the conductivity then reduces to

$$\sigma = \frac{ne^2}{m}(\mathcal{J}_a + \mathcal{J}_b),$$

$$(1.10)$$

where n is the number of electrons per unit volume actually in the zone(b), and thus the number of holes in zone(a). The first term represents the current carried by the positive holes, the second by the electrons.

For the transition metals we have two zones, the d zone and the s zone, to take into consideration. In the d zone the density of states is large. From this it follows that, if $\mathcal{J}_a$ and $\mathcal{J}_b$ are comparable, the current is nearly all carried by the electrons in the s zone. On the other hand, the transition probability from one state to another is proportional to the density of states in the final state. Therefore transitions in which the

electron jumps from the s zone to an unoccupied state in the d zone are more probable than the ordinary scattering processes, in which an electron jumps from one s state to another. This appears to be the reason for the low conductivity of the transition metals.

I.3 Anderson Model for Transition Metals

Anderson[5] proposed a model to study the occurence of a localized magnetic moments on iron-group atoms which are dissolved as dilute impurities in nonmagnetic metals. He introduced a model Hamiltonian which takes into account the presence of both free electron states and localized states. Included in his Hamiltonian are terms for the hybridization of the conduction electrons with localized d-electrons and for the Coulomb interaction between electrons of opposite spins occupying the localized orbital state.

In Anderson.'s' theory the Coulomb repulsion between localized atomic orbitals gives the appropriate energy

$$U = \int \left| \phi_d(r_1) \right|^2 \frac{a^2}{r_{12}} \left| \phi_d(r_2) \right|^2 d^3r_1 d^3r_2 \sim 10 \text{ eV.} \tag{1.11}$$

For a single hondegenerate d-level the Anderson Hamiltonian is

$$H = \sum_{k,\sigma} \epsilon_k c^+_{k\sigma} c_{k\sigma} + \sum_{j,\sigma} E_j d^+_{j\sigma} d_{j\sigma} + \left[\sum_{j,k,\sigma} V_{kj} c^+_{k\sigma} d_{j\sigma} \right.$$

$$\left. + \sum_{j,k,\sigma} V^*_{jk} d^+_{j\sigma} c_{k\sigma} \right] + \frac{1}{2} U \sum_{j,\sigma} d^+_{j\sigma} d_{j\sigma} d^+_{j-\sigma} d_{j-\sigma}, \tag{1.12}$$

where σ labels the spin orientation. C_k^+, C_k are the creation and destruction operators for s-electrons of momentum k; d_j^+, d_j are the creation and destruction operators for d-electrons located at a lattice site R_j.

The first term is the unperturbed energy of the free electrons where $\epsilon_k = \dfrac{\hbar^2 k^2}{2m}$ for free electrons.

The second term is the energy of the bound d-electrons where E_j is the binding for the orbital.

The third term is the overlap term where V_{kj} is the matrix element that connects the localized state at position j and the conduction state with the momentum k.

The fourth term is Coulomb energy.

By using Hartree-Fock approximation;

$$d_{j\sigma}^+ d_{j\sigma} d_{j-\sigma}^+ d_{j-\sigma} \longrightarrow \langle n_\sigma \rangle d_{j-\sigma}^+ d_{j-\sigma} + \langle n_{-\sigma} \rangle d_{j\sigma}^+ d_{j\sigma}$$
$$- \langle d_{j\sigma}^+ d_{j-\sigma}^+ \rangle d_{j-\sigma} d_{j\sigma}$$
$$- \langle d_{j-\sigma} d_{j\sigma} \rangle d_{j\sigma}^+ d_{j-\sigma}^+ , \qquad (1.13)$$

and let

$$\Delta_d = U \langle d_{j-\sigma} d_{j\sigma} \rangle , \qquad (1.14)$$

be the fluctuation due to the Coulomb repulsion.

With this approximation, the Hamiltonian becomes:

$$H = \sum_{k,6} \epsilon_k c^+_{k6} c_{k6} + \sum_{j,6} (E_j + U\langle n_6 \rangle) d^+_{j6} d_{j6}$$

$$+ \sum_{j,k,6} (V_{kj} c^+_{k6} d_{j6} + V^*_{jk} d^+_{j6} c_{k6}) \qquad (1.15)$$

$$-\tfrac{1}{2} \Delta_d \sum_{j6} d^+_{j6} d^+_{j-6} - \tfrac{1}{2} \Delta^*_d \sum_{j6} d_{j-6} d_{j6} .$$

The Hartree-Fock approximation leads to an overestimate of the effect of the Coulomb correlation energy, U, on the production of a localized magnetic moment. Since we are only interested in the model for transition metals, the criterion for the occurrence of the localized magnetic moment will not be met in the transition metals we are interested and therefore should not be of any concern to this study.