How to Tell Diamagnetic Materials from Paramagnetic

I wrote these notes as a followup to the *Material Physics* web pages of Dr. Rudolf Winter's from Aberystwyth University (Wales, UK):

- diamagmetism and paramagnetism;

- paramagnetism in metals;

- ferromagnetism et al.

Dr. Winter explains the physical origin of diamagnetism, paramagnetism, and collective magnetic behaviors such as ferromagnetism and antiferromagnetism. In these notes I explain how to tell whether a particular material is going to be diamagnetic or paramagnetic. I say 'is going to be' rather than simply 'is' because some of the would-be paramagentic materlals develop collective behaviors such as ferromagnetism. Alas, predicting such collective magnetic behavior is way beyond the scope of this class, so I limit these notes to diamagnetism and paramagnetism.

Let's start with individual atom or molecules As explained in Dr.~Winter's notes, in *all* atoms, the external magnetic field induces magnetic moments in the opposite direction to the applied field,

$$\mathbf{m}(\mathbf{B}) \;=\; \mathbf{m}_0 \;-\; \alpha_d \mathbf{B} \tag{1}$$

where $\mathbf{m}_0$ is the built-in magnetic moment of the atom in the absence of the external field, and

$$\alpha_d \;=\; \frac{e^2}{4m_e} \sum^{\text{electrons}} \left\langle r^2 \right\rangle . \tag{2}$$

Although Dr. Winter's notes explains eqs. (1) and (2) in classical terms, they also hold true in the quantum theory of atoms. Moreover, eq. (1) applies not just to individual neutral atoms but also to the ions and the molecules, although the coefficient α_d for the molecules is given by a more complicated formula than eq. (2).

In light of eq. (1), all atoms, ions, and molecules are inherently diamagnetic. However, the atoms and molectles with built-in magnetic moments $\mathbf{m}_0 \neq 0$ are also paramagnetic,

since in external magnetic field such moments $\mathbf{m}_0$ tend to align with $\mathbf{B}$. Indeed, the energy of a magnetic dipole in an external $\mathbf{B}$ field is $U = -\mathbf{m}\cdot\mathbf{B}$, which favors $\mathbf{m} \upuparrows \mathbf{B}$. Although the thermal motion of molecules tries to randomize the directions of their magnetic moments, the magnetic energy biases the statistical distribution of directions in favor of magnetic field's direction, so *on average*

$$\langle \mathbf{m}_0 \rangle \;=\; +\alpha_p \mathbf{B} \tag{3}$$

for

$$\alpha_p \;=\; \frac{\mathbf{m}_0^2}{kT} \tag{4}$$

where T is the temperature and k is the Boltzmann's constant. At room temperatures, $\alpha_p \gg \alpha_d$, so if paramagnetism is present at all, it wins over the diamagnetism. Thus:

- For atomic and molecular gases, liquids, or solids, or for ionic crystals: if the atoms / molecules / ions have non-zero bulit-in magnetic moments $\mathbf{m}_0 \neq 0$ then the substance is paramagnetic; otherwise it's diamagmetic.

For an atom or ion, the built-in magnetic moment follows from the angular momentum:

$$\mathbf{m}_0 \;=\; -\frac{e}{2m_2}(\mathbf{L} + 2\mathbf{S}) \tag{5}$$

where $\mathbf{L}$ is the net orbital angular momentum of all the electrons in the atom or ion while $\mathbf{S}$ is the net spin of all the electrons. Both $\mathbf{L}$ and $\mathbf{S}$ are quantized in units of $\hbar$, namely

$$\mathbf{L}^2 \;=\; \hbar^2 L(L+1) \quad \text{for integrer } L = 0, 1, 2, 3, \ldots, \tag{6}$$

$$\mathbf{S}^2 \;=\; \hbar^2 S(S+1) \quad \text{for integer or half-integer } S = 0, \tfrac{1}{2}, 1, \tfrac{3}{2}, 2, \ldots. \tag{7}$$

The specific values of L and S for a particular atom or ion follow from the shell model: Each electron's orbit belongs to a particular shell and subshell according to the radial and orbital quantum numbers, each sub/shell has room for so many electrons, the inner shells of an atom/ion are filled up, while the outer shell may be only partially filled. Any closed (*i.e.*, completely filled up) shell or subshell has zero net angular momentum, $L = S = 0$, while the open (incomplete) shell usually have $L \neq$ or $S \neq 0$ or both; the specific values of the L and S of an open shell follow from the Hund rules, but you don't need them for this class.

Note that ions have more/fewer electrons than the corresponding neutral atoms, so their shell structure is different. Thus, to find out if some ionic crystal is diamagnetic or paramagnetic, your should check the shell structure of the constituent ions rathar than the neutral atoms.

EXAMPLE: THE TABLE SALT, NaCl.

The solid sodium chloride is an ionic crystal, made from the positive sodium ions Na^+ and negative chlorine ions Cl^- rather than neutral atoms. A neutral sodium atom has electron structure $[Ne]3s^1$, but the Na^+ misses the outer 3s electron and has only the complete neon-like shells. Consequently, the sodium ion has $L = S = 0$ and hence no built-in magnetic moment. As to the chlorine, a neutral Cl atom has electron shell structure $[Ne]3s^23p^5$, but the negative ion has an extra 3p electron and hence a complete argon-like outer shell, $[Ne]3s^23p^6 = [Ar]$. Thus, the chlorine ion also has $L = S = 0$ and hence no built-in magnetic moment. so the net magnetic moment of the ion is zero. Altogether, none of the ions in the sodium chloride crystal have built-in magnetic moments, so the table salt is diamagnetic.

EXAMPLE: COPPER CHLORIDE $CuCl_2$.

This is another ionic crystal made from necgative Cl^- and Cu^{++} ions. As in the previous example, the negative chlorine ions have argon-like closed shell structure and hence no build-in magnetic moment. As to the copper, a neutral copper atom has electron shell structure $[Ar]4s^13p^{10}$, with one electron in an open subshell $4s$, hence $L = 0$ but $S = \frac{1}{2}$ and $\mathbf{m}_0 \neq 0$. A singly-charged positive copper ion Cu^+ loses this electron, so it has only closed shells or sub-shells and hence $\mathbf{m}_0 = 0$. But a doubly-charged ion Cu^{++} loses another electron, this time from the 3d subshell, so that subshell becomes open. A single *hole* in the 3d subshell gives it $L = 2$ and $S = \frac{1}{2}$, hence $\mathbf{m}_0 \neq 0$.

Altogether, the copper chloride is paramagnetic because it has ions with $\mathbf{m}_0 \neq 0$.

Molecules

In molecules, the electrons on the atom's outer shells are involved in chemical bonds, they no longer orbit a single nucleus, so instead of tracking their L and S quantum numbers it is more convenient to track the *electron pairing*. To electrons in a pair have similar quantum numbers, except for opposite directions of their orbital angular momenta and of their spinds.

Consequently, the paired electrons do not contribute to the net magnetic moment of the molecule, only the un-paired electrons do. Therefore:

⋆ If all electrons in a molecule are paired up, then the molecule has no net magnetic moment and the substance is diamagnetic.

⋆ But if a molecule has some un-paired electrons, then it generally has $\mathbf{m} \neq 0$ and the substance is paramagnetic.

Here are some rules for finding paired and un-paired electrons in molecules:

• All electrons in a closed shell of any atom or ion are paired up.

• For open sub-shells in *standalone* atoms or ions: In a subshell (n, ℓ) — which has a room for $4\ell + 2$ electrons — but has only k electrons,

  ○ For $k < 2\ell + 1$, all k electrons are un-paired.

  ○ For $k > 2\ell + 1$, $2(k - 2\ell - 1)$ electrons form pairs while the remaining $4\ell + 2 - k$ electrons are un-paired.

• Each covalent chemical bond involves two electrons, one from each atom.

  ∗ A single bond involves 2 electons, which are paired with each other.

  ∗ A double bond involves 4 electrons, 2 of which are paired with ech other while 2 are un-paired.

  ∗ A triple bond involves 6 electrons, which form 3 pairs.

To see how these rules work, let's consider a few examples.

EXAMPLE: CARBON.

A standalone carbon atom has electron structure $[He]2s^22p^2$, with 2 un-paired 2p electrons and hence $\mathbf{m} \neq 0$. This makes atomic carbon vapor paramagnetic. But in a solid carbon — either diamond or graphite — each carbon atom has 4 covalent chemical bonds with 4 neighboring atoms, so the whole carbon crystal acts as a single giant molecule. In both diammond and graphite, all carbon-carbon bonds are single, so all the electrons making these bonds are paired-up. As to the electron not involved in the chemical bonds, 4 bonds per atom use up all 4 outer electrons of the carbon atom — both 2s and 2p — so the remaining

helium-like inner electrons are all paired up. Consequently, all electrons in solid carbon are paired up, which leaves it with no built-in magnetic moments. Thus, both forms of solid carbon — the diamond and the graphite — are diamagnetic.

EXAMPLE: WATER.

A standalone hydrogen atom has a single 1s electrons — which is obviously un-paired. A standalone oxygen atom has 8 electrons in the $[He]2s^2 2p^4$ structure; the inner helium-line electrons and the two electrons in the 2s subshell are apired, while the 4 electrons in the 2p subshell follow the rule for $k = 4 > 2\ell + 1 = 3$: $2(n - 2\ell - 1) = 2$ electrons are paired, while the remaining 2 electons are un-paired. In the water molecule H_2O, each hydrogen atom is connected to the oxygen atom by a single bond, which pairs up the hydrogen's electron with one of the previously unpaired oxygen's 2p electrons. Altogether, all the electrons in the water molecule are paired up, which leaves without a bult-in magnetic moment. Consequently, the water — vapor or liquid — is diamagnetic. The ice — which is a molecular solid with strong hydrogen bonds between the molecules — is also diamagnetic.

EXAMPLE: OXYGEN O_2.

An oxygen atom has $[He]2s^2 2p^4$; the two 2s and two out four 2p electrons are paired-up while the remaining two 2p electrons are un-paired. When two oxygen atoms form the O_2 molecule, the two un-paired electrons from each atom form a double chemical bond $O = O$. In such a double bond, two electrons (one from each atom) pair up, but the other two electrons remain un-paired. Consequently, the oxygen molecule O_2 has net magnetic moment $\mathbf{m} \neq 0$, which makes oxygen — gas or liquid — paramagnetic.

Nitrogen N_2: A nitrogen atom has electronic structure $[He]2s^2 2p^3$; the two 2s electrons are paired-up while the three 2p electrons are un-paired. When two nitrogen atoms form the N_2 molecule, the three un-paired electrons from each atom form a triple chemical bond, $N \equiv N$. The six electrons involved in this triple bond form three spin-up/spin-down pairs, so there are no un-paired electrons left, and the net magnetic moment of the N_2 molecule is zero. Consequently, the nitrogen — gas or liquid — is diamagnetic.

EXAMPLE: SULFUR.

A sulfur atom has oxygen-like electron structure $[Ne]3s^2 3p^4$, where both 3s and two of the 3p electrons are paired-up while the remaining two 3p electrons are un-paired. But the

molecular structure of sulfur is quite different from the oxygen: Solid sulfur is a molecular crystal made from the cyclic S_8 molecules, where each sulfur atom has two neighbors to which it is connected by single bonds. Each single bond involves two paired-up electrons (one from each atom), and for each atom, two bonds take care of both of is un-paired electrons. Consequently, the whole molecule has no un-paired electrons, so its magnetic moment is zero. This makes the solid sulfur diamagnetic.

The liquid sulfur is a mixture of several molecular types, but they are all cyclic like the S_8 or else form long polymer chain. In all such molecules, each atom has two single bonds to its neighbors, which pair-up all the electrons. Consequently, the liquid sulfur is diamagnetic just like the solid sulfur.

Finally, the sulfur vapor is a mixture of several molecular types, mostly cyclic just like the S_8 and therefore diamagnetic. The only paramagnetic sulfur molecule is the oxygen-like S_2.

Metals

In metallic solids, the outer electrons are not bound to individual atoms but blow though the whole piece of metal as a kind of gas; that's why the matals are so good at conducting electricity. The remaining ion cores usually have closed electron shells only, with all the electrons paired up, so they are diamagnetic. On the other hand, the gas of conducting electrons is weekly paramagentic, as explained in Dr. Winter's notes. However, since the electron gas obeys quantum Fermi–Dirac statistics rather than classical Boltzmann statistics, with the Fermi energy level much larger than the thermal energy kT, the paramagentism of the electron gas is much weaker that the paramagnetism of an atomic or molecular gas of comparable density. In fact, the paramagnetic susceptibility of the electron gas has comparable magnitude to the diamagnetic susceptibility of the ion cores, with the numerical balance between the two suceptibilities determining whether the metal as a whole is diamagnetic or paramagnetic.

- The alkaline metals (lithium, sodium, potassium *etc.*) and the alkaline-earth metals (magnesium, calcium, *etc.*) have largeish neutral atoms, but once stripped from their outer electrons, the remaining ion cores have rather small radii. Consequently, the

ion-core diamagnetism in these metals is rather weak, so on the whole the alkaline and alkaline-earch metals are paramagnetic.

— For the same reason, aluminum is paramagnetic.

• In contrast, the post-transition metals — like copper, zinc, silver, gold, or lead — have larger ion cores, with correspondingly stronger diamagnetic effects. Consequently, most post-transition metals are diamagnetic, although there are a few exception to this rule.

• Finally, the transition metals — whose atoms have open d-subshells — are mostly paramagentic. However, iron, cobalt, nickel, and some rare-earth metals are ferromagnetic, while chromium is antiferromagnetic.