

## Chapter III

### Theoretical Model

According to the previous chapter, the Stoner collective electron model is useful in the case where one is interested in the magnetic behavior of the system containing itinerant electrons or itinerant magnetic moments. Stoner obtained a graphical relationship between the relative saturation magnetic moment,  $M/M_0$ , and temperature,  $T$ . In this study, the effect of nitrogenation on the Sm-Co compounds is looking at. The addition of nitrogen into Sm-Co compounds is assumed to be like the addition of electrons or holes into semiconductor materials, i.e., doping. When excess electrons are doped into semiconductor, the Fermi energy is shifted without any change in the band structure. In the metallic compounds, doping electrons leads to a distortion of the band structure. In our approximation, the band shape is slightly distorted and is therefore neglected. This implied that the doping of an electrons only change the Fermi energy level. The small distortion of the band structure is shown in the figures 3.1 and 3.2. Figures 3.1 and 3.2 show the density of states of  $\text{Nd}_2\text{Fe}_{17}$  and  $\text{Nd}_2\text{Fe}_{17}\text{N}_x$  which have rhombohedral  $\text{Th}_2\text{Zn}_{17}$  structure, the same as that of  $\text{Sm}_2\text{Co}_{17}$ .

The orthogonalized linear combination of atomic orbital (OLCAO) was used to determine the density of states of this compounds (Gu and Lai, 1992) shown in these figures. When we compare the density of states of  $\text{Nd}_2\text{Fe}_{17}$  in figure 3.1 to the density of states of  $\text{Nd}_2\text{Fe}_{17}\text{N}_x$  in figure 3.2 for each of lattice site, figure 3.1 c, d and e, figure 3.2 c, d and e, we see that there is a small change in the shape of the density of states. In the rigid band model, it is believed that the band structure of transition elements especially in Ni, Fe and Co are the same. The difference between the electronic structure of those elements is mainly the difference in the

level of Fermi energy as shown in figure 3.3 (Madelung, 1982). We observe that higher number of valence electrons lead to an increase in the Fermi energy. As seen in the figure 3.3. The Fermi energy of Ni is above that of Co which is above that of the Fe.

For our propose, we are not concerned with the exact shape of the real band structure of Co in the Sm-Co compounds. We are interested in the change in a magnetization, i.e., the change in the number of spin up and spin down electrons due to the absorption of nitrogen which in turn will lead to excess electrons being doped into the system.

We start with an arbitrary shape of the density of states which is assumed to be close to the density of states of free electrons, i.e.,

$$D(E) = -E^2 + 4 \sin E + 3 \cos \frac{E}{2} - \sin 3E + \pi^2. \quad 3.1$$

Figure 3.4 shows the shape of this equation. This density of states is chosen to give a rough estimate of the different number of the spin up and down electron. If we return to figures 3.1, 3.2 and 3.5 it is obvious that the real 3-d band structure, is more complicated than the one shown in figure 3.4. The band structure of Fe in Nd-Fe compounds and Ni look like a superposition of the density of state of a free electron and a density of a rigid band model. The arbitrary shape of the density of states of Co in Sm-Co compounds is taken to be the same with free electrons density of states (the extra peaks in a rigid band model being dropped).

In this discussion of band structure we neglect its temperature dependence. This corresponds to setting  $T$  equal to zero. At  $T = 0\text{K}$  the highest value of an electron energy is the Fermi energy  $E_f$ . All states above  $E_f$  are unoccupied, while all states below  $E_f$  are occupied. This leads to

$$D(E) = \begin{cases} 0 & E > E_f \\ D(E) & E < E_f \end{cases} \quad 3.2$$

$D(E)$  is a density of states in equation 3.1. The number of electrons in  $3d$  band is determined

$$n = \int_{E_{\min}}^{E_f} D(E) f(E) dE \quad 3.3$$

where  $f(E) \rightarrow 1$  as  $T \rightarrow 0K$ .

The density of state of  $3d$  band split into two subband when the exchange interaction is switched on as shown in figure 3.6. The energy gap is  $\mu_B \gamma M$ . The difference in the spin up and down electrons is proportional to the difference in the area under the two curves shown in figure 3.6, i.e.,

$$n = n_{\uparrow} - n_{\downarrow} = \int_{E_{\min}}^{E_f} [D(E) - D(E - 2\mu_B^2 \gamma M)] dE \quad 3.4$$

where  $M$  is replaced by  $n\mu_B$ .

The difference in the number of spin up and down electrons,  $n$ , appears on both sides of equation 3.4. The dependence of  $n$  on  $E_f$  is nonexplicit dependence and so the only way to solve this relation is by numerical method. This is done by expanding the integral on the right hand side to the finite series of a small area under the two curves as shown in figure 3.6. Equation 3.4 becomes

$$n = \sum_i^k \Delta E [D(E_i) - D(E_i - 2\mu_B^2 \gamma m)] \quad 3.5$$

This equation is valid only in the range  $E_{min} < E < E_f$  where  $E_{i+1} = E_i + \Delta E$ . For more accurate value, smaller areas i.e., small  $\Delta E$  are required. For each  $E_f$  we get the number of net magnetic moment in the form of  $n=g(n)$  where  $g(n)$  is obtained by evaluating the right hand sides of equation 3.5, for different  $n$  values. The solution for  $n$  is the intersection  $y = n$  and  $y = g(n)$  as shown in figure 3.7.

In the simple picture, it is reasonable to treat the energy gap  $2\mu_B \gamma M$ , as a constant. In actuality, there is a small change in the energy gap when the Fermi energy is shifted. The energy gap is slightly less than 1eV while the energy of  $3d$  band is in the order of 10 eV. The integral term in the right hand side of equation 3.4 is analytic function and the relation of  $n$  with  $E_f$  is obtained as shown in figure 3.8. It is obvious that there is a decrease and increase region. As one shifts the Fermi energy one sees an increase in  $n$  until it reaches a maximum, then one sees  $n$  decrease. This means that the magnetization will increase initially as the Fermi energy is shifted. It increases until it reaches a maximum after which the magnetization (or  $n$ ) will decrease as the Fermi energy is further shifted. This result corresponds to our observation which will be discussed in detail later.

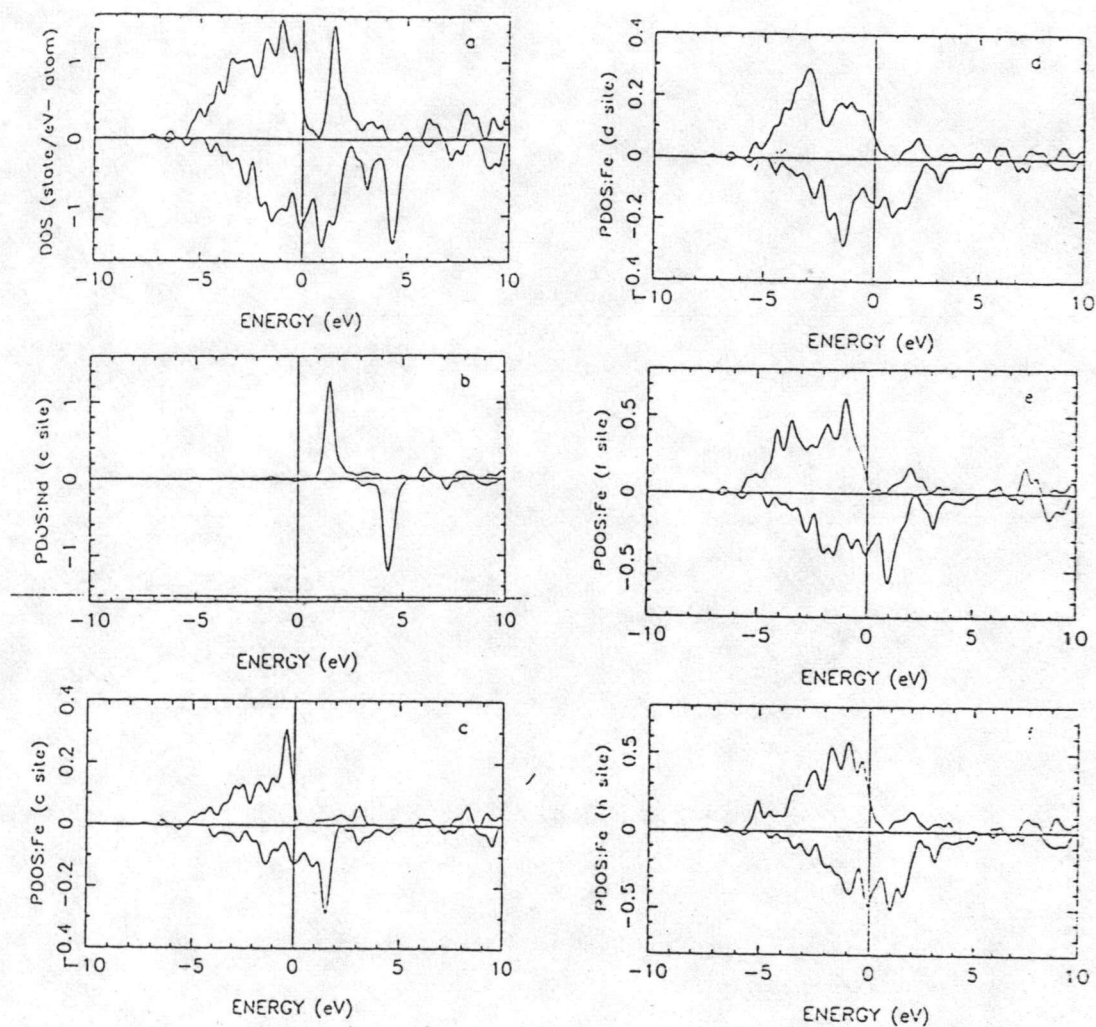


Figure 3.1 Total and partial density of state at different atom site in  $\text{Nd}_2\text{Fe}_{17}$  (a) total (b) Nd(6c), (c) Fe(6c), (d) Fe(9d), (e) Fe(18f), (f) Fe(18h). Note that the DOS for one spin appears to be a shifted upside DOS for the other spin electrons.

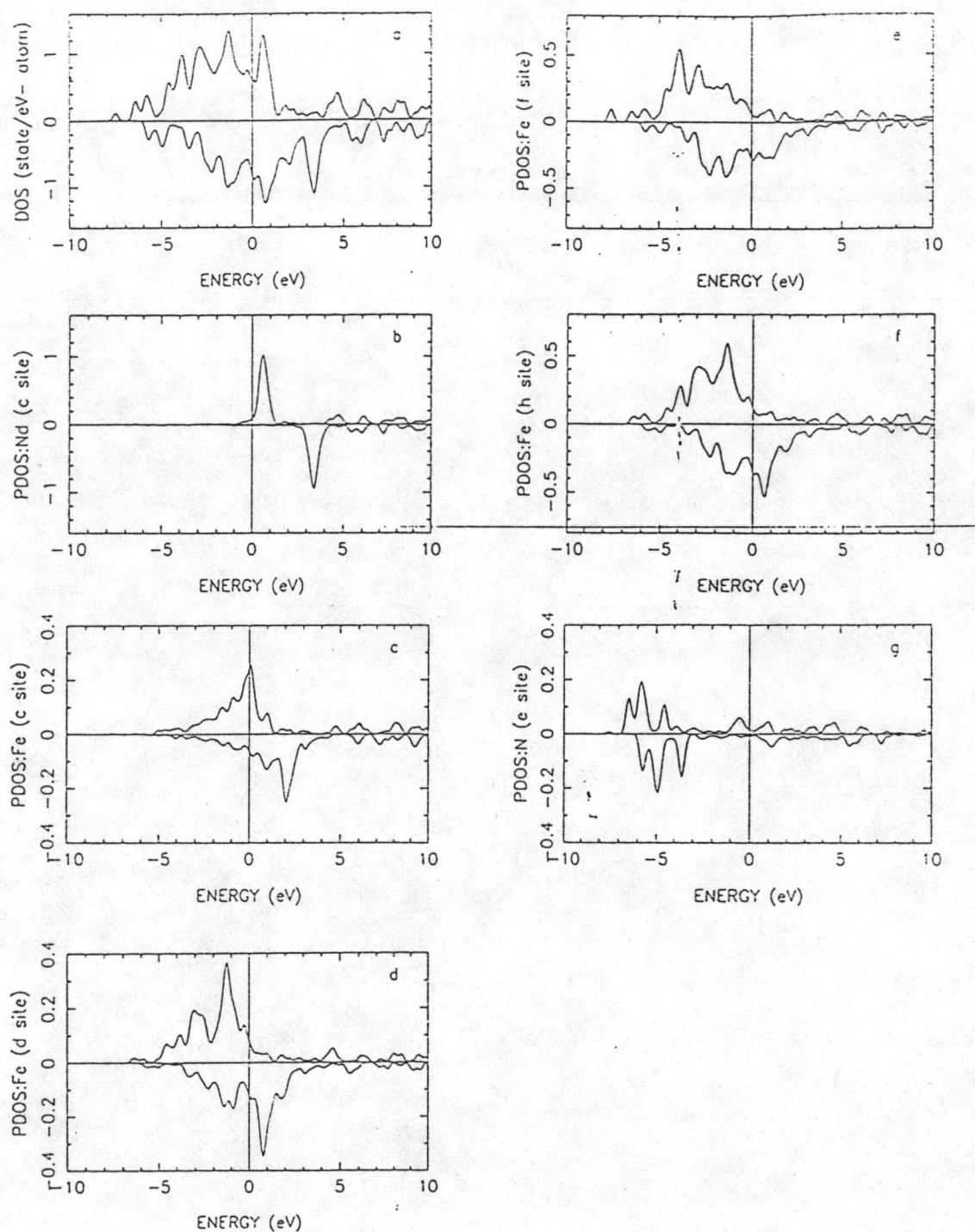


Figure 3.2 Total and partial density of state at different atom site in  $\text{Nd}_2\text{Fe}_{17}\text{N}_x$  (a) total (b) Nd(6c), (c) Fe(6c), (d) Fe(9d), (e) Fe(18f), (f) Fe(18h), (g) N(9e). Again the upside down DOS looks similar to the right side up DOS except for a shift it the right.

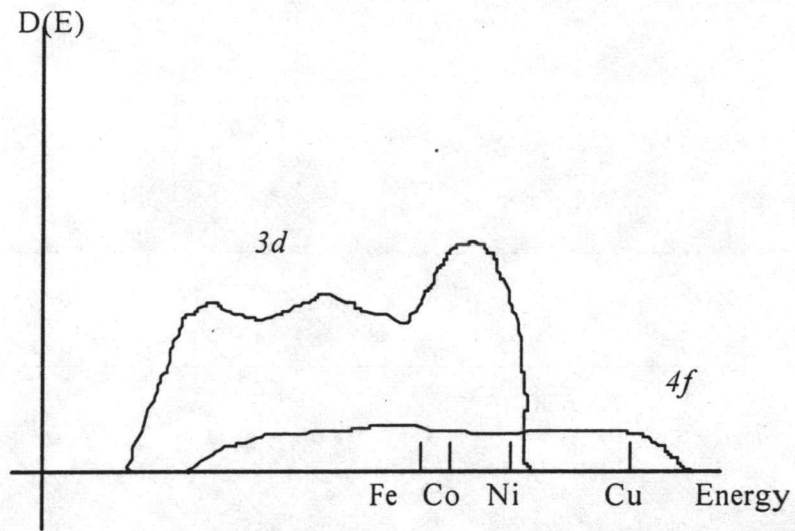


Figure 3.3 Schematic representation of the density of states of the transition metals with the assumption that all these elements have approximately the same band structure.

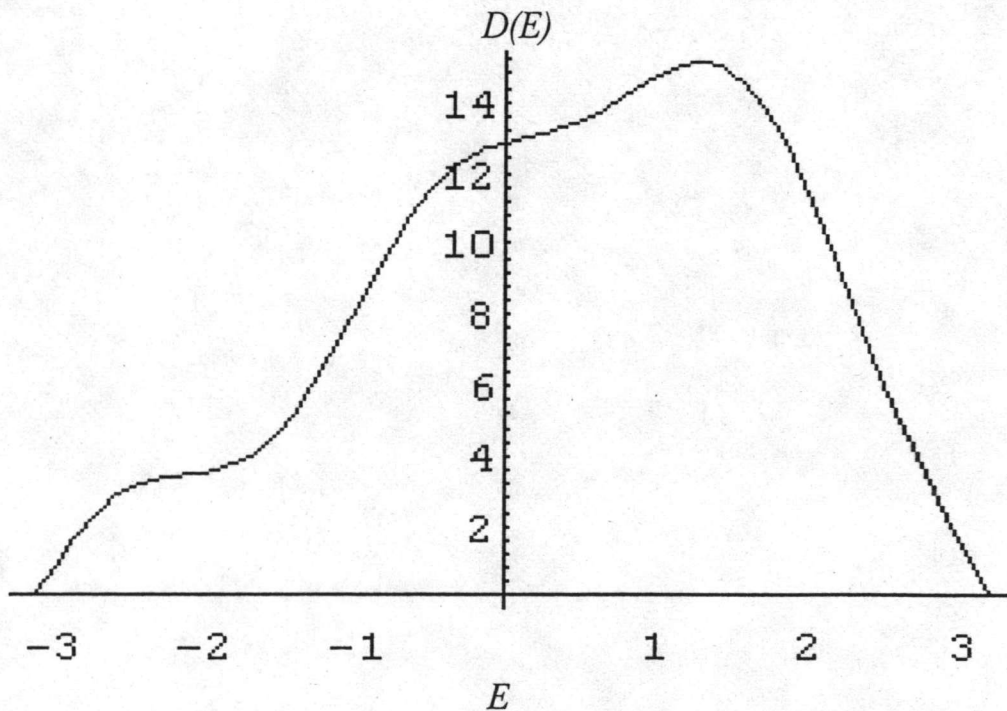


Figure 3.4 Schematic representation of nearly free electron density of state in equation 3.1

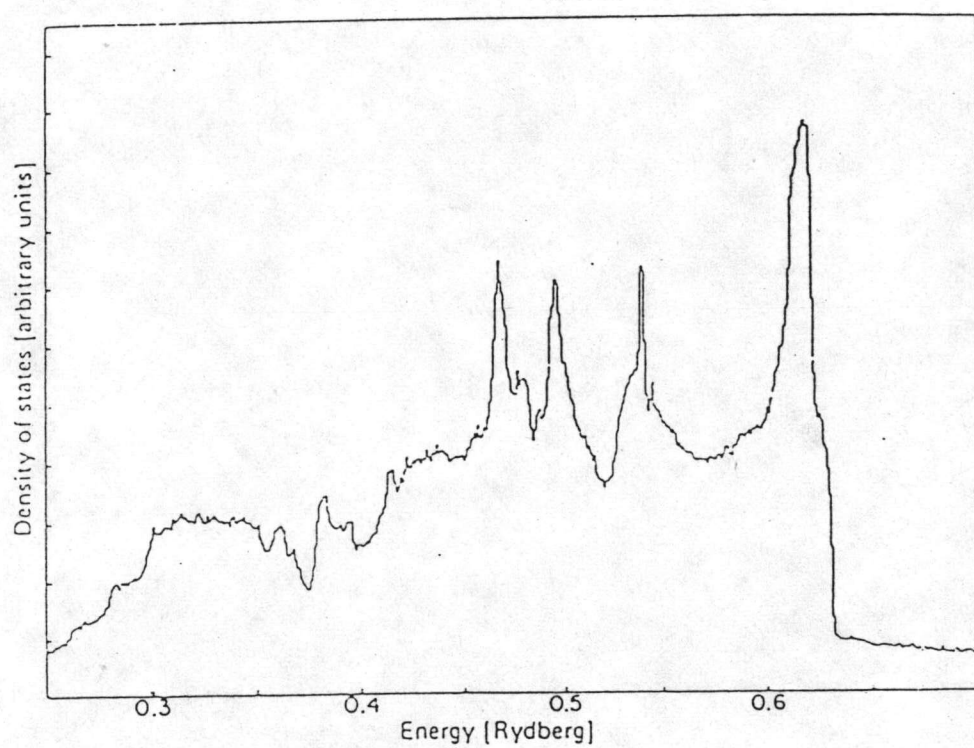


Figure 3.5 Density of states of nickel in the energy range of the *d* bands.  
(Madelung, 1982)



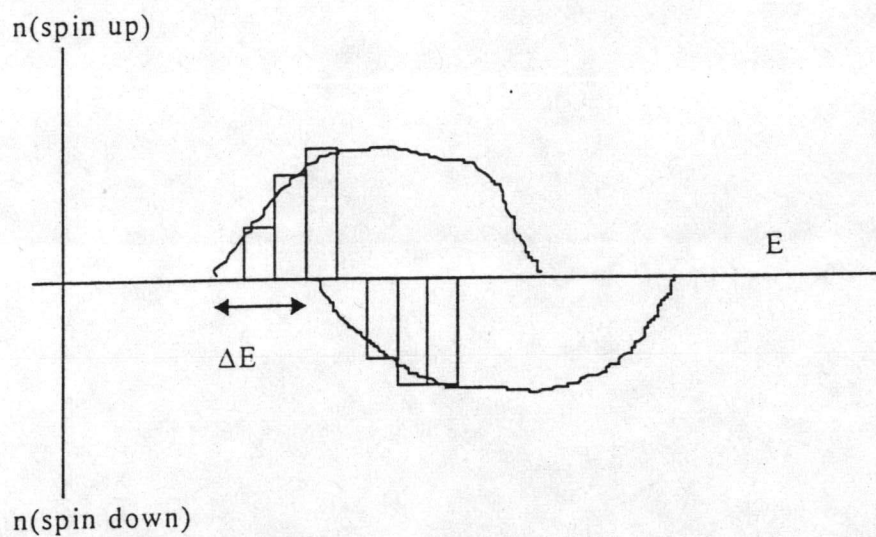


Figure 3.6 The energy shift cause by an exchange interaction,  $\Delta E = 2\gamma m\mu_B^2$  and a small area under the two curves.

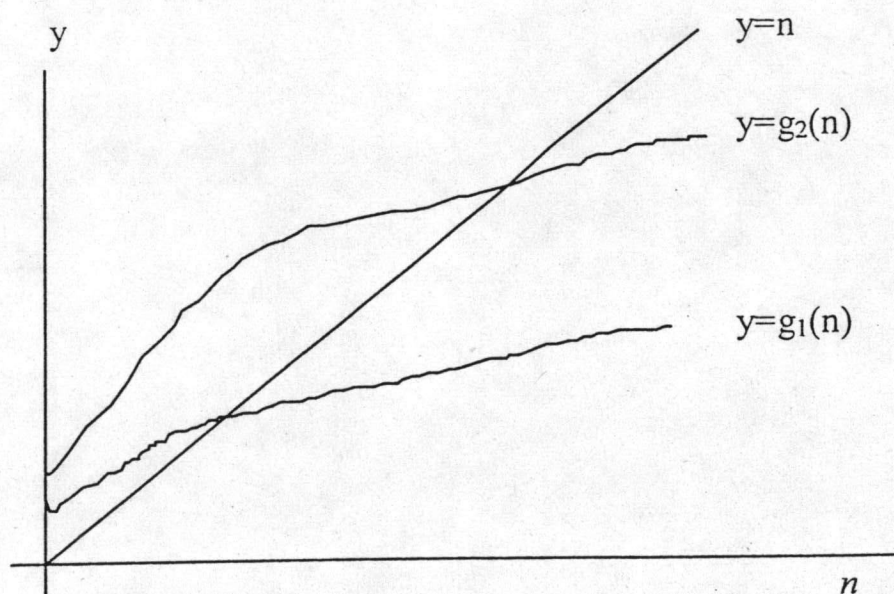


Figure 3.7 Graphical diagram of the calculation value of  $n$ , a number of total magnetic moments which for each intersection point represent a number of total magnetic moment for a given  $E_f$ .

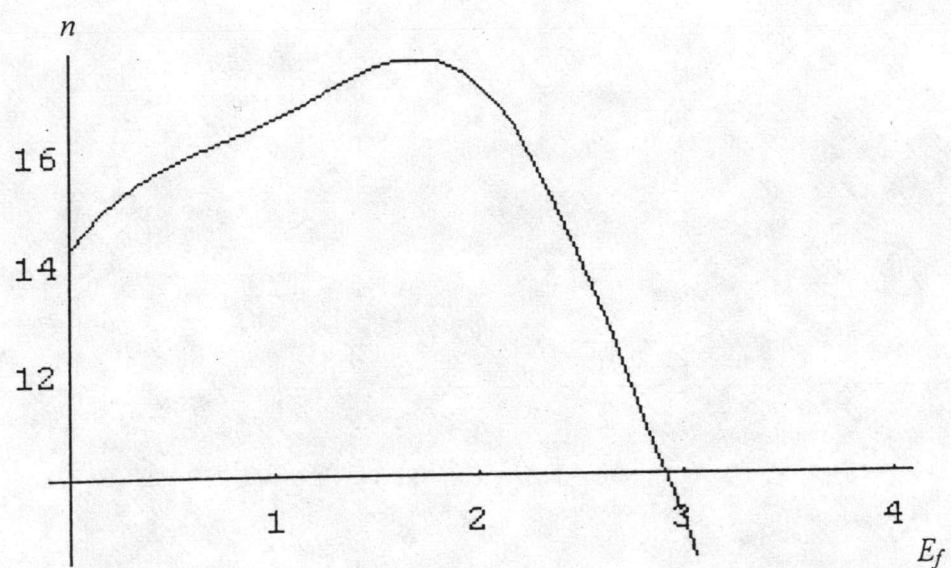


Figure 3.8 Graphical relation of total magnetic moments and Fermi energy employed equation 3.1 as the density of state and the splitting energy is assumed to be constant.