Day 28: Diamagnetism, paramagnetism, and ferromagnetism

"Magnetism is the funnest thing no one understands" —

Materials are classified by how their dipoles respond to applied magnetic fields.

Paramagnetic materials:

Upon adding a magnetic field, the previously randomized dipoles align only slightly, leading to some small internal field in the same direction as the applied field. That makes the internal $\vec{B}$ just a bit bigger. We have:

$\vec{M} = \chi_m \vec{H}$ (note $\vec{B}$ & $\vec{H}$ are always parallel)

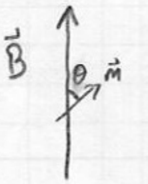
For parametic materials, χ_m is positive and very small $(10^{-3} - 10^{-6})$ so in everyday situations we don't notice the effects.

Paramagnetism comes about when individual atoms have a net intrinsic magnetic moment, either spin or orbital (or both).

With paramagnetism there are two competing effects:

1) Thermal interactions tend to randomize the dipoles.
2) The magnetic field applied tries to uniformly orient them.

What wins? Let's do some stat mech.



The angle θ between $\vec{B}$ & $\vec{m}$ is a measure of the alignment of the dipoles. Let's take the thermodynamic average of $\cos\theta$ (why $\cos\theta$? we'll see presently)

$$\langle\cos\theta\rangle = \frac{\int e^{-U/kT}\cos\theta\, dU}{\int e^{-U/kT}\, dU}$$

A weighted average with the Boltzmann factor as the weighting function.

Here, $U = -\vec{m}\cdot\vec{B} = -mB\cos\theta$, so $dU = mB\sin\theta\, d\theta$

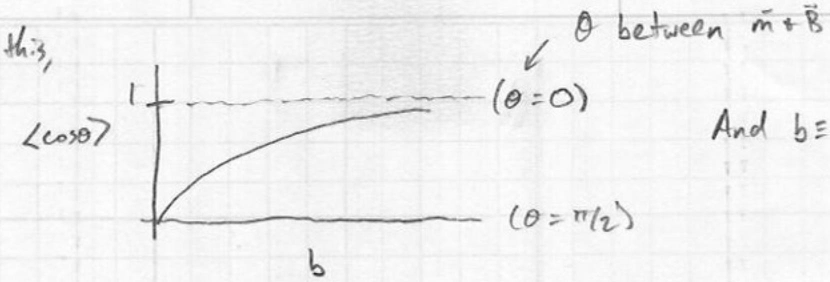
$$\Rightarrow \quad \langle\cos\theta\rangle = \frac{\cancel{mB}\int_0^{\pi} e^{mB\cos\theta/kT}\cos\theta\sin\theta\, d\theta}{\cancel{mB}\int_0^{\pi} e^{mB\cos\theta/kT}\sin\theta\, d\theta}$$

We evaluate this and get (with $b \equiv mB/kT$)

$$\langle\cos\theta\rangle = \frac{(\cancel{2}b\cosh(b) - \cancel{2}\sinh(b))/b^{\cancel{2}}}{\cancel{2}\sinh(b)/\cancel{b}} = \frac{\cancel{b}\cosh(b)}{\cancel{b}\sinh(b)} - \frac{\sinh(b)}{b\sinh(b)}$$

$$= \coth(b) - \frac{1}{b}$$

Sketching this,



And $b \equiv mB/kT$

So for low T (high b), $\langle\cos\theta\rangle = 0$, meaning $\vec{m}$ + $\vec{B}$ are aligned. This is what happens when the dipole interaction energy is large compared to the ambient thermal energy, $mB >> kT$.

If $kT >> mB$, $b \to 0$ and the dipoles are on average unaligned.

In reality at room temperature, kT is sufficiently large that thermal effects dominate (mostly), which is why χ_m is so small.

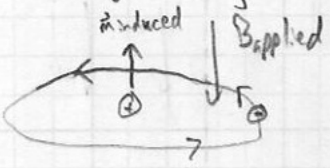
Diamagnetic materials

These have no net atomic (or molecular) magnetic moments, on account of closed electron shells and a spin up e^- for every spin down e^-.

(technically all materials exhibit diamagnetism, but only in these materials is it not dominated by something stronger like paramagnetism)

Like para- and ferromagnetism, diamagnetism is intrinsically quantum mechanical, and the proper treatment is outside the scope of this class. We'll resort to a classical argument.

Consider any individual atom in a material, with an electron orbiting a nucleus. The electron constitutes a current loop.



If we apply a B-field, there's an interval over which the flux through the loop is changing, inducing an EMF in the loop. By Lenz's law the EMF is in such a direction as to oppose the change that made it, which means slowing down the electron + changing the orbital dipole moment of the system such that $\vec{m} \propto -\vec{B}$.

Alternately: The $q\vec{v}\times\vec{B}$ force on the electron given a downward $\vec{B}$ is outward, so there's less centripetal force on the electron and it slows down. The orbital magnetic moment becomes weaker, and so there ends up being an induced $\vec{m}$ upward.

Ferromagnetism

Very, very generally, if you put two dipoles (think bar magnets) next to each other, they antialign:

or ↑↓

This minimizes the energy associated with the magnetic interaction, and minimizing energy is a thing nature does quite well (though its sometimes balanced against maximizing entropy)

In ferromagnetic materials, the structure of the outermost orbitals leads to a different kind of energy that dominates the simple dipole-dipole interaction.

✶ Disclaimer: What follows is a very casual, handwavy description of ferromagnetism. A precise treatment involves detailed calculations of orbital structure for large atoms and evaluation of scary things like "exchange integrals".

The dominant energy in ferromagnetic materials is the exchange energy. You've seen exchange forces in quantum. Wavefunctions (including the spinor) have to be antisymmetric under exchange of two particles if we're dealing with fermions. Examples:

Spin antisymmetric
Spatially symmetric
Overall antisymmetric

(allowed state)
(bonding, for H_2)

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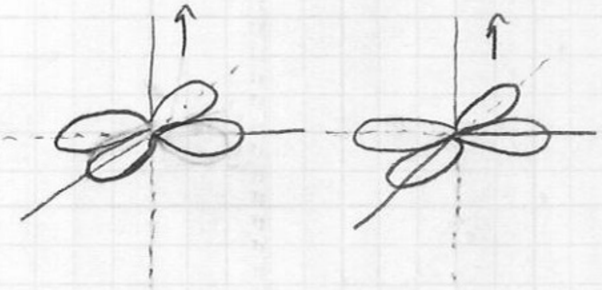
Three elements are ferromagnetic at room temperature:

Fe	(26)	$4s^2 3d^6$
Co	(27)	$4s^2 3d^7$
Ni	(28)	$4s^2 3d^8$

Consecutive on the periodic table, with a particular electronic structure

The valence electrons are in d shells with $m \neq 0$; the orbitals look like:



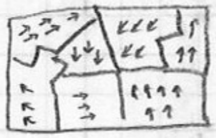
In every other material, the preferred energy state involves symmetric wavefunctions and antisymm. spins.

For these elements, antisymmetric wavefunctions and symmetric spins work out to be strongly favorable.

The antisymmetric wavefunctions lead to the atoms being farther apart (much as in the H_2 antibonding case), and the reduced electrostatic repulsion dominates all other terms, so atoms bond spin-parallel.

Something about the geometry of the $m \neq 0$ d shells makes this all work out when you do the detailed exchange energy calculations

Now, you might expect all of the dipoles in, say, iron to line up automatically. But they don't. The iron will have defects (impurities, dislocations, etc) where alignment tends to get "snagged." In practice spins form clusters called domains:



The domains are usually randomly oriented at first.

(discussion question w/ curie temperature hint)

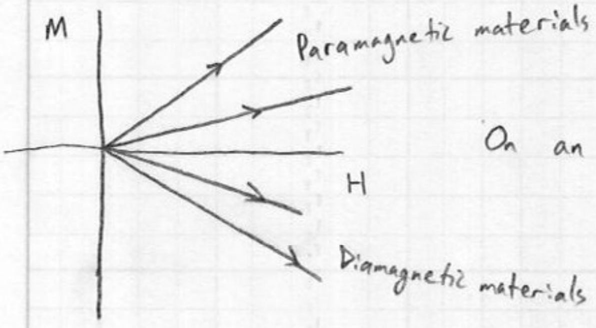
Now, with a strong enough applied magnetic field, one can force the domains into alignment, at which point they'll stay there and we'll have a permanent magnet.

$B = \mu H$
$M = \chi H$

Memory + Hysteresis

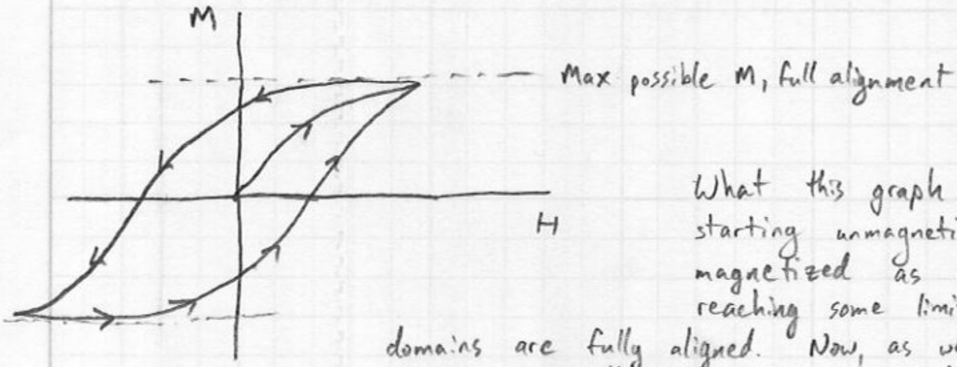
Ferromagnetic materials have a memory that others don't.

In a diamagnetic or paramagnetic material, the magnetization is always proportional to the field. Take away the field, and $\vec{M}$ leaves too. Furthermore, the relationship is usually linear in $\vec{H}$, $\vec{M} = \chi_m \vec{H}$



On an M vs H plot, the slope is χ_m

For ferromagnetic materials, we get curves such as:



What this graph shows is a material starting unmagnetized. It then becomes magnetized as we turn up $\vec{H}$, eventually reaching some limiting value where the domains are fully aligned. Now, as we turn $\vec{H}$ back town, the domains will relax, but not completely. As we apply $\vec{H}$ in the opposite direction, it will actually take quite a bit of field to flip the domains all the way over.

So χ_m is variable and depends not just on $\vec{H}$ but on the history of the material. This is referred to as hysteresis, and the sketch is a hysteresis loop.

(slides, link)