

FoP3B Part I Lecture 9: Anisotropy and Magnetic Ordering

Magnetocrystalline anisotropy

The transition metal elements, Fe, Co and Ni are known for their ferromagnetic properties.

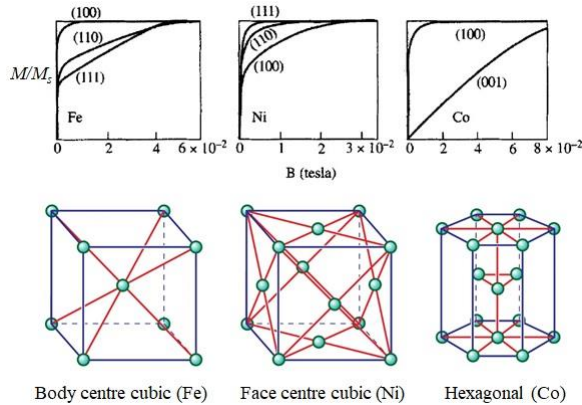


Figure 1

The crystal structure of these elements are all different, with Fe being body centred cubic, Ni face centred cubic and Co hexagonal (Figure 1). It is found that the elements are readily magnetised along certain crystallographic directions than others. For example, for hexagonal Co the **easy** direction of magnetisation is normal to the *basal planes*, i.e. it takes a lower **B**-field to reach saturation magnetisation M_s along the easy axis compared to other crystal directions (Figure 1).

The reasons for the so-called **magnetocrystalline anisotropy** are somewhat complex. There are ‘crystal field’ effects that arise due to the anisotropic shape of electron orbitals, especially *d*-orbitals as found in transition metals, where some electron orbitals are subjected to greater Coulomb repulsion from electrons in neighbouring atoms than others. This results in *orbital quenching* where the net orbital angular momentum $L = 0$ (note that Hund’s rules for an isolated atom states that L must be maximised, so orbital quenching is a phenomenon arising from the crystal environment surrounding the atom). The orbital quenching modifies the spin orbit interaction so that the Hamiltonian is now dependent on the crystal direction.

Because of magnetocrystalline anisotropy there is an energy penalty for magnetisation in a direction other than the easy axis. This results in an **energy density** (i.e. energy per unit volume). As an example for hexagonal crystals the energy density is:

$$E = K_1 \sin^2 \theta + K_2 \sin^4 \theta$$

where θ = angle between magnetisation direction and easy axis, and K_1, K_2 = anisotropy constants. Note that if magnetisation is along the easy axis $\theta = 0^\circ$ and there is no energy penalty (i.e. $E = 0$). The above formula is only valid for hexagonal crystals; alternative expressions can be found for crystals of other symmetry, such as, cubic.

Antiferromagnetism

We will now examine other forms of magnetic moment long range ordering. In ferromagnetism $J_{ij} > 0$, so that the triplet has lowest energy, and all the spins are aligned parallel to one another. If $J_{ij} < 0$ the singlet is the ground state and neighbouring spins are aligned anti-parallel to one another. This form of long range ordering is known as **antiferromagnetism**. An example is MnO, where the spin orientation of magnetic Mn^{2+} ions on alternate (111) planes are anti-parallel to one another (Figure 2). Since neighbouring magnetic moments are anti-parallel and are of the same magnitude the *net* magnetisation of an antiferromagnet is zero. In **ferrimagnetism** (e.g. Fe_3O_4) the neighbouring spins are anti-parallel, but have different magnitude, resulting in non-zero magnetisation.

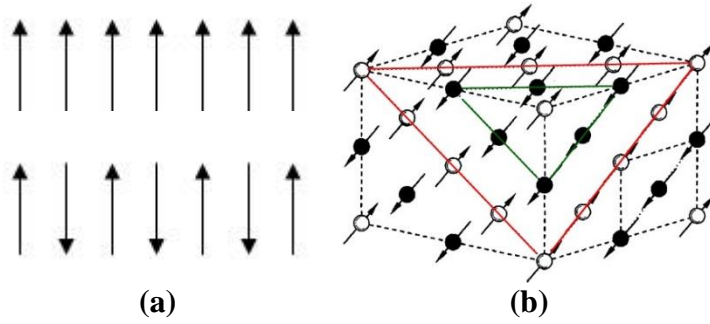


Figure 2: (a) ferromagnetic (top) and antiferromagnetic (bottom) spin ordering and (b) the antiferromagnetic solid MnO. The dark and white circles represent Mn^{2+} ions on alternate (111) planes (indicated by the coloured lines).

We can extend the Weiss model of ferromagnetism to antiferromagnets as well. The concept is illustrated in Figure 3, where the antiferromagnetic spin lattice is separated into two ferromagnetic *sub-lattices* (spin up and spin down).

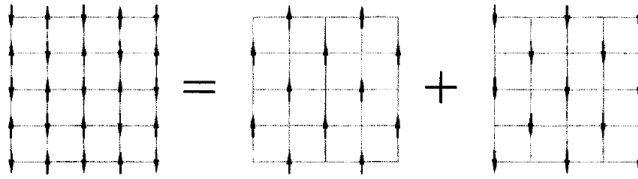


Figure 3

Magnetisations on each sub-lattice are equal and opposite. The molecular field imposed by one sub-lattice on the other is given by (+ is spin 'up' and - is spin 'down'):

$$B_{\text{mf}}^+ = -|\lambda|M^-$$

$$B_{\text{mf}}^- = -|\lambda|M^+$$

Note that the molecular field constant is $-|\lambda|$ rather than λ , since the sign of J_{ij} for an antiferromagnet is opposite to that of a ferromagnet.

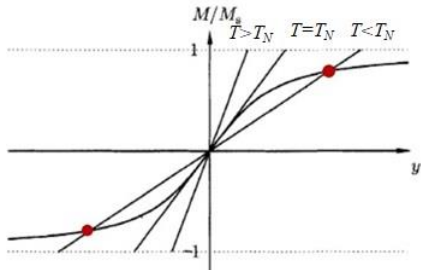


Figure 4

Applying Weiss' theory to a ferromagnetic sub-lattice:

$$\frac{M^\pm}{M_s} = B_J(y^\pm) \dots (1)$$

$$\text{and } y^\pm = \frac{g_J \mu_B J (B + B_{\text{mf}}^\pm)}{kT} = \frac{g_J \mu_B J (B - |\lambda| M^\mp)}{kT} \dots (2)$$

The graphical solution of this problem at zero applied field is shown in Figure 4. The spontaneous magnetisation of a sub-lattice decreases to zero at the **Néel temperature** (T_N).

Above the Néel temperature the antiferromagnet becomes paramagnetic. The magnetic susceptibility of the paramagnetic phase can be calculated by solving Equations 1 and 2 under a small applied field B . The graphical solution is illustrated in Figure 5.

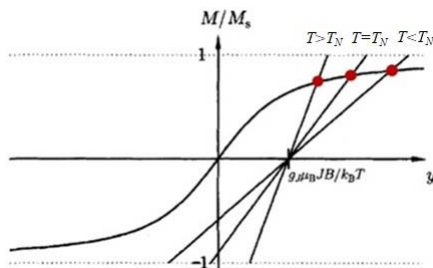


Figure 5

For a $J = 1/2$ solid Equation 1 gives:

$$\frac{M^\pm}{M_s} = \frac{\mu_B (B + B_{\text{mf}}^\pm)}{kT} = \frac{\mu_B (B - |\lambda| M^\mp)}{kT}$$

Since the magnetisation on each sub-lattice is equal in magnitude ($M^+ = M^- = M$):

$$\frac{M}{M_s} \left(1 + \frac{|\lambda| \mu_B M_s}{kT} \right) = \frac{\mu_B B}{kT}$$

For small magnetisations $\chi = \mu_0 M/B$:

$$\chi = \frac{\mu_0 \mu_B M_s}{k \left[T + \frac{|\lambda| \mu_B M_s}{k} \right]} \propto \frac{1}{T + T_N}$$

In general the paramagnetic susceptibility above the transition temperature is found to vary as $\chi \propto 1/(T - \theta)$, where θ is the **Weiss temperature**. If the material is paramagnetic at low temperature $\theta = 0$ (Curie's law), $\theta > 0$ (Curie-Weiss law) for ferromagnetic materials, and $\theta < 0$ for antiferromagnets.

Since the net magnetisation of an antiferromagnet is zero the question arises what would be the susceptibility below the Néel temperature. In fact, the magnetic susceptibility is different for a **B**-field applied parallel or perpendicular to the magnetisation direction. This is illustrated in Figure 6.

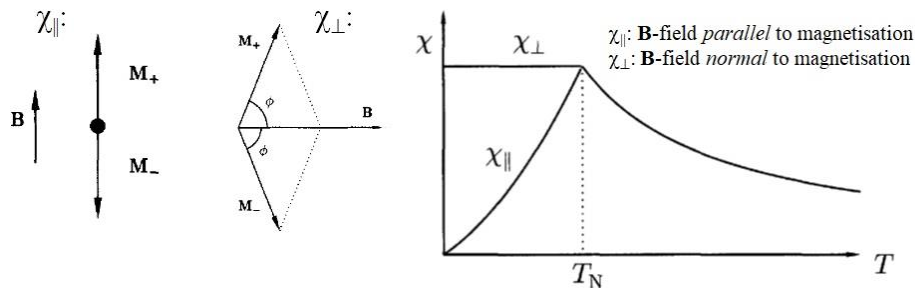


Figure 6

The explanation is as follows:

χ_{\parallel} : At $T = 0$ K all the spins are perfectly aligned and sub-lattices have saturation magnetisation M_s . The spin up sub-lattice is favourably aligned with the **B**-field, but not the spin down sub-lattice. Provided the **B**-field is small spin down cannot flip to spin up. Therefore χ_{\parallel} is zero at 0 K. Higher temperatures will tend to cause deviations from perfect spin alignment, which can be restored by the applied field, at least for the spin up sub-lattice, causing χ_{\parallel} to increase with temperature until T_N .

χ_{\perp} : the magnetisation of the two sub-lattices will partly tilt towards the direction of the applied **B**-field. Complete tilting is prevented by the energy penalty due to magnetocrystalline anisotropy. χ_{\perp} is approximately independent of temperature below T_N .

Helimagnetism

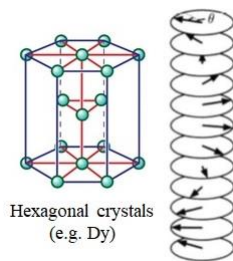


Figure 7

Another form of long range order is **helimagnetism**, where the spin rotates by an angle θ between successive planes (e.g. basal planes in hexagonal crystals such as dysprosium Dy; Figure 7). Here the exchange constant between spins in neighbouring (J_1) and next-neighbour (J_2) planes are important. Let us determine the conditions that favour helimagnetic ordering. The exchange energy term $-J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$ is:

$$E = -2NS^2(J_1 \cos \theta + J_2 \cos 2\theta)$$

where N = number of atoms in the plane. The factor of 2 in $2NS^2$ is due to the fact atom pairs i and j are counted twice in $-J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$.

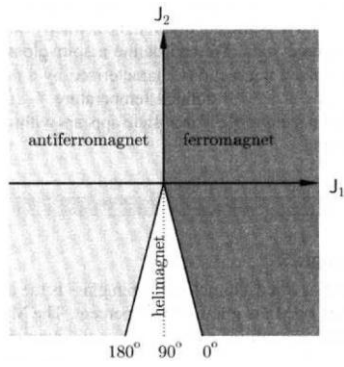


Figure 8

The minimum energy condition must satisfy $dE/d\theta = 0$, or $(J_1 + 4J_2 \cos \theta) \sin \theta = 0$. The solutions are $\sin \theta = 0$ and $\cos \theta = -\frac{J_1}{4J_2}$. The former is satisfied for $\theta = 0^\circ$ (ferromagnetism) and $\theta = 180^\circ$ (antiferromagnetism). The latter represents helimagnetism. For an energy minimum $d^2E/d\theta^2 > 0$ and it is easy to show that for helimagnetism this is satisfied when $J_2 < 0$. The helimagnetism stability region is therefore as shown in Figure 8.