SOLUTIONS

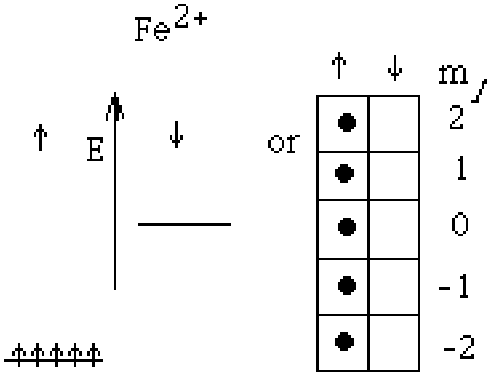
5.2 i)Free iron atoms $3d^6\,4s^2$, energy of $3d > 4s$. Hund's rule applied to $3d^6$ results in $l = 2$, $s = 4/2$ and $j = 4$ so the moment is 4 μ_B/Fe. These moments are independent and so behave as a paramagnet with susceptibility $\chi = N_v\mu_m^2\mu_o/kT$.

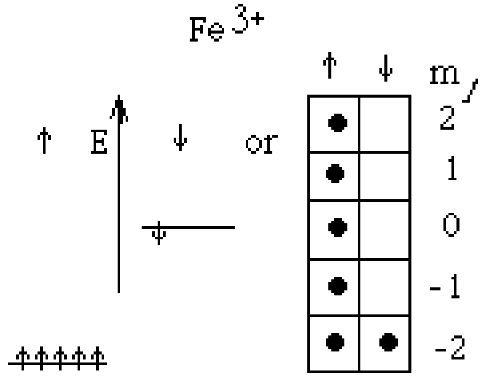
ii) $3d$ and $4s$ states broaden into overlapping bands with $3d^7 4s^1$, approximately, with spin up and down $3d$ states shifted relative to each other. d states are broad in energy and while more spin up states are filled, some spin down states are also filled. Moment is 2.2 μ_B/Fe. Sketch band DOS.

iii) Fe^{3+} is $3d^5$ $\mu_m = 5\,\mu_B$

F^{2+} is $3d^6$ $\mu_m = 4\,\mu_B$

d states are narrow as fully spin split, fully spin, i.e. all spin up fill before any spin down $3d$.





5.3 Add	Cu, $n_v = 11$,	to Ni, $n_v = 10$.
No. of s electrons	$n_s = 1.0$	$n_s = 0.6$
d electrons	$n_d = 10$	$n_d = 9.4$
d spin up	$n_d^+ = 5$	$n_d^- = 5$
d spin down	$n_d^+ = 5.0$	$n_d^- = 4.4$.
$n_d^+ - n_d^-$	0	0.6
alloy moment	$0x$ +	$0.6(1 - x)$

Ni has 0.6 holes in minority spin band. As Cu is added, the holes fill at a rate of 1 electron per Cu, so the holes are gone, moment = 0, when 60% of alloy is Cu.

5.4 The contribution of the d-band electrons to the stability of an alloy can be expressed

$$E_d = \int_{-W/2}^{E_F} EZ(E)\,dE$$

which gives

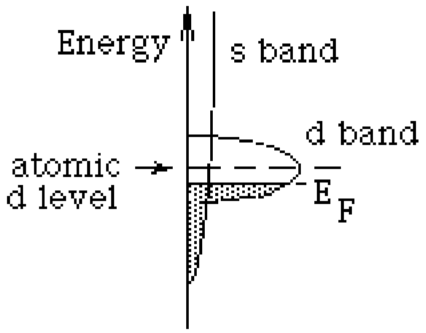
$$E^2 / 2]_{\square\square/2}^{E_F} = (E_F^2 \ \square \ \frac{\square^2}{4}) / 2$$

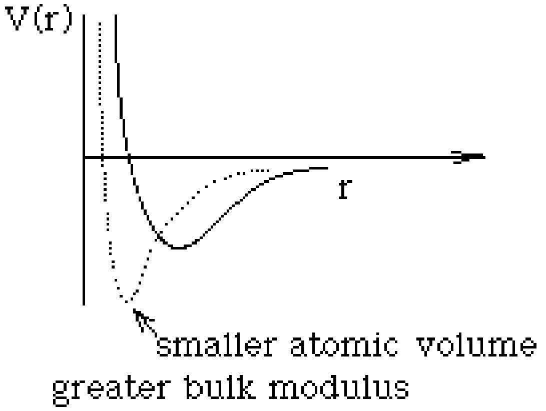
which is parabolic in the value of the Fermi energy (Fig. 5.12).

5.6 a) Early transition metals have broader *d* bands (lower density of states) than do later transition metals because the sparsely-filled *d* orbitals of the early transition metals see a weaker core potential than the electrons of the later transition metals. This in itself favors moment formation in the later transition metals based on the Stoner criterion which states that the product of the density of states times an exchange integral (that is related to the energy favoring parallel spins) be greater than unity. In addition, in Ni the Fermi energy is near the top of the *d* band where the states are of antibonding character; this further enhances the density of states near E_F for Ni. In Ti on the other hand, the Fermi energy is in the lower half of the *d* band which is more bonding in character and thus has an even lower density of states.

b) *p* orbitals are more involved in bonding ($l = 1$) than are *d* orbitals ($l = 2$). Thus they are less localized and form more free-electron-like states than do *d* electrons. The Stoner criterion then favors moment formation in the *d* series considerably more than in the *p* series.

5.8 a) The band structure of the transition metals is approximately as sketched below. The center of the *d* band is well below the electronic energy of the free-atom *d* states (otherwise the condensed state would not be stable). Half the *d*-band states are below and half above the center of the *d* band. The states near the bottom of the *d* band (bonding in nature) fill first and account for the dramatic increase in stability (depth of interatomic potential) and stiffness (related to the curvature of the interatomic potential) and concomitant decrease in interatomic volume in the first half of the series. The occupation of higher-energy, antibonding states in the second half of the series cancels the energy stabilization gained in the first half and the trends reverse.



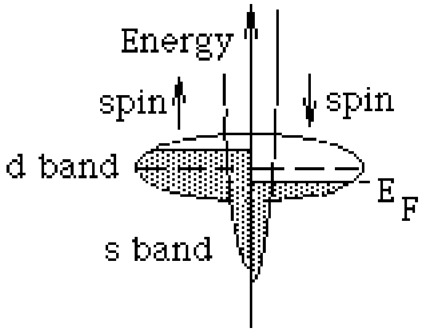


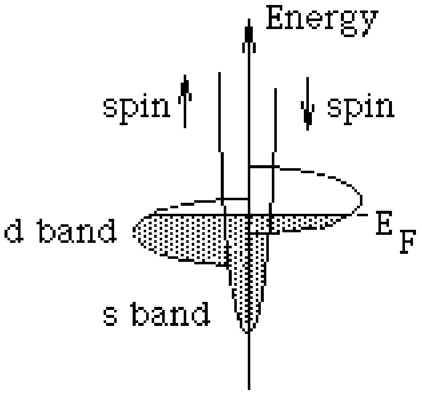
Magnetic moments are known to form on atoms in the 3*d* series metals Cr, Mn, Fe, Co, Ni. [In the first two, these moments order antiferromagnetically, i.e. $\square\boldsymbol{\square}m = 0$

over a unit cell, and in the latter three, the moments order ferromagnetically]. The exchange energy drives the establishment of an unequal spin population in the two sub-bands; electrons below the Fermi energy in one band must move to empty states above E_F in the other. Kinetic energy is measured from the bottom of the band. Hence, a net kinetic energy increase for the *d* electrons results from satisfying Hund's rule (even partially) because more electrons now find themselves in states farther from the bottom of the spin-up band.

$$\langle E_K \rangle = \int_0^{E_F} E_K Z(E) f(E) dE$$

Here E_K is the kinetic energy of the *d* electrons and *Z(E)* and *f(E)* are the density of states and the Fermi function, respectively. Just as increased kinetic energy in a gas causes expansion, so too, in metals, moment formation increases the kinetic energy of the *d* electrons causing an increase in atomic volume.





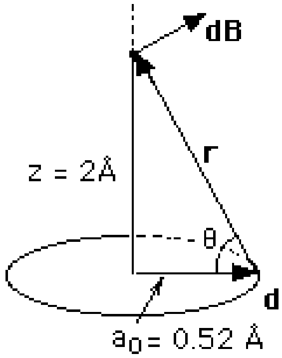
b) This moment formation leads to a giant internal pressure. From Fig. 5.20, a volume change is seen for Fe to be of order 1 part in 7 (14%) corresponding to a linear strain of more than 4%. The change in bulk modulus of Fe due to its magnetic moment appears from Fig. 5.20 to be of order 1.0×10^4 kg/mm^2 (100 GPa or 1.5 megabar)! Alternatively, using a nominal value of 1.7×10^{11} N/m^2 for the bulk modulus of Fe, the magnetic stress is of order $14\% \times 1.7 \times 10^{11}$ = 24 GPa or 0.24 megabars.

Now it should be clearer why Fe finds itself in the BCC structure rather than in a close-packed structure expected for a metal at room temperature. It needs the extra atomic volume of the more open BCC structure to accommodate this giant internal pressure.

5.9. a) If the second spin is located along the axis of the first spin, its moment will align parallel to that of the first. If the second spin is located in the plane perpendicular to the first, its moment will be antiparallel to that of the first electron. In Ch. 4, we had estimated the *B* field seen by an electron due to its relative motion about the nucleus (a_0 = 0.52Å) to be of order 1 T (this is the field associated with the spin-orbit interaction). For two spin 1/2 electrons 2Å apart, the *B* field should be smaller than 1 T. We cannot use the dipole field formula for the field of one spin at the position of the other because that equation is for the *far field* of a dipole; closer to a dipole the field does not vary as r^{-3}.

Instead we use the Biot-Savart law, Eq. 1.14, and calculate the field at z = 2 Å along the axis of symmetry as shown in the figure below.

$$B_z = \frac{\mu_0}{4\pi} I \oint \frac{\mathbf{dl} \times \mathbf{r}}{r^3} = \frac{\mu_0}{4\pi} ev \frac{\sqrt{r_0^2 + a^2}}{(r_0^2 + a^2)^{3/2}} \cos\theta = \frac{\mu_0}{4\pi} \frac{ev}{r_0^2 + a^2}$$

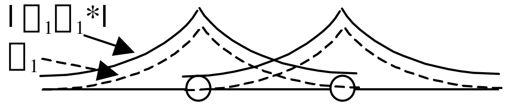


Here a_0 = 0.52 Å is the Bohr radius, θ is the angle between $\boldsymbol{r}$ and the plane of the orbit, and we have used $I = e\omega/2\pi$. Taking $v = (2E/m)^{1/2} = 2.2 \times 10^6$ m/s^2, with E = 13.6 eV, we get I = 1.07 mA and B = 0.826 T directed along the z axis.

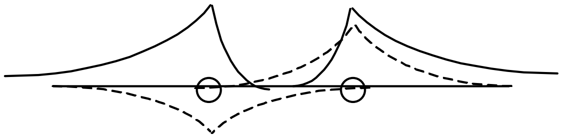
The energy of a spin-one-half particle (one Bohr magneton) in this dipole field is $-\mu_B B = 7.66 \times 10^{-24}$ J = 0.05 meV.

b) The strength of the Coulomb interaction of two electrons separated by 2 Å is $e^2/(4\pi\varepsilon_0 r) = 1.15 \times 10^{-18}$ J = 7 eV.

c) The *Coulomb integral* is expected to be of the same order of magnitude as the classical Coulomb interaction, 7 eV. The probability densities, $|\psi_1\psi_1^*|$ and $|\psi_2\psi_2^*|$, of the two electrons drop off as exp[$-2r/a_0$] and exp[$-2(r-2\text{Å})/a_0$]. Their integration over all space represents the net electrostatic interaction of the distributed electronic charge of the two electrons. The Coulomb *exchange* integral can be estimated from the value of the above Coulomb interaction times a factor that accounts for the fact that the two electrons, now having parallel spins, stay on average farther from each other; their wave functions combine in a spatially antisymmetric way, and hence their probability density has a nodal plane between their centers. This could be approximated by replacing the 2Å above with a slightly larger number or by using an asymmetric wave function on each site as illustrated below, right.



Coulomb integral



Exchange integral

In any case, this exchange integral is much stronger than the *dipole* interaction but it is due to an entirely different mechanism, and it is not as strong as the pure Coulomb interaction.

5.10. a) p orbitals or p bands in Al are too delocalized (essentially free electrons), to support any moment formation which must arise from a highly localized electronic wave function. The nearly atomic like (high density of states) 3d wave functions of Ni allow intra-atomic exchange (Hund's rule) to establish a moment. Interatomic exchange allows the moment to order over long range.

b) The early transition metals have bonding valence states that are more delocalized than those of the late transition metals which are antibonding. The result is that the late transition metal valence states are more highly localized and so a moment can form. They overlap enough so that long range order can be sustained.