Magnetic Effects in Solids #1: Diamagnetism

Magnetic effects in solids go back in history far before electric effects, back to the ancient civilizations. The reason for this is simple: ferromagnetism - the magnetic analogue of ferroelectricity – is naturally occurring (particularly in a iron ore called magnetite) and is *very strong*. Whereas two ferroelectric samples placed side-by-side will have a very weak interactive force, two ferromagnetic samples can interact so strongly as to "fly" together or apart, depending on their orientation. One of our goals in covering ferromagnetic effects is to explain this fascinating phenomena – a phenomena that was the basis for the first recorded electromagnetic device in history – the magnetic compass ! We will see that ferromagnetism is so strong because of a "hidden" nonclassical force – the quantum-mechanical interaction between particle *spins*. Unfortunately for ferroelectrics, no such interaction occurs, so that they are stuck with the relatively weak classical interaction between electric dipoles.

Another important distinction between magnetic and electric effects is the nature of the fundamental particles. In electric effects, there exists monopoles (i.e., negative electrons and positive protons) and dipoles (positive-negative pair). This creates the important distinction between conductors (dominated by monopoles) and insulators (dominated by dipoles) in response to externally applied electric fields. In magnetic effects, there are only dipoles.[1] But unlike electric effects, the dipoles originate from two fundamentally-different sources: (1) electrons in orbital motion, and (2) particle spin. While both are similar forms of *angular momentum*, they have radically different interactive strengths and, therefore, lead to different macroscopic effects. Specifically, electronic orbital motion leads to true diamagnetism, unpaired spins usually lead to paramagnetism, and under special conditions (to be defined later) create ferromagnetism.

As in insulating electric materials, the fundamental quantity in magnetic quantities is the atomic magnetic dipole, m. The definition of m and the other important quantities in magnetic solids follow by analogy with electric quantities:

$\vec{p} = q \cdot \vec{d}$ (charge, separation) $\qquad \vec{m} = i \cdot \vec{A}$ (current, area)

$\vec{E} \rightarrow \vec{B}$ magnetic induction

$\vec{P}_e \rightarrow \vec{M}$ magnetization

where $\vec{M} = n \cdot \vec{m}$, $\vec{m} = i \cdot \vec{A}$

$n \rightarrow$ number per unit volume

$\vec{A} \rightarrow$ area vector (points along perpendicular direction to current loop according to right-hand rule)

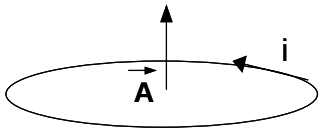


Fig. 1. Classical magnetic dipole with area A and current i.

[1] The search for magnetic monopoles has proceeded, off-and-on, for over a century. One of the more recent endeavors was conducted by Prof. L. Alvarez of of the Physics Dept. at U.C. Berkeley while the author was an undergraduate there in the early 1970s. Unfortunately, all such endeavors have failed.

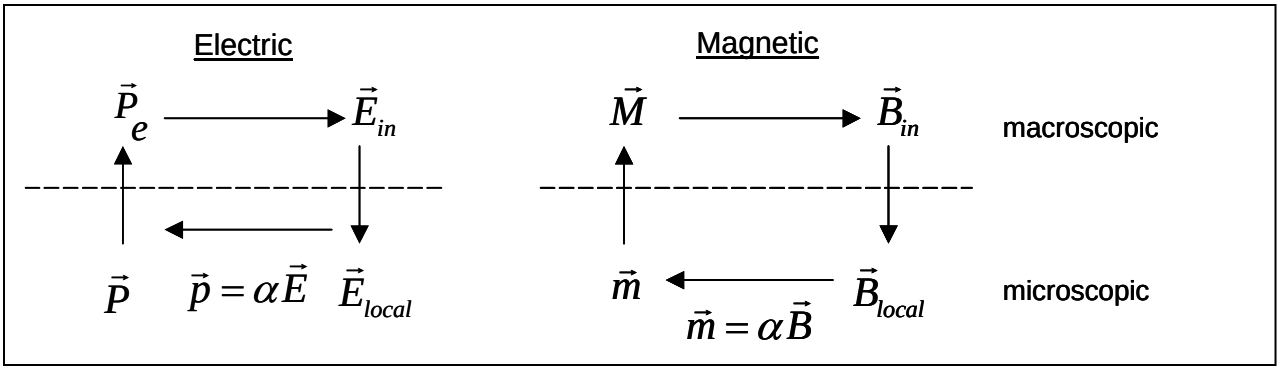
$\chi_e \rightarrow \chi_m$ magnetic susceptibility: $\chi_m \equiv \frac{d\vec{M}}{d\vec{H}_{in}} = \mu_0 \frac{d\vec{M}}{d\vec{B}_{in}}$ or $\vec{M} = \frac{\chi_m \vec{B}_{in}}{\mu_0}$ in most materials, the exception being ferromagnets.

$\chi_m > 0$: with permanent magnetic dipoles $\Rightarrow$ paramagnetic

$\chi_m >> 1$: with ordered permanent dipoles $\Rightarrow$ ferromagnetic

$\chi_m < 0$: diamagnetic

Recall that in electrostatic phenomenology, there was no true diaelectric response ("dielectric" meant simply that the solid opposed the flow of electric current). But in magnetic phenomena, there is a true "dia"response, meaning that the internal magnetization is opposite in direction to the internal magnetic field. Hence, there is a distinct possibility of negative magnetic susceptibility.



And as in electrostatics we have a built-in feedback loop (see diagrams above) between the microscopic and the macroscopic levels. In other words, there is a "local" magnetic induction that the atomic magnetic dipoles sense, and that can be different than the macroscopic induction B_{in} inside the solid.

(1) Sample Geometrical Effects

As in the "depolarization" effect of electrostatics, there is a screening of the internal magnetic induction owing to dipoles (current loops) that build up on the surface of the sample. These surface current always tend to reduce the internal induction to a degree that

depends on the shape of the sample. If we write $\vec{B}_1$ as the "response" induction created by the surface currents, then the mascroscopic induction inside the solid is given by

$$\vec{B}_{in} = \vec{B}_0 + \vec{B}_1 = \vec{B}_0 - N\mu_0\vec{M}$$

$N = \frac{1}{3}$ for sphere; $N = 1$ for slab

where N is the depolarization factor.

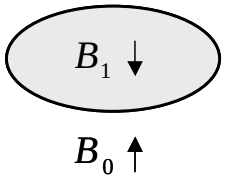


Fig. 2. Relative orientation of response induction B_1 and external induction B_0 for a simple (ellipsoidal) geometric shape.

(2) Microscopic Effects

Magnetostatic analysis shows that

$$\vec{B}_{local} = \vec{B}_{in} + \mu_0\frac{\vec{M}}{3}$$

Note: μ_0 is in numerator

This is the magnetic analog of the *Lorentz condition* for dielectric and, again, only approximate.

In general:

$$\vec{B}_{local} = \vec{B}_{in} + b\mu_0\vec{M}$$

$$\frac{1}{3} \lesssim b \lesssim 1$$

The microscopic connection to the macroscopic is, again, just the sum over atomic dipoles:

$$\vec{M} = n\vec{m} = n\alpha_m\vec{B}_{local} = n\alpha_m\left(\vec{B}_{in} + b\mu_0\vec{M}\right)$$

(analogous to $\vec{P} = n\vec{p} = n\alpha_e\vec{E}_{local}$)

where α_m is the magnetic polarizability. So we can write

$$\vec{M} = \left(1 - n\alpha_m b\mu_0\right) = n\alpha_m\vec{B}_{in}$$

$$\vec{M} = \frac{n\alpha_m\vec{B}_{in}}{1 - n\alpha_m b\mu_0} \quad \text{and} \quad \chi_m \equiv \frac{n\alpha_m\mu_0}{1 - n\alpha_m b\mu_0}$$

As in the calculation of the electric polarizability (for atomic, ionic, and ferroelectric responses), the calculation of α_m is a great exercise in microscopic physics. We will do it separately for the diamagnetic, paramagnetic, and ferromagnetic responses.

Classical model of atomic diamagnetism.

The much greater mobility of electrons compared to protons creates a generic magnetic response analogous to the atomic polarizability derived for electrostatics. We start by assuming that the electrons execute circular orbits around a fixed nucleus. To maintain the orbits, there must be a centripetal (inward radial) force

$$F = \frac{m_e \mathrm{v}^2}{R} = \frac{m_e}{R}\left(2\pi R \cdot f_{tot}\right)^2 = m_e \omega_0{}^2 R$$

where f_{rot} is the rotational frequency. For such an orbit, without there is a built-in magnetic moment along the z axis of

$$\vec{m}_z = i \cdot A \cdot \hat{z} = e\left(\frac{\omega_0}{2\pi}\right)\pi R^2 \hat{z}\,.$$

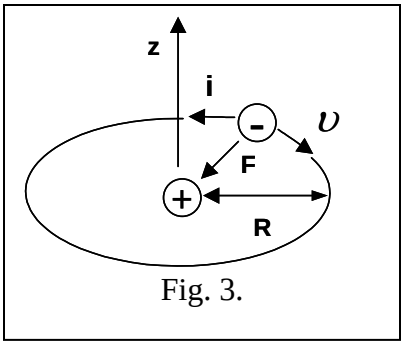


Fig. 3.

This assumes that the orbit is occurring in the equatorial plane as shown in Fig. 3, moving with negative helicity with respect to the velocity vector and the z axis.[2]

But as in the case of electrostatics, an analysis of real atoms must start with a three-dimensional *distribution* of charge, not just an orbit. The simplest model assumes a spherical charge distribution that can be built up from circular orbits by a taking a vector sum of a very large number of such orbits in random orientation. This can be expressed mathematically by pointing each area vector along the radial vector $\vec{A} = A \cdot \hat{r}$, so that $\vec{m} = i \cdot A \cdot \hat{r}$ (recall that in spherical coordinates $\hat{r}$ by itself can be pointing in any direction until θ and ϕ are specified). We get the total magnetic moment by summing over θ in spherical coordinates at an arbitrary value of ϕ, ϕ_0 , with equal weighting at all angles.

$$\vec{m}_{tot} = \int_0^{2\pi} iA\hat{r}\,d\theta\,d\varphi = \int_0^{2\pi} iA(\hat{x}\sin\theta\cos\varphi_0 + \hat{y}\sin\theta\sin\varphi_0 + \hat{z}\cos\theta)d\theta = 0\ .$$[3]

[2] "Helicity" pertains to the direction of rotation of a physical quantity with respect to a chosen axis. Right-hand-circular (RHC) means that when the thumb of the right hand points along the chosen axis, the fingers wrap along the rotation of the chosen variable. So while Fig. 3 above is RHC with respect to the z axis and electrical current, it is left-hand circular (LHC) with respect to the z axis and electron velocity.

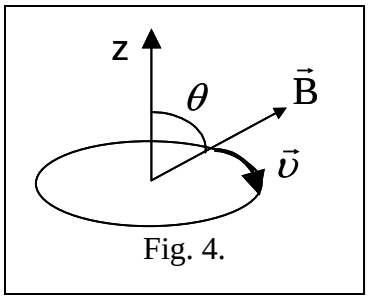


Fig. 4.

Important points: to achieve a spherical distribution starting with one orbit, we integrate over θ from 0 to 2π; we do not need to integrate over ϕ because this is taken care of by the rotating current in the orbit.

From the zero result, there is no built-in magnetic dipole from a rotating spherical charge distribution. This is intuitively obvious.

With an external magnetic field applied, the situation changes. There is now a *Lorentz force* on the electron that is always given by

$$\vec{F} = -e\vec{\upsilon} \times \vec{B}$$

Without loss of generality, we can start with a current loop that lies in the equitorial plane of a spherical coordinate system such that $\vec{A}$ is along the z axis, as shown in Fig. 4. The applied B must be along some direction $\vec{B} = B_0\hat{r}$ (θ,ϕ) such that it can be always be decomposed into a z component B_Z and an equitorial component B_ρ. Clearly, the equitorial component will generate no net Lorentz force around an orbit since at any point on the circle, the Lorentz force is exactly cancelled (in amplitude and direction) by the Lorentz force on the diametrically-opposed side of the circle. But the B_Z component will generate an orbit-constant force

$$\left\langle \vec{F} \right\rangle = evB_Z\hat{\rho} = e(2\pi R\frac{\omega}{2\pi})B_Z\hat{\rho} = e\cdot R\cdot\omega\cdot B(\cos\theta)\hat{\rho}$$

where < > again denotes angular averaging, and B = $|\vec{B}|$ and $\hat{\rho}$ is the radial vector lying in the equitorial plane and unspecified in direction (same as radial vector in cylindrical coordinates). Note that this force is *centrifugal* (i.e., directed outward from the center of rotation) if 0 < θ < π/2 or 3π/2 < θ < 2π, but is *centripetal* otherwise.

[3] Using the useful identity from vector spherical coordinates, $\hat{r} = \hat{x}\sin\theta\cos\varphi + \hat{y}\sin\theta\sin\varphi + \hat{z}\cos\theta$

To proceed further, we make the educated assumption that the Lorentz force does not change the orbit radius.[4] And since the mass must stay fixed, then the Lorentz force can be counterbalanced by a change of the *always centrifugal* force of orbital motion only if there is a change in orbital frequency. We denote this by the change in orbital frequency from ω_0 to $\omega_0 + \Delta\omega$, for which the equitorial-plane force counter-balance condition becomes:

$$m_e(\omega_0 + \Delta\omega)^2 R = m_e\omega_0{}^2 R - eR\omega_0 B\cos\theta$$

If $\Delta\omega << \omega_0$, we can drop terms of order $(\Delta\omega)^2$ and obtain

$$-e\omega_0 B\cos\theta \approx 2m_e\Delta\omega\cdot\omega_0$$

or

$$\Delta\omega \approx -\frac{eB\cos\theta}{2m_e}$$

where $\frac{eB}{2m_e}$ is called the Larmor frequency – a pervasive quantity in magnetic calculations and magnetic-based systems, and derived before the development of quantum theory. For example, it is a common quantity in (nuclear) magnetic resonance imaging (MRI).

Of great interest is the new magnetic moment, if any, in the presence of B. To calculate this we must, as with zero B, form a spherically-symmetric charge distribution by rotating the orbit in Fig. 4. But common sense dictates that this is equivalent to keeping the orbit fixed and rotating B over all possible orientations via the random expression $\vec{B} = B_0\hat{r}$. This is a convenient trick because we already know that the Lorentz force only depends on B_Z as $B_0\cos\theta$ where, again, θ is the angle between $\vec{B}$ and $\vec{A}$. So the total magnetic dipole moment is,

$$\vec{m}_{tot} = \int_0^{\pi} (1/2)e\cdot\omega\cdot R^2\hat{r}\sin\theta d\theta$$

[4] An assumption justified by the shell model of electronic orbitals via the Pauli exclusion principle.

This is slightly different than the case for B = 0 because the orbit is staying fixed and the magnetic induction is being rotated down at an arbitrary value of $\phi = \phi_0$. Hence, we need to multiply by $\sin\theta$, the Jacobian in spherical coordinates. This leads to

$$\vec{m}_{tot} = \int_0^{\pi} (1/2)e(\omega_0 + \Delta\omega)\cdot R^2(\hat{x}\sin\theta\cos\varphi_0 + \hat{y}\sin\theta\sin\varphi_0 + \hat{z}\cos\theta)\sin\theta d\theta$$

$$= 0 + \int_0^{\pi} (1/2)e(-eB_0/2m_e)\cos\theta\cdot R^2(\hat{x}\sin\theta\cos\varphi_0 + \hat{y}\sin\theta\sin\varphi_0 + \hat{z}\cos\theta)\sin\theta d\theta$$

from integral tables we have $\int_0^{\pi} \sin\theta\cos^2\theta\cdot d\theta = \frac{-\cos^3\theta}{3}\Big|_0^{\pi} = \frac{2}{3}$ and $\int_0^{\pi} \sin^2\theta\cos\theta\cdot d\theta = 0$

So we get $$\langle\vec{m}\rangle = -\frac{e^2B_0}{4m_e}\frac{2}{3}R^2\hat{z} = -\frac{e^2B_0}{6m_e}R^2\hat{z}$$

The fact that this is nonzero and *negative* means that the response of the spherical current orbit is truly "dia"magnetic.

Note that the direction of the magnetic moment is exactly along the z axis. This is because of the trick we invoked of fixing the orbit and rotating $\vec{B}$. By deduction, if we had kept the magnetic induction fixed and rotated the orbit to all possible orientations, then the magnetic moment would have ended up pointing along $\vec{B}$. This an important bit of deduction for all magnetic-field effects with atoms. Since there is an arbitrariness in the orientation of the electron orbits in any isolated atom (related to the point-like nature of the nucleus), then the external magnetic induction removes this arbitrariness and defines a preferred direction in space. By convention, the direction of $\vec{B}$ is usually set along the $\hat{z}$ axis in spherical coordinates. This allows us to determine the electronic magnetic polarizability as

$$\alpha_m \equiv \frac{\langle \vec{m} \rangle}{\vec{B}} = \frac{-e^2 R^2}{6m_e}$$

an expression that makes it clear that the MKSA units for α_m are [Cb^2-m^2/KG]. It should also be compared to the classical expression we previously derived for the atomic electric polarizability, $\alpha_e = 4\pi\varepsilon_0 R^3$. As in the electrostatic case size matters, although not as much for diamagnetism as for the electric case. The most important difference is the sign. Our analysis predicts that all atoms contribute a diamagnetic effect (i.e., χ_m negative) in contrast to the paraelectric effect (i.e., χ_e positive) they display from electrostatics.

Refinements to Diamagnetic Model:

(1) It is easy to deduce that we should get one unit of this polarizability for each electron orbit in an atom, of radius R_i. So we can generalize to get the total atomic polarizabilty by,

$$\alpha_{m,tot} \equiv \sum_{i=1}^{N} \frac{\langle \vec{m}_i \rangle}{\vec{B}} = \sum_{i=1}^{N} \frac{-e^2 R_i^2}{4m_e}$$

Knowing the polarizability, we can find go back to the macroscopic level and find the magnetic susceptibility,

$$\chi_m = \frac{n\alpha_m \mu_0}{1 - n\alpha_m b\mu_0} = \frac{-n\mu_0 e^2 \sum_{i=1}^{N} R_i^2 \Big/ 6m_e}{1 + nb\mu_0 e^2 \sum_{i=1}^{N} R_i^2 \Big/ 6m_e}$$

where n is the density of atoms in the solid.

Example: Silicon, 14 electrons per atom, $n = 8/a^3 = 8/(5.43\times10^{-10} m)^3 = 5\times10^{28}/m^3$, $\mu_0 = 4\pi\times10^{-7}(MKSA)$. From the section on atomic polarizability, we have for silicon an average radius of the electron cloud of $\langle\rho\rangle \sim 1.5$ Å $\Rightarrow \alpha_{m,tot} =$

$\sum_{i=1}^{14} e^2 \rho_i^2 / 6m \approx 14 \cdot e^2 < \rho >^2 / 6m = 1.5\text{x}10^{-27}$. And $n \cdot \alpha_{m,tot} \cdot \mu_0 = 9.3\text{x}10^{-5}$. This is so much less than unity that the Lorentz-condition term in the denominator of χ_m above can be ignored. Hence $\chi_m \approx - n \cdot \alpha_{m,tot} \cdot \mu_0 = -9.3\text{x}10^{-5}$. This is typical of atomic susceptibilities in solids… not large enough to be important in normal electronics, but large enough to be measurable.

Quantum Mechanical Derivation: The Landau Formalism

We start with the fact that there is a diamagnetic term in the electronic *Hamiltonian*.

$$H_{magnetic} = \frac{je\hbar}{2m}\left(\vec{\nabla} \cdot \vec{A} + \vec{A} \cdot \vec{\nabla}\right) + \frac{e^2}{2m} A^2$$

where $\vec{B} \equiv \vec{\nabla} \times \vec{A}$

In a uniform field,

$$A_x = -(1/2)\text{ x B}$$
$$A_y = 1/2\text{ y B} \qquad \text{Landau gauge}$$
$$A_z = 0$$

$$\Rightarrow 2nd\ term = \frac{e^2 B^2}{4m} < \left|x^2 + y^2\right| >= \frac{e^2 B^2}{4m} < \left|r^2\right| >$$

But for a three-dim charge distribution, we should replace r by R, the mean radius for a uniformly filled spherical shell. The relationship between the two quantities is simply $R^2 = \frac{3}{2} r^2$.

Hence, $\left\langle \vec{m}_i \right\rangle = \frac{-e^2 B_0 \rho_i^2}{6m_e} \hat{z}$, and $\alpha_{m,i} = \frac{-e^2 \rho_i^2}{6m_e}$.

$$< \psi_2 \left| H' \right| \psi_1 >= \frac{e^2 B^2}{8m} < \left|x^2 + y^2\right| >= \frac{e^2 B^2}{6m} < \left|r^2\right| >$$

Since $U_{mag} = -B \cdot (MV)$

$$M \cdot V = \frac{dU}{dB} = \frac{-e^2 B}{6m} < \left|r^2\right| >$$

So quantum result is the same as classical ! It just brings a different interpretation of $<r^2>$.