

Day 28: Diamagnetism, paramagnetism, and ferromagnetism.

This is an almost intractably complex topic, full of special cases and exceptions. If you think of an objection to something in here based on some example you're familiar with, there's a fair chance that you're not wrong about it. But the resolution may be rather non-trivial.

I have a nice book chapter in pdf form available by request that gives a readable survey-level treatment of these topics while still being essentially correct. Just FYI.

Materials can be categorized based on how they respond to applied B-fields.

Paramagnetic materials produce weak internal fields in the same direction as applied fields.

Diamagnetic materials produce (usually) weak internal fields antiparallel to applied fields, effectively screening out applied fields.

Ferromagnetic materials produce very strong ^{parallel} internal fields in response to applied fields.

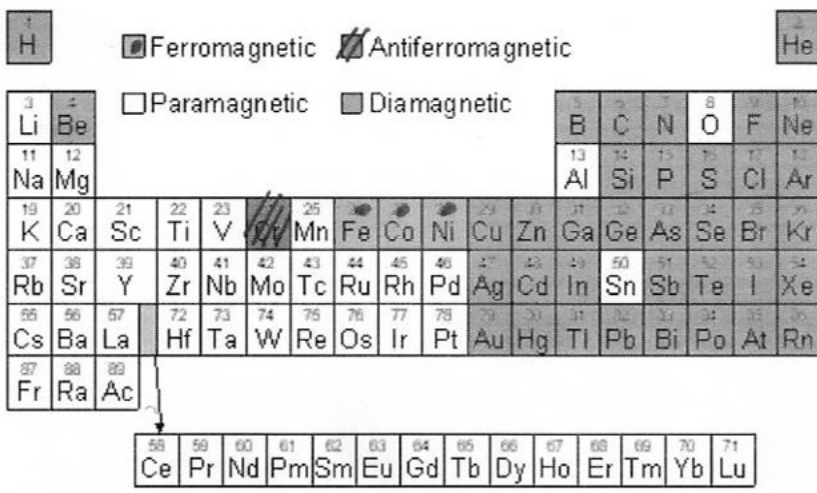
Of course, you know you're in for some trouble when the standard junior-level text on E&M says things like:

"<diamagnetism> is typically much weaker than paramagnetism, and therefore is observed mainly in atoms with even numbers of electrons, where paramagnetism is absent"

"Paramagnetism usually occurs in atoms or molecules with an odd number of electrons"

And then you look at an actual periodic table marked out by magnetic category:

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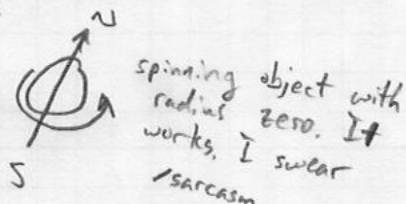
There's also ferrimagnetic & antiferromagnetic,
 plus ridiculously complex temperature dependences!

Ugh. This is going to get worse before it gets better, isn't it?

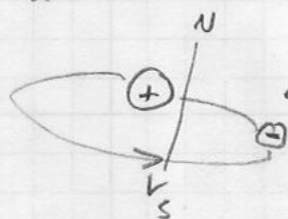
We'll start at the beginning. Material response to magnetic fields come mostly from electron response; nuclei have magnetic moments too but they don't really contribute much to the total.

Electrons can have magnetic moments two different ways:

- 1) Because of their spin. Classically, because they're "spinning balls of charge" <enough>
Quantum mechanically, it's intrinsic magnetism related to quantum number s or m_s

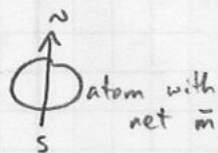


- 2) Because of their orbital angular momentum. Classically, by orbiting a nucleus the electrons constitute current loops, the fundamental magnetic dipole. QM: associated with quantum number l



current loop. Because it is totally rotating...
...yeah.

The net magnetic moment of an atom or molecule comes from the combination of all the orbital & spin terms for all the electrons present. Adding angular momenta in QM (basically the same thing as combining dipoles) is hard. We will simply abstract that out and say that an atom either ends up with a nonzero \vec{m} or it does not



atom such that all the terms add to $\vec{m}=0$

S, L
Clebsch-Gordan

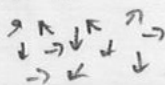
Curie Paramagnetism: Understandable classically
 Strong temperature dependence
 Common in isolated atoms, rare in solids

Consider some loose collection of magnetic dipoles. There are a couple competing effects that govern their ordering:

1) If there's a B-field, the dipoles minimize their energy ($U = -\vec{m} \cdot \vec{B}$) by aligning with \vec{B}



2) If $T > 0$ (and it always is) thermal energies $\propto kT$ are going to serve to randomize the orientations of the \vec{m}_i 's



In Curie paramagnetism, if $mB \gg kT$, the constituent dipoles align and reinforce the applied field. If $kT \gg mB$, thermal randomization dominates. There's a transition region in between. We can characterize things reasonably well using some stat mech:

$\vec{m} \cdot \vec{B} = mB \cos \theta$, so let's take the thermodynamic average of $\cos \theta$ for dipoles in this field to characterize the average bulk orientation:

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

A weighted average with the Boltzmann factor as the weighting function

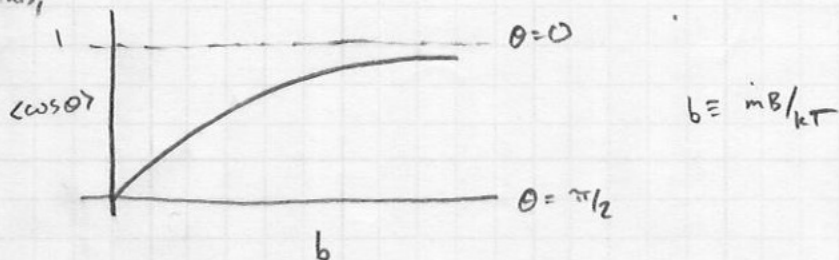
Let $U = -\vec{m} \cdot \vec{B} = -mB \cos \theta$, $dU = mB \sin \theta d\theta$

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

Let $b \equiv mB/kT$

Which evaluates to $\langle \cos \theta \rangle = \coth(b) - 1/b$

Sketching this,



For low T (high b), $\langle \cos \theta \rangle \rightarrow 1$, meaning $\vec{m} \parallel \vec{B}$ are aligned. This is what happens when the dipole interaction energy is large compared to the ambient thermal energy, $mB \gg kT$.

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

For most real Curie paramagnets, at room temperature kT is dominant + χ_m is small.

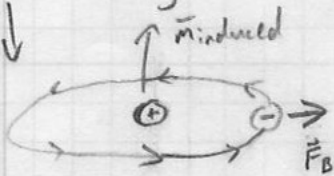
Curie paramagnetism occurs only if you have weakly-coupled atoms/molecules that each have nonzero \vec{m} . It's much more common (esp. in solids) for your spin + orbital \vec{m} terms to add to zero, or for atoms to line up with their \vec{m} 's antiparallel so as to cancel on a small scale. When that happens, a weaker but more universal effect manifests:

Diamagnetism: This is present in every material, but is noticeable only in materials where there isn't anything stronger (paramagnetism, ferromagnetism) masking it.

In a nutshell: When you apply a \vec{B} -field to an atom or molecule, there's an induced \vec{m} in a direction opposite to the applied \vec{B} . The induced \vec{m} 's screen some of the applied \vec{B} out. In extreme cases, the induced \vec{m} is strong enough to levitate an object.

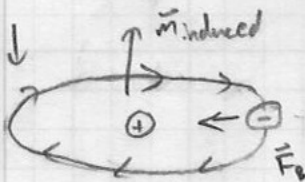
This is intrinsically quantum, but that won't stop us from constructing a semiclassical model that works better than it has any business doing:

applied \vec{B}
↓ ↓ ↓



So an atom has an electron orbiting a nucleus. Say we apply a B -field. No matter the sense of the orbit (clockwise vs. counterclockwise), the B -field will cause a radially outward force on the electron. This will cancel some of the attraction to the nucleus, changing the centripetal force, and thus slowing down or speeding up the electron.

\vec{B}
↓ ↓ ↓



The change in speed changes the current + thus the orbital \vec{m} . It is always in a direction so as to oppose \vec{B} (check it yourself)

So we'd expect many solids to be diamagnetic. But there are a couple of very special things that can happen in metals.

Pauli paramagnetism

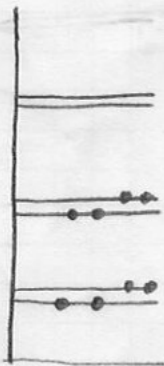
What makes a metal a metal? It's band structure, mostly.

One atom has an energy level spectrum, which fills in from the bottom:

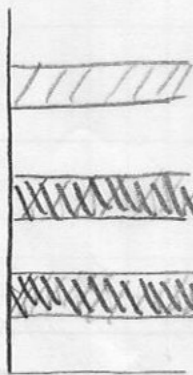


Note that they fill in in spin up/down pairs

If you have two atoms bound together, the energy levels split:



If you have many atoms (say, like in a solid), the energy levels split many times, forming nearly continuous bands.

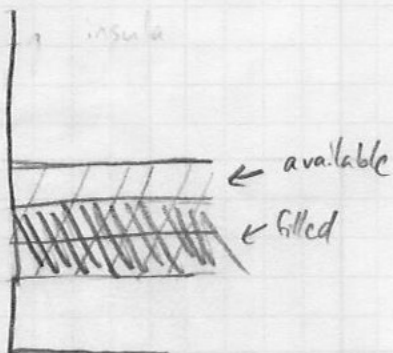


available, empty

filled

filled

In insulators + semiconductors, the bands stay separate so that there's a big energy gap between the electrons & the unoccupied states. Note that electrons still fill in from the bottom in spin up/spin down pairs.



In a metal, the bands broaden to the point that a filled band and an empty band overlap, meaning that those electrons at the top edge have immediately available states at close to zero energy cost.

Suppose we apply a \vec{B} -field to a non-metal. It would be energetically favorable for some of the $\uparrow\downarrow$ pairs to flip to $\uparrow\uparrow$ in alignment with \vec{B} , but all the nearby $\uparrow\downarrow$ states are full. There'd have to be an energetically close empty \uparrow state for the \downarrow electron to move into. There isn't.

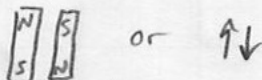
In a metal, there is. The energy of the system can be reduced overall if some of the electrons hop up to a slightly higher, unoccupied spin-parallel-to- \vec{B} state, reducing $-\vec{m} \cdot \vec{B}$.

So in a metal, applying \vec{B} leads to some of the \vec{m} 's lining up with \vec{B} and slightly reinforcing the applied \vec{B} , the essential feature of paramagnetism.

We call this Pauli paramagnetism.

Ferromagnetism

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

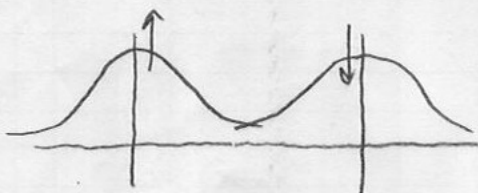


This minimizes the energy associated with the magnetic interaction, and minimizing energy is a thing nature does quite well (though it's sometimes balanced against maximizing entropy)

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

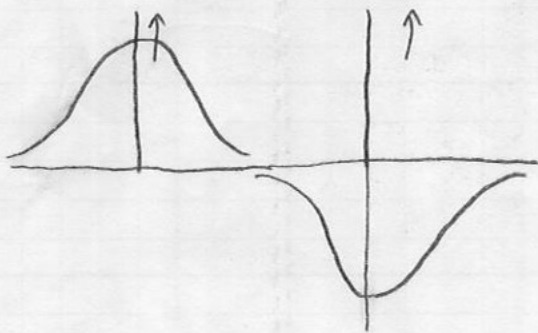
★ Disclaimer: What follows is a very casual, handwavy description of ferromagnetism. A precise treatment involves detailed calculations of orbital structure for large atoms and evaluation of scary things like "exchange integrals".

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: (vs. $U = -\vec{m} \cdot \vec{B}$ or kt)



Spin antisymmetric
Spatially symmetric
Overall antisymmetric

(allowed state)
(bonding, for H_2)



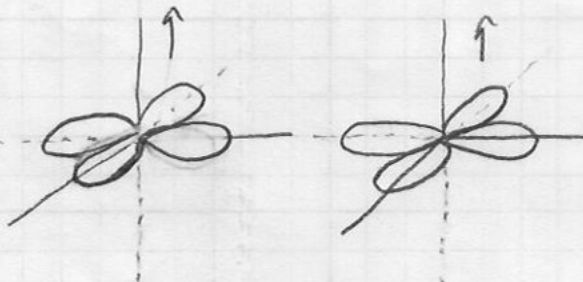
Spin symmetric
Spatially antisymmetric
Overall antisymmetric

(allowed state)
(antibonding, for H_2)

Three elements are ferromagnetic at room temperature:

Fe (26)	$4s^2 3d^6$	Consecutive on the periodic table, with a particular electronic structure
Co (27)	$4s^2 3d^7$	
Ni (28)	$4s^2 3d^8$	
(Cu 29)	$4s^1 3d^{10}$, Zn 30	

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



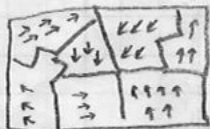
In every other material, the preferred energy state involves symmetric wavefunctions and antisymmetric spins.

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: (there's also an energy balance issue)



The domains are usually randomly oriented at first.

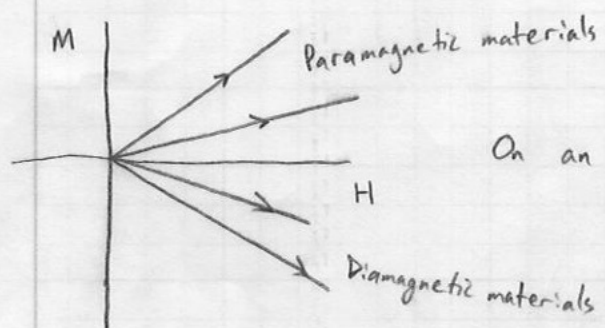
(discussion question w/ Curie temperature hint)

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.

Memory & Hysteresis

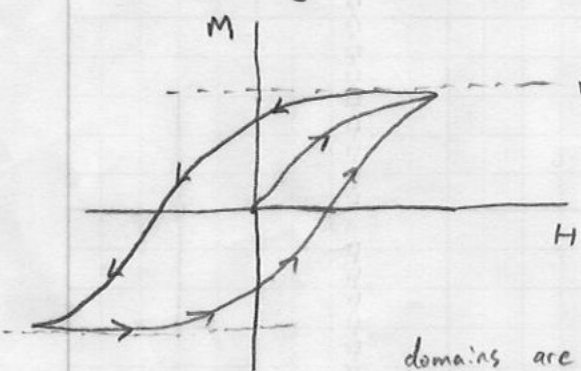
Ferromagnetic materials have a memory that others don't.

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 down, 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)