

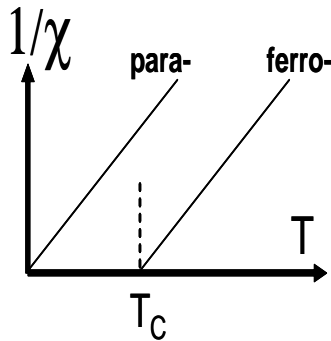
Chapter 4

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Paramagnets were found to have an inverse magnetic susceptibility which increased linearly with temperature. At zero temperature, fluctuations disappeared and the ensemble has perfect ordering with a divergent (infinite) susceptibility.

A ferromagnet is a material where ordering and infinite susceptibility persists up to a nonzero critical temperature. Furthermore, they have a spontaneous local remnant magnetization in the absence of any external field.

Experimentally, these qualities manifested themselves in a shifted inverse susceptibility plot and hysteresis in magnetization graphs. Divergent susceptibility persists until a critical temperature T_C , called the Curie temperature.



1 Magnetostatic Dipole Interaction

What causes the ordering at nonzero temperature? It must result in a coupling energy of nearest-neighbors like

$$E = -\beta\mu_1\mu_2 \cos\theta \quad (1)$$

where $\beta > 0$. (The case where $\beta < 0$ corresponds to *antiferromagnetism*, a topic for a later chapter.) The magnitude of this interaction must clearly be on the order of $k_B T_C$.

Naively, we could point to the magnetostatic energy of nearby moments. The magnetostatic energy is due to the stray field of one moment acting on another:

$$E_{dipole-dipole} = -\mu \cdot B = \mu_1 \cdot \frac{\mu_2}{r^3} \rightarrow \approx \frac{\mu_B^2}{a^3} \quad (2)$$

where a is the lattice spacing between moments. In cgs units, $\mu_B = \frac{e\hbar}{2mc}$, and the characteristic lattice spacing is a few Bohr radii.

The Bohr radius can be found (in terms of fundamental constants) by equating the centripetal force to the electrostatic Coulomb force:

$$\frac{mv^2}{r_0} = \frac{e^2}{r_0^2} \Rightarrow r_0 = \frac{e^2}{mv^2} \quad (3)$$

and imposing angular momentum quantization on an “orbiting” electron in an atom:

$$L = mvr = n\hbar \Rightarrow v = \frac{\hbar}{mr_0}. \quad (4)$$

We see that

$$r_0 = \frac{e^2 m^2 r_0^2}{m\hbar^2} \Rightarrow r_0 = \frac{\hbar^2}{e^2 m} \quad (5)$$

Therefore, if we use the Bohr radius in our calculations to get an upper bound on the magnetostatic energy, we find

$$E_{dipole-dipole} = \frac{\mu_B^2}{r_0^3} = \frac{\left(\frac{e\hbar}{2mc}\right)^2}{\left(\frac{\hbar^2}{e^2 m}\right)^3} = \frac{e^8 m}{\hbar^4 c^2} = \left[\frac{e^2}{\hbar c}\right]^4 mc^2 \quad (6)$$

The term in brackets is the dimensionless fine-structure constant, $\alpha \approx \frac{1}{137}$. The rest mass energy mc^2 for the electron is 511 keV, so we have

$$E_{dipole-dipole} = \left[\frac{1}{137}\right]^4 5.11 \times 10^5 eV \approx 1meV \quad (7)$$

This value corresponds to $T_C = \frac{E}{k_B} \approx 10K$, much smaller than what we would need to result in $\approx 1000K$ Curie temperature. Furthermore, is an upper bound on the magnetostatic dipole-dipole energy, since the inter-moment spacing is typically many times the Bohr radius and the energy decreases as the inverse third power of the distance.

So what is the origin of the interaction energy, if not magnetostatic? The solution to this problem is found by realizing that electrostatic energies are much larger than magnetostatic, and contemplating the coupling of the spin degree of freedom to the charge degree of freedom through the Pauli exclusion principle known as the exchange energy.

2 Exchange Energy

Let's examine the simplest interacting two-electron system like the neutral Helium atom. Our Hamiltonian is something like

$$H = H_1 + H_2 + H_{12} \quad (8)$$

where H_1 is the Coulombic interaction of electron 1 with the nucleus, H_2 is the Coulombic interaction of electron 2 with the nucleus, and H_{12} is the repulsive interaction between electrons 1 and 2.

2.1 Pauli Exclusion Principle

In solving this problem, it would help to guess the proper form of the solution. To do so, consider that indistinguishability of electrons 1 and 2 results in the necessity that the total probability of measuring 1 and 2 is the same as 2 and 1:

$$\|\Psi(1,2)\|^2 = \|\Psi(2,1)\|^2. \quad (9)$$

Here, 1 and 2 are labels which include all quantum numbers defining each particle, including the spin degree of freedom. The solution to this problem is

$$\Psi(1,2) = \pm\Psi(2,1) \quad (10)$$

where the + or - is an intrinsic property of the particle in question. For electrons, the latter is necessary. This defines the property of a *Fermion*, whereas particles requiring the + sign are known as *Bosons*. Through the Dirac equation, we can see that Fermions have half-integer spin (like the spin 1/2 electron) and Bosons have integer spin. This is known as the *spin statistics theorem*.

A simple way of imposing the asymmetry of particle interchange is the following wavefunction:

$$\Psi(1,2) = \frac{1}{\sqrt{2}} (\psi_\alpha(1)\psi_\beta(2) - \psi_\alpha(2)\psi_\beta(1)) \quad (11)$$

Switching 1 and 2 gives

$$\Psi(1, 2) = \frac{1}{\sqrt{2}} (\psi_\alpha(2)\psi_\beta(1) - \psi_\alpha(1)\psi_\beta(2)) = -\Psi(2, 1). \quad (12)$$

Note that if the quantum numbers are equal, the wavefunction is zero. This is the Pauli exclusion principle.

2.2 Imposing Antisymmetry

So, the Pauli principle states that the total wavefunction (product of spatial and spin) is antisymmetric under particle exchange. If the spatial wavefunction is symmetric, then the spin wavefunction must be antisymmetric and vice versa.

If $\phi_1(r_1)$ and $\phi_2(r_2)$ are the single-particle spatial wavefunctions of electron 1 and 2, respectively, then we can assume the two-particle spatial wavefunction to be either

$$\Psi_S = \frac{1}{\sqrt{2}} [\phi_1(r_1)\phi_2(r_2) + \phi_1(r_2)\phi_2(r_1)] \quad (13)$$

(the spatially symmetric wavefunction) and

$$\Psi_A = \frac{1}{\sqrt{2}} [\phi_1(r_1)\phi_2(r_2) - \phi_1(r_2)\phi_2(r_1)] \quad (14)$$

(the spatially antisymmetric wavefunction).

The energies of these wavefunctions are given by calculating the diagonal matrix elements of the Hamiltonian:

$$H\Psi = E\Psi \rightarrow \Psi^*H\Psi = \Psi^*E\Psi = E\Psi^*\Psi \quad (15)$$

and integrating:

$$\int \Psi^*H\Psi dr_1 dr_2 = E \int \Psi^*\Psi dr_1 dr_2 = E \quad (16)$$

So we have to perform a number of integrals involving the terms H_1 , H_2 , and H_{12} . Since the first two terms are dependent on variables r_1 and r_2 exclusively, the cross terms in distributing the multiplication in the integrals vanish, for instance:

$$\frac{1}{2} \int [\phi_1(r_1)\phi_2(r_2) \pm \phi_1(r_2)\phi_2(r_1)]^* H_1(r_1) [\phi_1(r_1)\phi_2(r_2) \pm \phi_1(r_2)\phi_2(r_1)] dr_1 dr_2 \quad (17)$$

$$= \frac{1}{2} \int \phi_1(r_1)^* \phi_2(r_2)^* H_1(r_1) \phi_1(r_1) \phi_2(r_2) dr_1 dr_2 \quad (18)$$

$$+ \frac{1}{2} \int \phi_1(r_2)^* \phi_2(r_1)^* H_1(r_1) \phi_1(r_2) \phi_2(r_1) dr_1 dr_2 \quad (19)$$

$$\pm \frac{1}{2} \int \phi_1(r_1)^* \phi_2(r_2)^* H_1(r_1) \phi_1(r_2) \phi_2(r_1) dr_1 dr_2 \quad (20)$$

$$\pm \frac{1}{2} \int \phi_1(r_2)^* \phi_2(r_1)^* H_1(r_1) \phi_1(r_1) \phi_2(r_2) dr_1 dr_2 \quad (21)$$

Since H_1 depends only on r_1 , the r_2 integral can be done separately:

$$\pm \frac{1}{2} \int \phi_2(r_2)^* \phi_1(r_2) dr_2 \int \phi_1(r_1)^* H_1(r_1) \phi_2(r_1) dr_1 \pm \quad (22)$$

$$\frac{1}{2} \int \phi_1(r_2)^* \phi_2(r_2) dr_2 \int \phi_2(r_1)^* H_1(r_1) \phi_1(r_1) dr_1 \quad (23)$$

But the wavefunctions are orthogonal, so the r_2 integrals vanish. The same happens for the cross terms in the H_2 integrals. However, H_{12} depends on both r_1 and r_2 , so this procedure cannot be carried out, and the cross terms remain, along with the symmetric/antisymmetric $+/-$ signs. These are known as *exchange integrals*, and we can write the energy of the wavefunction as

$$E = E_1 + E_2 + E_{12} \pm J \quad (24)$$

where J is the exchange integral. The $+$ is for the spatially symmetric and $-$ is for the spatially antisymmetric wavefunction.

2.3 Exchange “Force”

How does this affect spin interaction energy?

Assume $J < 0$. Then, the symmetric spatial wavefunction is lowest in energy. Since the total product of the spatial and spin wavefunctions must be antisymmetric under particle exchange, the corresponding spin wavefunction must be antisymmetric, like the spin “singlet”:

$$|\uparrow_1\downarrow_2\rangle - |\downarrow_1\uparrow_2\rangle \quad (25)$$

If one of the spins is flipped, for instance spin 1, our spin wavefunction then looks like

$$|\downarrow_1\downarrow_2\rangle - |\uparrow_1\uparrow_2\rangle \quad (26)$$

This spin wavefunction is now *symmetric* under particle exchange. Therefore, in order to maintain total wavefunction antisymmetry, the spatial wavefunction must be antisymmetric. This causes the energy to increase from

$$E = E_1 + E_2 + E_{12} + J \quad (27)$$

(remember $J < 0$) to

$$E = E_1 + E_2 + E_{12} - J \quad (28)$$

a difference of $2J$. Since the magnitude of J is determined by electrostatic interaction on the order of eV, the system would have to acquire an enormous amount of energy to overcome the *exchange force* to flip spins.

3 Heisenberg Model

The exchange interaction explains the magnitude of the Curie temperature. However, we don’t want to worry about spatial wavefunctions. We’d like to distill the essential physics of exchange by itself. For this, we turn to the simplest Hamiltonian for exchange between two spins:

$$H = JS_1 \cdot S_2 \quad (29)$$

where

$$S_1 = \sigma_{x1}\hat{x} + \sigma_{y1}\hat{y} + \sigma_{z1}\hat{z} \quad S_2 = \sigma_{x2}\hat{x} + \sigma_{y2}\hat{y} + \sigma_{z2}\hat{z} \quad (30)$$

and the σ s are the 2×2 Pauli matrices. Clearly, from a classical viewpoint, if $J < 0$, this system favors ferromagnetism since its lowest-energy ground state occurs when the spins align. How do we calculate $S_1 \cdot S_2$? Using the *direct* or *tensor product* indicated by the symbol \otimes . If A and B are 2×2 matrices,

$$A \otimes B = \begin{bmatrix} a_{11}B & a_{12}B \\ a_{21}B & a_{22}B \end{bmatrix} \quad (31)$$

so that

$$H = JS_1 \cdot S_2 = J[\sigma_{x1} \otimes \sigma_{x2} + \sigma_{y1} \otimes \sigma_{y2} + \sigma_{z1} \otimes \sigma_{z2}] \quad (32)$$

becomes

$$H = J \left(\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \otimes \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} + \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \otimes \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} + \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \right) \quad (33)$$

$$H = J \left(\begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} + \begin{bmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{bmatrix} + \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \right) = J \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \quad (34)$$

To find the energy levels for this Hamiltonian, we need to solve the time-independent Schrödinger equation

$$H\Psi = E\Psi \quad (35)$$

Which is a simple eigenvalue problem. The (normalized) eigenvectors are

$$\frac{1}{\sqrt{2}} \begin{bmatrix} 0 \\ 1 \\ -1 \\ 0 \end{bmatrix}, \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \frac{1}{\sqrt{2}} \begin{bmatrix} 0 \\ 1 \\ 1 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix} \quad (36)$$

with associated eigenvalues $-3J, J, J, J$ respectively.

3.1 Identifying the states

Using the tensor product, we can decompose the 2-body states into component 1-body states, for example

$$\frac{1}{\sqrt{2}} \begin{bmatrix} 0 \\ 1 \\ -1 \\ 0 \end{bmatrix} = \frac{1}{\sqrt{2}} \left(\begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \begin{bmatrix} 0 \\ 1 \end{bmatrix} - \begin{bmatrix} 0 \\ 1 \end{bmatrix} \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix} \right) \quad (37)$$

$$\begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad (38)$$

$$\frac{1}{\sqrt{2}} \begin{bmatrix} 0 \\ 1 \\ 1 \\ 0 \end{bmatrix} = \frac{1}{\sqrt{2}} \left(\begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \begin{bmatrix} 0 \\ 1 \end{bmatrix} + \begin{bmatrix} 0 \\ 1 \end{bmatrix} \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix} \right) \quad (39)$$

$$\begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \otimes \begin{bmatrix} 0 \\ 1 \end{bmatrix} \quad (40)$$

Identifying

$$\begin{bmatrix} 1 \\ 0 \end{bmatrix} \rightarrow \parallel \uparrow \rangle, \begin{bmatrix} 0 \\ 1 \end{bmatrix} \rightarrow \parallel \downarrow \rangle \quad (41)$$

or “spin up” and “spin down”, we can see how the singlet ($S_{total} = 0$) state

$$\parallel \uparrow \downarrow \rangle - \parallel \downarrow \uparrow \rangle \quad (42)$$

and the triplet ($S=1$) states

$$\parallel \uparrow \uparrow \rangle, \parallel \uparrow \downarrow \rangle + \parallel \downarrow \uparrow \rangle, \parallel \downarrow \downarrow \rangle, \quad (43)$$

arise from this simple treatment.

3.2 N-body problem

For a lattice of N moments, we can generalize the 2-body problem to

$$H = J \sum_{i, j \neq i} S_i \cdot S_j \quad (44)$$

To simplify this intractable problem, we consider nearest neighbors

$$H = J \sum_{i, \delta} S_i \cdot S_{i+\delta} \quad (45)$$

If we include a Zeeman term to the Hamiltonian due to an external field, we have

$$H = \sum_i S_i \cdot \left[J \sum_{\delta} S_{i+\delta} \right] - \mu_i \cdot H \quad (46)$$

Since $S_i = \frac{\mu_i}{g\mu_B}$, we can write

$$H = - \sum_i \mu_i \cdot H_{eff} \quad (47)$$

where

$$H_{eff} = H - \frac{J}{g\mu_B} \sum_{\delta} S_{i+\delta} \quad (48)$$

We now use the *mean field approximation* to eliminate the sum over nearest-neighbors δ by assuming each term is the same and averaging. This effectively treats all sites i the same. Therefore we have

$$H_{eff} = H - \frac{Jz}{g\mu_B} \langle S_{i+\delta} \rangle = H - \frac{Jz}{g^2\mu_B^2} M = H + wM \quad (49)$$

where $w = -\frac{Jz}{g^2\mu_B^2}$. So now we have a single-particle Hamiltonian corresponding to an ensemble of noninteracting magnetic moments in a magnetic field given by H_{eff} . This is similar to our treatment of the paramagnetic response of noninteracting spins where $H \rightarrow H + wM$.

3.3 Ferromagnetic state ($T < T_C$)

For spin 1/2,

$$M = N\mu \tanh \alpha \quad (50)$$

where

$$\alpha = \frac{\mu(H + wM)}{k_B T}. \quad (51)$$

Assume that $H = 0$. Expanding to second order gives

$$M = N\mu \tanh \alpha \approx N\mu \left(\alpha - \frac{\alpha^3}{3} \right) \quad (52)$$

and allows us to write

$$M = N\mu \left(M\gamma - \frac{M^3\gamma^3}{3} \right) \quad (53)$$

where $\gamma = \frac{\mu w}{k_B T}$. Solving:

$$M = \sqrt{\frac{3}{\gamma^3} \left(\gamma - \frac{1}{N\mu} \right)} \quad (54)$$

The spontaneous magnetization in zero field disappears when $\gamma = \frac{1}{N\mu}$. This defines the critical Curie temperature

$$T_C = \frac{N\mu^2 w}{k_B} \quad (55)$$

3.4 Near T_C

We have

$$M = \frac{\sqrt{3}}{\gamma} \left(1 - \frac{1}{N\gamma\mu} \right)^{1/2} \quad (56)$$

Applying our definition of T_C gives

$$M = \frac{\sqrt{3}}{\gamma} \left(1 - \frac{T}{T_C} \right)^{1/2} \quad (57)$$

3.5 Paramagnetic State ($T > T_C$)

At high temperature $\alpha \ll 1$, so we can expand the $\tanh \alpha$ to first order and write

$$M = N\mu\alpha \quad (58)$$

which can be substituted into Equation 51, yielding

$$M = \frac{k_B T M}{N\mu^2 w} - \frac{H}{w} \quad (59)$$

Which can be solved when $H \neq 0$:

$$M\left(1 - \frac{k_B T}{N\mu^2 w}\right) = -\frac{H}{w} \quad (60)$$

$$M = -\frac{H}{w\left(1 - \frac{k_B T}{N\mu^2 w}\right)} = \frac{N\mu^2/k_B}{T - wN\mu^2/k_B} H = \frac{C}{T - T_C} H \quad (61)$$

Thus,

$$\chi = \frac{C}{T - T_C} \quad (62)$$

This is similar to the Curie Law, except it is modified due to the molecular field w , dependent on the ferromagnetic exchange energy J . It is known as the Curie-Weiss law.

This theory reproduces the existence of a critical temperature (dependent on the strength of the molecular field w), below which spontaneous ordering takes place.

4 Band Ferromagnetism

From the Weiss model, the magnetic moment should be the same in the ferromagnetic ($T < T_C$) and paramagnetic ($T > T_C$) state, and should be an integral multiple of μ_B . However, this is not observed experimentally. This is due primarily to the fact that the electrons contributing their magnetic moments to ferromagnetism are delocalized from the lattice sites. Therefore, a more correct model is based on bandstructure. This can be modeled to first order by considering the free electron gas, as we did in the case of Pauli paramagnetism. We only need to include the effects of the molecular field.

The number density of up and down electrons is given by

$$N_{\uparrow/\downarrow} = \int_0^\infty D_{\uparrow/\downarrow}(E) f_{\uparrow/\downarrow}(E) dE \quad (63)$$

where

$$D_{\uparrow/\downarrow}(E) = \frac{3}{4} \frac{N}{E_F^{3/2}} E^{1/2} \quad (64)$$

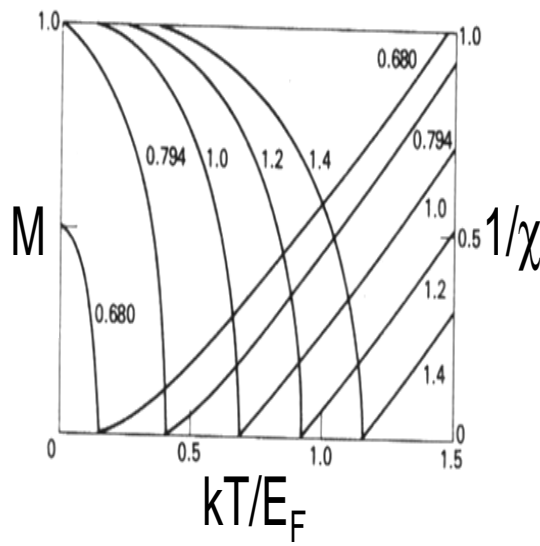
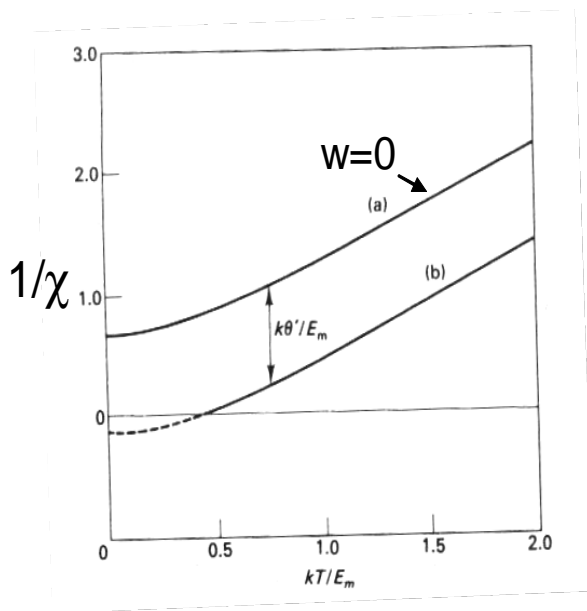
and

$$f_{\uparrow/\downarrow}(E) = \frac{1}{e^{(E - E_F \pm \mu(H + wM))/k_B T} + 1}. \quad (65)$$

where the \pm is for up or down spins. Since the magnetization is given by

$$M = \mu(N_\uparrow - N_\downarrow), \quad (66)$$

we have a nonlinear equation for M . Furthermore, the integrals cannot be evaluated analytically. We can, however, calculate the magnetization for different magnetic field conditions and determine the susceptibility numerically. In the case where $w = 0$, we have the case of Pauli paramagnetism. This gives a nearly constant susceptibility as a function of temperature. When the molecular field is present, this curve moves down toward the temperature axis. If it intersects, the intersection defines the critical Curie temperature; the susceptibility is valid only for temperatures above T_C in the paramagnetic state. Below T_C , ferromagnetic ordering takes place and the magnetization in the absence of a magnetic field can be calculated.



This model, postulated first by Stoner in the early 1950's, essentially reduces to the idea that in a ferromagnet, the bands of one spin species were rigidly shifted (i.e. their energy changes, but their shape does not) to account for spin polarization and spontaneous magnetization. First-principles calculations done decades later have supported this view. Specifically, when the Fermi energy lies within the shifted d bands, ferromagnetism occurs (as in Ni, Co, and Fe). Metals with higher Fermi energies such as Zn and Cu are not ferromagnetic because these shifted bands are essentially completely filled.

