Chapter II

Theoretical Background

In this chapter we will consider the theoretical models which describe the magnetic state of matter. It is found that some of the elements in the periodic table show spontaneous magnetic moment in the absence of external magnetic fields. These elements are called a ferromagnetic, ferrimagnetic or antiferromagnetic depending on the orientation of their magnetic moments or their electron spins. The origin of spontaneous magnetization was unknown prior to the development of quantum mechanics. At that time, Weiss proposed a model to describe the spontaneous magnetization which did not treat the origin of the phenomena. Nevertheless, it gave good agreement to the experimental results.

In order to explain spontaneous magnetization, Weiss assumed that the orientation of a spin moment is due to field which acts on each lattice site, occupied by a spin moment. The field is called the molecular field model. With the advent of quantum mechanics, Heisenberg explained spontaneous magnetization as being due the interaction of nearest neighbor electrons with each other. This interaction term is called the exchange integral or exchange interaction which will be discussed in detail later. Weiss's model is a first approximation to Heisenberg's model. Unfortunately, Weiss's model encounters some serious problems when it was applied to the system in which the itinerant electrons contribute strongly to the spontaneous magnetization. These systems are the metals and metallic compounds. Stoner (1938,1946-1947) constructed a model in which the itinerant electron play the important part. Our consideration in this chapter is based on both the Weiss molecular fields model and Stoner collective electron model.

Exchange Interaction

In all condensed matter exhibiting the magnetic behavior, no matter whether they be ferromagnetic, ferritmagnetic or antiferromagnetic, there is an ordering orientation of the magnetic moments which arise from the electron spins. In the classical interpretation, the spin orientation is due to the energy between two electron spins or two magnetic moments similar to the energy due to magnetic dipole moment. In the quantum mechanics interpretation, the ordering of magnetic moments or the electron spins is due to the overlap of wave function of electrons belonging to neighboring ions. We start here with the wave function of N electrons. It was well known that the wave function which is used to describe the state of N electrons must be an antisymmetric wave function. An antisymmetric function is one for which the interchange of coordinate, both of spin and space coordinate, of any two electrons lead to a change in sign of the wave function, i.e.,

$$\Psi(r_1, r_2) = -\Psi(r_2, r_1) \qquad\qquad 2.1$$

where $\Psi(r_1, r_2)$ is denoted as the total wave function for the two electrons, one which is located at r_1 and the other is located at r_2, keeping in mine that two electrons are identical. If the wave function of each electron are denoted as φ_1 and φ_2, the total wave function becomes

$$\Psi(r_1, r_2) = \varphi_1(r_1)\varphi_2(r_2) - \varphi_1(r_2)\varphi_2(r_1) \qquad\qquad 2.2$$

This wave function satisfies equation 2.1 as is seen as follows

$$\varphi_1(r_1)\varphi_2(r_2) - \varphi_1(r_2)\varphi_2(r_1) = -(\varphi_1(r_2)\varphi_2(r_1) - \varphi_1(r_1)\varphi_2(r_2)). \qquad\qquad 2.3$$

Equation 2.2 is the two electron wave function. If $r_1 = r_2$ or $\varphi_1 = \varphi_2$, the two electron wave function vanishes, thus confirming that Pauli exclusion principle is operating.

From the two electrons wave function we can generalize to N electrons wave function as a summation of N multiple term at every possible different coordinate, i.e.,

$$\Psi = \sum (1)^{k+1} P_k(\Pi \varphi_i(r_j))$$ 2.4

$$\Psi = \varphi_1(r_1)\varphi_2(r_2)\,\varphi_3(r_3)...\varphi_n(r_n) - \varphi_1(r_2)\varphi_2(r_3)\varphi_3(r_4)...\varphi_n(r_1) + ...(N\ terms).$$ 2.5

Where P_k is a permutation of r_j, that form of a total wave function which is called the Slater determinant, i.e.,

$$\psi_N = \begin{vmatrix} \varphi_a(1) & \varphi_b(1) & \cdot & \cdot & \cdot & \varphi_n(1) \\ \varphi_a(2) & \varphi_b(2) & \cdot & \cdot & \cdot & \varphi_n(2) \\ \cdot & \cdot & & & & \cdot \\ \cdot & \cdot & & & & \cdot \\ \varphi_a(n) & \varphi_b(n) & \cdot & \cdot & \cdot & \varphi_n(n) \end{vmatrix}.$$ 2.6

The one electron wave function, $\varphi_1(r_1)$, satisfied

$$H_i\varphi_a(r_i) = E_a\varphi_a(r_i).$$ 2.7

Where H_i is a one electron Hamiltonian, the total Hamiltonian, H_{total}, contains N free electrons Hamiltonian plus the interaction term, H_{in}.

$$H_{total} = H_1 + H_2 + H_3 + ... + H_n + H_{in} = \sum H_i + H_{in}$$ 2.8

H_i is the free electron Hamiltonian which depends only on the coordinate of i electron, H_{in} contains the interaction term of N electrons.

The energy eigen value is obtained from the total Hamiltonian and total wave function. The energy of state is computed from

$$E = <\Psi H_{total} \Psi>.$$ 2.9

In the above, H_{total} can be separated in the individual Hamiltonian of each electron, which are independent with each other, and the interaction term which is regarded as the perturbation term. The energy of state, in the first approximation, would be

$$E = <\Psi [H_1 + H_2 + H_3 + \dots H_n + H_{in}] \Psi>$$ 2.10

$$E = \sum E_i + <\Psi H_{in} \Psi>$$ 2.11

where H_{in} depends on a pair of an electrons that interacted each other. Then $H_{in} = \sum_{ij} H_{ij}$. When the existence of spin is taken into account, the energy state due to a perturbation term can be separated into two parts, one depending on the occupation state of a parallel spins and the other depending on everything except the spin configuration. The first term denoted by J_{ij} depends on the orientation of a parallel spin and is called the exchange integral.

$$J_{ij} = <\varphi_i^*(n)\varphi_j^*(m)H_{mn}\varphi_j(n)\varphi_i(m)>$$ 2.12

Heisenberg Hamiltonian

In 1928, Heisenberg employed the interaction term, the exchange integral, to constructed the Hamiltonian would describe the state of interacting spins which led to spontaneous magnetization. This Hamiltonian is called the Heisenberg Hamiltonian, i.e.,

$$H = \sum_{ij} J_{ij}\, \mathbf{S}_i \cdot \mathbf{S}_j \qquad\qquad 2.13$$

The summation over ij is taken only in nearest neighbor of a localized electron base on the fact that J_{ij}, the exchange interaction, is due to the Coulomb interaction which fall off rapidly with the increase in the interatomic distance. The solutions of this model are easily obtained if one uses the Weiss molecular field model. It should be noted that in the case of 1/2 spin, the Hamiltonian is called the Ising model which exact solution in 1 and 2 dimension. The exact solution of two dimensional Ising model is called the Onsagar solution in honor of the person who first solved the model. Exact solution of three dimensional model has not yet been obtained. This problem is not of concern in this study.

Weiss Molecular Field Model

In 1907, Pierre Weiss propose a model which is now named after him. He assumed that there is a field acts on each spin or magnetic moment at each of the lattice sites. This field causes the ordering alignment of a spin or magnetic moment and is called the molecular field or mean field. Using standard statistical mechanics, he obtains the dependence of the magnetization on temperature. The development of these ideas proceed as follows.

Consider the Heisenberg Hamiltonian which was introduced after the Weiss model for a spin located at ith lattice site interact with other spin on other lattice site.

$$H_i = \sum_j J_{ij}\, \mathbf{S}_i \cdot \mathbf{S}_j \qquad\qquad 2.14$$

where the summation over j is taken only in nearest neighbor of a spin lattice site i. Assuming J_{ij} is constant for nearest neighbor lattice site i and j, we get

$$H_i = JS_i \cdot \Sigma_j S_j \qquad\qquad 2.15$$

$$H_i = -g\mu_B S_i H_e \qquad\qquad 2.16$$

where $H_e = \dfrac{2J}{g\mu_B} \sum_{j=1}^{z} S_j$. H_e is treated as the magnetic field that acts on a spin located at the lattice site i. Applying statistical mechanics, we obtain the temperature dependence of a magnetization in the form

$$M = Ng\mu_B sB_s\left(\dfrac{g\mu_B Hs}{k_B T}\right) \qquad\qquad 2.17$$

where μ_B is a Bohr magneton, s is a spin quantum number, g is a Lande' g-factor, H_o is the effective field, $H = \gamma M$ which γ is the effective field coefficient, $B_s(x)$ is a Brillouin function. It is seen that M, the magnetization appear on both sides of equation 2.17. The solution of this equation, M, can be obtained by the graphical method as shown in figure 2.1. This method is discussed in detail in many standard solid state text book (Christman, 1988, Kittel, 1986, Martin, 1967 and Smart, 1966). This model has been applied to real system. Prayoonwech and Tang (1979) extended the molecular field model to compute the temperature dependent of a magnetization of a spinal ferrite Fe_3O_4 with random arrangement of Fe^{3+} and Fe^{2+}. Qiao et. al (1992) also used this model to investigate the temperature dependence of the magnetization and to determine the exchange integral and the molecular field coefficients of $Sm_2Fe_{17}C_x$ and $Er_2Fe_{17}C_x$ compounds. Both investigations agree with the experimental results. However, the molecular field model has some serious problems when it applied to systems in which the magnetic moments are almost entirely due to the itinerant electrons. The evidence of the deficiencies of Weiss model is seen when comparing the values of the molecular field coefficients deduced from the observation of the Curie temperature. For nickel, if J_{ij} is assumed to be constant, the transition from ferromagnetic state to paramagnetic state leads to a

molecular field coefficient 13,400 while a transition from paramagnetic state to ferromagnetic state leads to a molecular field coefficient 18,500. (Martin, 1967) Other evidence of the failure of the Weiss model is a non-integer value time to Bohr magneton of a magnetic moment per ion is determined by the magnitude of a spontaneous magnetization at $T = 0$ K i.e. $\dfrac{M}{N} = g\mu_B J B_J (\dfrac{g\mu_B J H_o}{k_B T})$ if T become zero then $B_J(\infty) \rightarrow 1$ and M/N should be equal to the integer number time Bohr magneton. The value of a magnetization per ion of Ni, Fe and Co are $0.6\mu_B$, $2.2\mu_B$ and $1.72\mu_B$ respectively. This is due to the fact that Weiss model is concerned with localized electron (in fact, only with localized spin at a lattice site, which interact with each other through the exchange interaction). These interaction depends strongly on a wave function of a pair localized electron. This model is valid only in a non-metallic magnet such as a spinal ferrite and some of the oxide compound of transition elements. Because of the deficiencies of Weiss model, Stoner (1938) proposed his model to explain the magnetic behavior in the system that contain a non-local electrons, the itinerant electrons.

Stoner Collective Electron Model

As we emphasize above, the spontaneous magnetization of metal or metallic compounds of transition element, especially Ni, Co and F, are mainly due to itinerant electrons in $3d$ band. In both models, Weiss and Stoner, the spin orbit coupling term is neglected. Numerical calculation (Friedel, 1969) showed a spin orbit coupling term was small compare to the width of d band, the spin orbit term being less than 0.1 eV while the width of d band is in order of electron volts. The magnetization per unit volume of a transition alloys would be equal to the Bohr magnetron, μ_B, time a number of electron per unit volume, $M = N\mu_B$. In 1938 Stoner proposed his model to interpret the magnetic behavior of the system in which the electrons responsible to a magnetization are the itinerant electrons. It is based on the Fermi-Dirac distribution function and the shape of the density of states. The electrons having free particle energy, are those near the edge of the Fermi level. When the interaction

between a magnetic moment is switched on, the d band structure is splitted into two levels, The subband for the spin up electrons is shifted down and the subband for the spin down electrons is shifted up.

In his paper, Stoner obtained the graphical interpretation of M versus T by employing statistical mechanics and using the Fermi-Dirac distribution function. He assumed the energy of state to be that of the free electron density of state in three dimension i.e. $D(E) \propto E^{1/2}$. The number of electrons per unit volume in a whole range of energy is then defined as

$$N = \int_0^\infty D(E)f(E)dE.$$
2.18

Where $D(E)$ is the density of state and $f(E)$ is a Fermi-Dirac distribution function. When we switch on the interaction, exchange interaction, J_{ij}, appears and the density of state split in to two levels as shown in figure 2.2. The energy shift results from molecular field, M, which acts on each of the spin moment. The energy of a spin moment interacting with a magnetic field, H, is

$$H = -\gamma\mu\cdot M$$
2.19

looking at both spin up and spin down we have $H = \pm\gamma\mu M$ where minus corresponds to the energy of the spin up electrons while the plus corresponds to the energy of the spin down electrons. The difference in energies of spin up and spin down is $2\gamma\mu M$. The magnetic moment is proportional to the difference in the numbers of spin up and spin down electrons, i.e.,

$$M = (N_{up}-N_{down})\mu_B.$$
2.20

The relative magnetic moment obtains from this assumption is

$$\xi = \frac{M}{M_o} = \frac{F(\alpha + \beta) - F(\alpha - \beta)}{F(\alpha + \beta) + F(\alpha - \beta)} \qquad 2.21$$

where $\alpha = \dfrac{E_t - E_f}{K_B T}$, $\beta = \dfrac{\mu_B(H + \gamma M)}{K_B T}$ and $F(\alpha) = \displaystyle\int_0^\infty \frac{x^{1/2}}{\exp(x - \alpha) + 1} dx$. Numerical

calculations by Stoner gave a set of relative magnetization versus temperature shown in figure 2.3 (Stoner, 1938). This relation gives better explanation of magnetic behavior of both below the Curie temperature and above or from ferromagnetic state to paramagnetic state than does the Weiss model.

Weiss molecular field model fails when one tries to apply it to the metallic compounds, or to system in which a non-integer value of a magnetization per formula unit occurs. In the latter system, there is a small overlap of *3d* and *4s* band so the valence electrons are both *3d* and *4s* like. This graphical interpretation is shown in the figure 2.4 and the overlapping of *3d* and *4s* band is shown in figure 2.5. In the case of Ni, ten valence electrons, 9.46 electrons are in the *3d* band while 0.54 electrons in *4s* band. When exchange interaction is switched on, two *d*-sub band appear, one contains only a spin down electrons and the other contains a spin up electrons. In Ni, the lower subband is fully filled leaving 0.54 electrons to the upper subband. This means the saturated magnetization per atom is equal to $0.54\mu_B$, 0.54 is a hole in a upper subband (Madelung, 1982). For cobalt, a magnetic moment per atom at very low temperature is $1.7\mu_B$. To explain, nine valence electrons of cobalt should be arranged among *4s* band and two *3d* subbands in the ratio 0.7:5.0:3.3. The spontaneous magnetization for iron is $2.2\mu_B$ per atom leading to the ratio in *4s* and two *3d* subband being 0.9:4.7:2.4 i.e. neither the upper subband nor lower subband are fully filled. Figure 2.6 shows a non magnetic band, one filled subband and both unfilled subbands.

In the next chapter the calculation on the Stoner magnetic band model for transition element is emphasized in order to determine a magnetization when one shifts the Fermi level by introduce more electrons into the system.
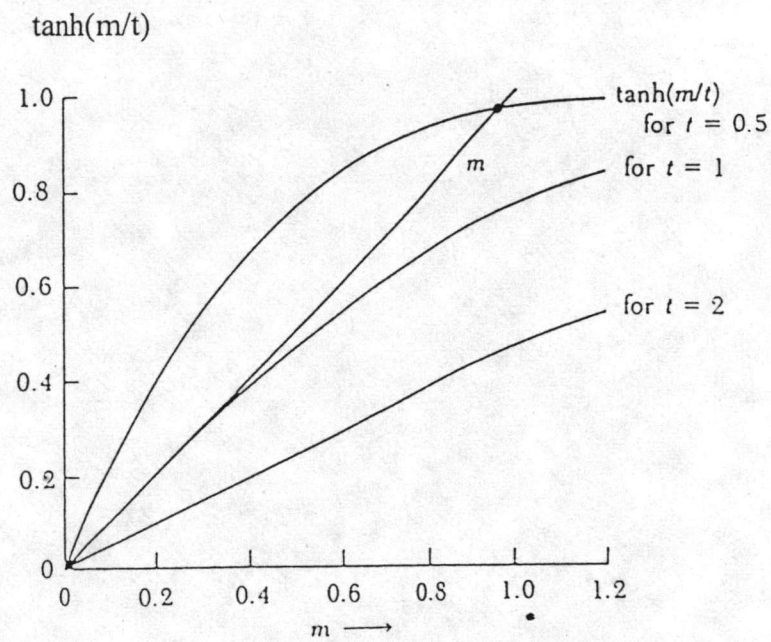
tanh(m/t)

Figure 2.1 Graphical solution of equation 2.17 for reduced magnetization, $m = M/M_o$, the left hand side of equation 2.17 is plotted as the straight line, the right hand side is plotted by fix the temperature and for $s = 1/2$, $B_{1/2}(x) = tanh(x)$, as shown in the figure. For each temperature, there is a intersect point and this point is the value of a relative magnetization for a given temperature. At the temperature higher than the Curie temperature, $t > 1$ there is no intersect point, $t = k_B T / N \mu^2 \gamma = T/T_c$ where $\mu = g \mu_B s$.
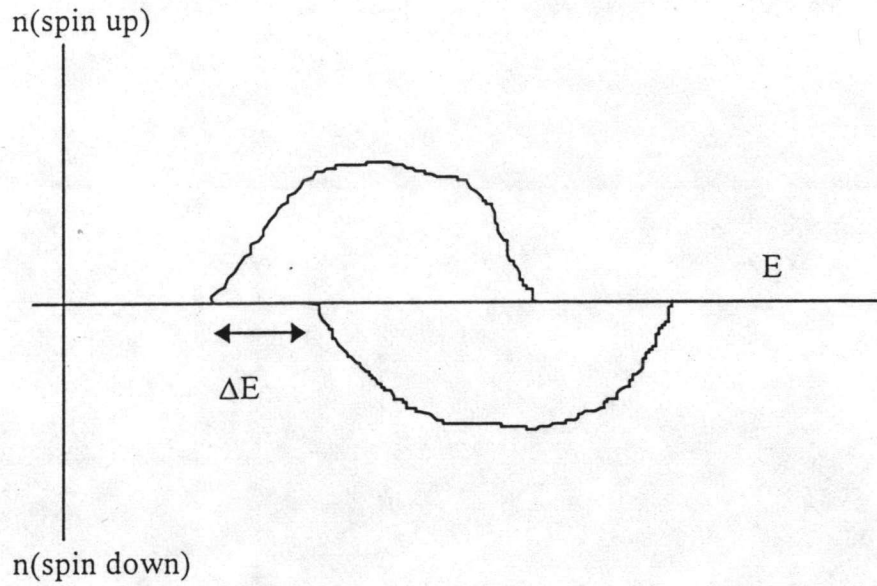
Figure 2.2 The energy shift caused by an exchange interaction, $\Delta E = \gamma m \mu_B^2$.
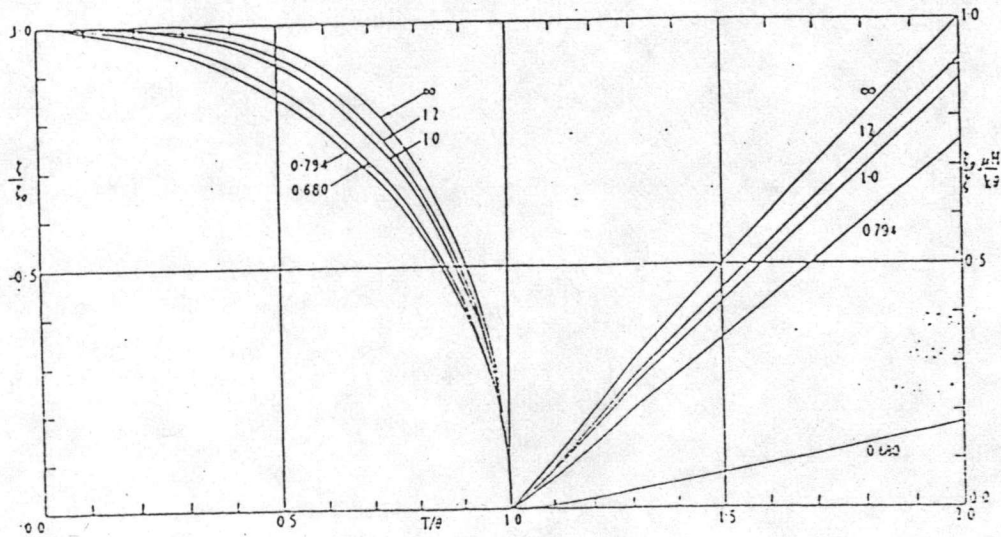
Figure 2.3 Calculation value of ζ/ζ_o and the reciprocal susceptibility in the collective electron model.(Stoner, 1938)
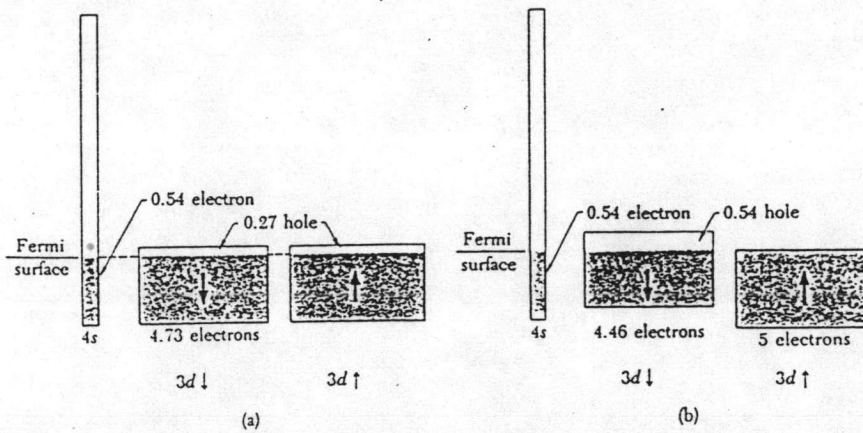
Figure 2.4.1a Schematic relationship of 4s and 3d bands in the metallic copper. The 3d band hold 10 electrons per atom and is filled in copper. The 4s band can hold 2 electrons per atom; it is show half filled, as copper has one valence electron outside the filled 3d shell.

Figure 2.4.1b The 3d band of copper shown as two separate sub-bands of opposite electron spin orientation, each band holding five electrons. With both sub-bands filled
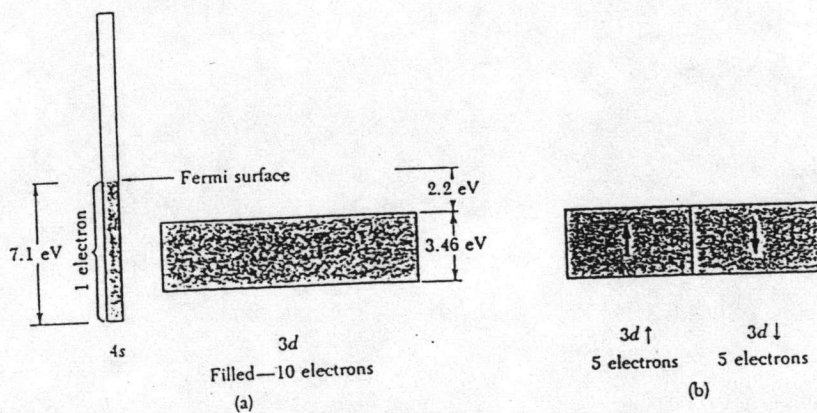

Figure 2.4.2a Band relationships of nickel above the Curie temperature. The net magnetic moment is zero, as there are equal numbers of holes in both 3d $\downarrow$ and 3d $\uparrow$ bands.

Figure 2.4.2b Schematic relationship of bands in nickel at absolute zero. The energy of 3d $\uparrow$ and 3d $\downarrow$ sub-bands are separated by an exchange interaction.(Kittle, 1986)
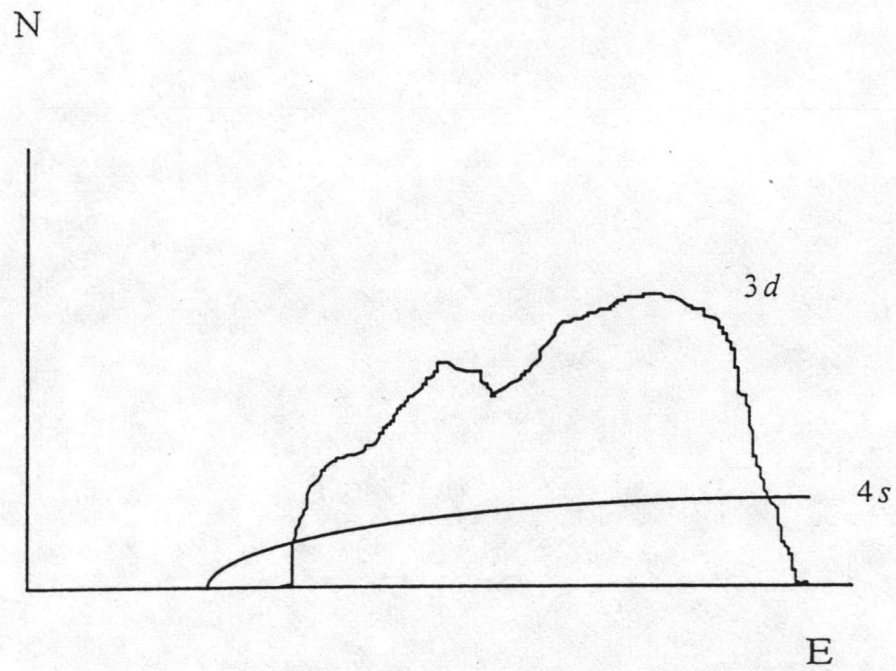
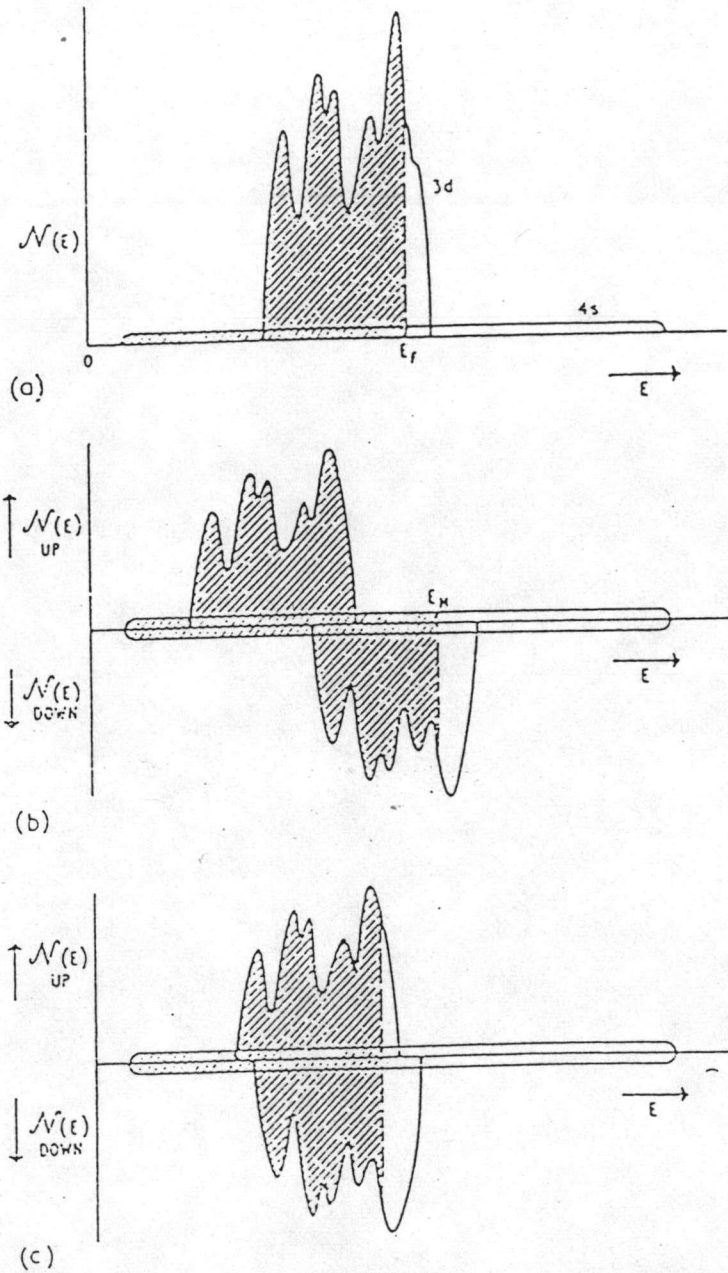Figure 2.5 Schematic relation of 3-*d* and 4-*s* overlapping.

Figure 2.6 Calculation reveal a high and narrow band within a low and broad 4s band in the vicinity of the Fermi level in the iron group transition metals. The 3d band contain five times as many states as 4s band, and its density of state is peaky as illustrated schematically here. (a) Is a non magnetic state and (b) and (c) different magnetic states (Martin, 1967).