

## Basic Concepts

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*The goal of theory is to make things as simple as possible, but no simpler.* attr. A. Einstein

At the start of a School on ‘Models in Magnetism’, it is necessary to fix some of the basic concepts. We are concerned with magnetism in solids, so we need to have a some idea of what is is, and how it arises.

*The beginnings.*

A basic relation, discovered by Oersted in 1821, is the connection between magnetism and electric currents. His discovery triggered the electromagnetic revolution which led to the electrification of the planet. It resolved the age old puzzle regarding the analogy between electrostatic and magnetic forces. Ampere then found that a magnet behaves like a current-carrying coil. The relation between a current loop of area  $A$  carrying a current  $I$  and the equivalent magnetic moment  $m$  is

$$\mathbf{m} = IA \quad (1)$$

This truth is nicely enshrined in our preferred system of units. Magnetic moment is measured in  $\text{A m}^2$ . More generally, the relation between magnetic moment and current density  $\mathbf{j}$  is  $\mathbf{m} = (1/2) \int \mathbf{r} \times \mathbf{j}(\mathbf{r}) d^3r$ .

*Magnetization*

The next step is to define *magnetization*  $\mathbf{M}$  in a volume  $\Delta V$  as  $\Delta m / \Delta V$ . We need to think carefully about the volume. If we choose it to be too small, we run into wild spatial and temporal fluctuations as we approach the atomic scale. If we choose it to be too big, we risk missing the spontaneous magnetization in domains. A good choice is the mesoscopic scale, or the continuum approximation of magnetostatics. Magnetization can be induced by a magnetic field in a paramagnet or diamagnet, or it can arise spontaneously in a magnetically ordered material like cobalt or magnetite. The relation between magnetization and current density is

$$\mathbf{j}_M = \nabla \times \mathbf{M} \quad (2)$$

*Magnetic fields*

Magnetic fields are created by electric currents. The field in free space created by a current element  $I d\ell$  is given by the Biot-Savart law;

$$\delta \mathbf{B} = -(\mu_0/4\pi) I(\mathbf{r} \times d\ell)/r^3 \quad (3)$$

Here we have chosen to use the  $\mathbf{B}$ -field, which is measured in Tesla. The constant  $\mu_0$  which appears in the equation is defined to be exactly  $4\pi \cdot 10^{-7} \text{ TmA}^{-1}$ . In free space, the  $\mathbf{B}$  and  $\mathbf{H}$  fields are practically interchangeable, with the relation

$$\mathbf{B} = \mu_0 \mathbf{H} \quad (4)$$

$\mathbf{H}$ , like  $\mathbf{M}$  is measured in  $\text{A m}^{-1}$ . In a material medium, the relation is

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}) \quad (5)$$

The *fundamental* magnetic field is  $\mathbf{B}$ . This is because there are no magnetic poles in Nature (or if they exist, we never managed to find them. String theorists are convinced they must be somewhere). Contrast this with electricity, where we have plenty of electric charges.

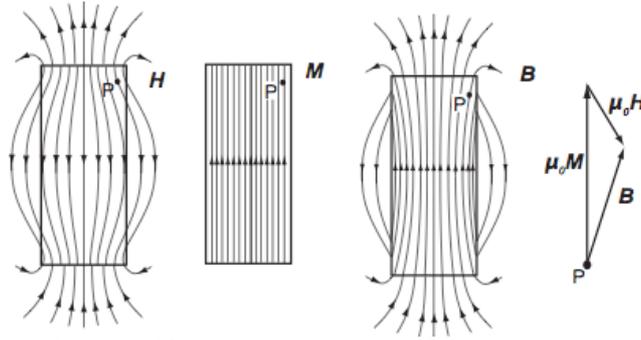


Fig 1.  $\mathbf{B}$ ,  $\mathbf{H}$  and  $\mathbf{M}$  for a uniformly-magnetized ferromagnetic bar. The vectors illustrate Eq.(5)

The absence of magnetic poles is enshrined in one of Maxwell's equations

$$\nabla \cdot \mathbf{B} = 0 \quad (6)$$

to be contrasted with the equation for the electric field in a medium  $\nabla \cdot \mathbf{D} = \rho$ , where  $\rho$  is the electric charge density.  $\mathbf{B}$  can be derived from a vector potential  $\mathbf{A}$ ,  $\mathbf{B} = \nabla \times \mathbf{A}$ .

So why do we need an  $\mathbf{H}$  field? The standard answer is that in Ampere's law, which relates  $\mathbf{B}$  to  $\mathbf{j}$  in a steady state,

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{j} \quad (7)$$

there are really two kinds of current. One is associated with the magnetization of the medium ( $\mathbf{j}_M$ ) where the currents are unmeasurable, because they are atomic in origin, while the other kind, the free currents ( $\mathbf{j}_f$ ) are the usual currents that flow around in conductors and can be measured with an ammeter. Hence,  $\nabla \times \mathbf{B} = \mu_0(\mathbf{j}_f + \mathbf{j}_M)$ . From (2), (5) and (7), we find

$$\nabla \times \mathbf{H} = \mu_0 \mathbf{j}_f \quad (8)$$

This is Ampere's law for the  $\mathbf{H}$ -field. The significance of  $\mathbf{H}$  is that matter responds to the  $\mathbf{H}$ -field acting in the material. Hysteresis loops are plotted as  $M$  versus  $H$ . In the continuum approximation, the internal  $\mathbf{H}$  field is the sum of an externally-applied field  $H'$  and the  $\mathbf{H}$ -field created by the magnetized material, as shown in Figure 1. The  $\mathbf{H}$ -field created by magnetized material is known as the *stray field* outside, and the *demagnetizing field* ( $H_d$ ) inside. Mathematically, we can represent the sources of the  $\mathbf{H}$ -field as fictitious 'magnetic charge'. The surface charge density is  $\sigma_m = \mathbf{M} \cdot \mathbf{e}_n$  and the volume charge density is  $\rho_m = \nabla \cdot \mathbf{M}$ . The field due to a fictitious magnetic charge  $q_m$  is  $\mathbf{H} = q_m \mathbf{e}_r / r^2$ . Positive and magnetic charges are the fabled 'North' and 'South' magnetic poles, which can be considered as the sources and sinks of the  $\mathbf{H}$ -field. The main use of magnetic charge is as a computational convenience, to calculate the  $\mathbf{H}$ -field. It can also be deduced from a magnetic scalar potential  $\phi_m$ ;  $\mathbf{H} = -\nabla \phi_m$ , but only when there is no contribution from electric currents.

### Response to a field

For paramagnetic and diamagnetic materials, the linear response of the magnetization to the field can be expressed in terms of the susceptibility  $\chi$ . Defined by the equation

$$\mathbf{M} = \chi \mathbf{H} \quad (9)$$

the susceptibility is a dimensionless quantity. There are several other definitions! In (9) the susceptibility is usually taken to be a scalar. For a crystal it is a second-rank tensor.

More generally, the response of a magnetically-ordered material to a magnetic field is nonlinear, irreversible and time-dependent. This is the *hysteresis loop*, which is the true icon of magnetism.

$$\mathbf{M} = \mathbf{M}(\mathbf{H}, t) \quad (10)$$

The *energy* of a moment in an external field is  $-\mathbf{m} \cdot \mathbf{B}$ , and the associated torque is  $\mathbf{m} \times \mathbf{B}$ . The energy density  $E \text{ J m}^{-3}$  of already-magnetized material in an external field  $\mathbf{H}'$  is

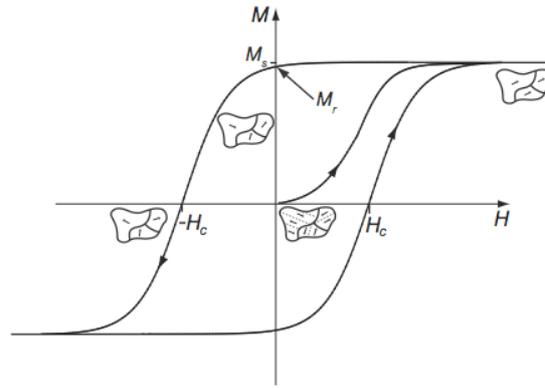


Fig 2. A hysteresis loop. Domain structures for a polycrystalline sample are indicated.

$$E = -\mu_0 \mathbf{M} \cdot \mathbf{H}' \quad (11)$$

Whenever the moment is induced by the field, as it is for a paramagnet, or whenever the field is created by the material itself, as it is for the demagnetizing field, a factor  $\frac{1}{2}$  must be included in the energy expression.

Energy in magnetic systems is a subtle and sometimes confusing issue. The point is that all magnetism basically is due to electric currents, and the magnetic force  $q\mathbf{v} \times \mathbf{B}$  on a charge  $q$  moving with velocity  $\mathbf{v}$  acts perpendicular to the velocity, and therefore does no work on the magnetic system. Overall, energy is conserved, but it may shift from one place to another. The energy density associated with a magnetic field is  $-\frac{1}{2}\mu_0 H^2$ .

*Magnetostatics* is the branch of magnetism associated with energy minimization in static conditions. The basic equations are (6) and (8), and the total energy to be minimized includes (11) and the energy density in the demagnetizing field  $-\frac{1}{2}\mu_0 \mathbf{M} \cdot \mathbf{H}_d$ , as well as terms representing exchange, anisotropy and magnetostriction.

### Origin of magnetism

The origins of magnetism were finally understood in the 1920s. In quantum mechanics, magnetic moments are associated with the *angular momentum of charged particles*, which is somehow equivalent to an electric current. The reality of the link between magnetization and angular momentum was demonstrated by the Einstein-de Haas experiment. The constant of proportionality is the gyromagnetic ratio  $\gamma$ . In solids, the charged particles we have to consider are the electrons. Their angular momentum has two distinct origins. One is the intrinsic spin angular momentum of  $\frac{1}{2} \hbar$ , the other is the orbital angular momentum, whose z-component is quantized in units of  $\hbar$ . The gyromagnetic ratio turns out to be almost exact twice as great in the first case ( $e/m$ ) as in the second ( $e/2m$ ). Hence the unit of magnetic moment for the electron is the Bohr magneton,  $\mu_B$ .

$$\mu_B = e\hbar/2m \quad (12)$$

The value of the Bohr magneton is  $9.27 \cdot 10^{-24} \text{ A m}^2$ .

The half-integral angular momentum of the electron was shown by Dirac to follow as a consequence of relativistic quantum mechanics. Theorists consider the electron as a point particle that possesses charge, mass and angular momentum. It helps to imagine a tiny spinning object, but it is only a prop for the imagination. Pauli formulated three spin

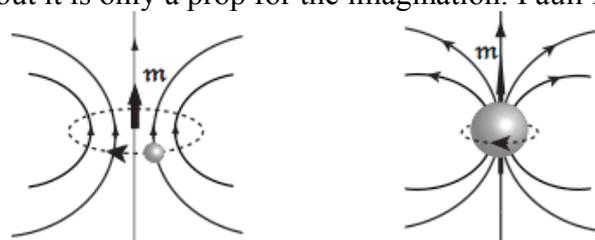


Fig 3. The orbital (left) and spin (right) angular momentum of an electron.

matrices which, when multiplied by  $\hbar/2$ , represent the three cartesian component of the spin angular momentum.

$$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad (13)$$

The orbital angular momentum is visualized in terms of the orbital motion in Bohr's planetary model of the atom. Its components are represented by three  $(2\ell+1) \times (2\ell+1)$  matrices.  $\ell$  is the orbital quantum number; the spin quantum number  $s = 1/2$

### Magnetism of the hydrogenic atom

A single electron in the central potential of an atomic nucleus  $Ze/4\pi\epsilon_0 r$  is the starting point for understanding chemistry and magnetism. Schrodinger's equation  $\mathcal{H}\psi_l = \epsilon_l\psi_l$ , where  $\mathcal{H}$  is the Hamiltonian,  $\epsilon_l$  is an eigenvalue and  $\psi_l$  is an eigenfunction known as the *electron orbital* is conveniently written in spherical polar coordinates  $r, \theta, \phi$ :

$$\left[ -\frac{\hbar^2}{2m_e} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{1}{\hbar^2 r^2} \hat{l}^2 \right) - \frac{Ze^2}{4\pi\epsilon_0 r} \right] \psi_l = \epsilon_l \psi_l \quad (14)$$

Here the angular variation is contained in the orbital angular momentum operator  $\hat{l}^2$ .

$$\hat{l}^2 = -\hbar^2 \left( \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \quad (15)$$

Solutions of the equation are of the form  $\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$ . The angular part is a spherical harmonic  $Y_l^m$ , where  $\ell$  and  $m$  are the orbital and magnetic quantum numbers.

$$Y_l^m = c_{l,m} P_l^m(\theta) \exp(im\phi) \quad (16)$$

Here  $c_{l,m}$  is a normalization constant,  $P_l^m$  is the associated Legendre polynomial which depends only on  $\theta$ , and the exponential part depends only on the azimuthal coordinate  $\phi$  and the magnetic quantum number  $m$ . The orbitals with  $\ell = 0, 1, 2$  and  $3$ , which are known as *s, p, d, f* orbitals for historical reasons, are respectively 2, 6, 10 and 14 fold ( $2\ell+1$  fold) degenerate. The orbitals with a given value of  $n$  (the principal quantum number, which determines the radial part of the wavefunction  $R(r)$ ) and  $\ell$  form a shell, e.g.  $2p, 3d \dots$

The single-electron orbitals can each hold two electrons, one with spin up,  $m_s = +1/2$  ( $\uparrow$ ), the other with spin down ( $\downarrow$ ),  $m_s = -1/2$ . The sign convention accounts for the fact that magnetic moment and angular momentum are oppositely directed because of the negative charge of the electron

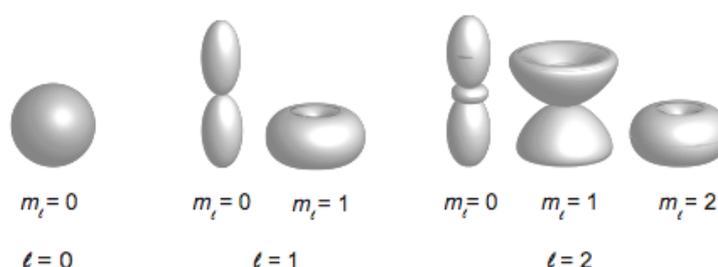


Fig 4. Single-electron orbitals for the free atom

### Magnetism of multi-electron atoms

When there are many electrons on the atom, Coulomb interactions among them complicate the solution of the Schrodinger equation. Nevertheless, the one-electron orbitals provide a basis for determining the electronic structure of the atom, and hence the periodic table. The blocks of atoms there are 2, 6, 10 or 14 atoms wide.

From a magnetic viewpoint, the key question is how do the spin and orbital moments of the electrons add together? Magnetism is associated with partly-filled shells, because when the orbitals are all filled with two electrons each with opposite spin there is no spin moment, and when the  $\pm m_l$  orbitals are occupied, there is no net orbital moment. The  $3d$  and  $4f$  shells are the ones of most interest. Hund developed his empirical rules to decide the orbital occupancy, and hence the magnetic moment of the *ground state* of a free atom with an unfilled shell.

- First maximise the spin by adding the spin angular momenta of the electrons, consistent with Pauli's principle (the spins of two electrons occupying the same orbital must be opposite) to yield the total spin angular momentum  $S$
- Next, couple orbital angular momenta of the individual electrons to give the maximum resultant orbital angular momentum  $L$ , consistent with the first rule.
- Finally couple  $L$  and  $S$  together to yield the total angular momentum  $J$ .  $J = L+S$  if the shell is more than half-full and  $J = L-S$  otherwise.

There are higher-energy optically-excited states, but for magnetism we need only consider the ground state. The last rule is a result of the weak spin-orbit coupling that can be understood by considering the nucleus from the electron's standpoint. The orbiting charged nucleus is like a current loop that creates a magnetic field at the electron, coupling its spin moment to its orbital moment. Represented by the Hamiltonian  $\mathcal{H}_{so} = \lambda \mathbf{L} \cdot \mathbf{S}$ , this interaction is much weaker than the Coulomb correlations among the electrons, represented by the Hamiltonian  $\mathcal{H}_0$  including the electrostatic interactions that give rise to the first two rules.

There are four orbital ground states possible for  $3d$  ions, with A, D and F terms, corresponding to  $L = 0$  ( $d^0$ ),  $L = 2$  ( $d^1, d^4, d^6, d^9$ ) and  $L = 3$  ( $d^2, d^3, d^7, d^8$ )

### The crystal field

Now we take a step closer to reality, by packing the atoms or ions into a solids. Unpaired electrons in an outer  $s$  shell tend to delocalise and form an unpolarized metallic band with equal  $\uparrow$  and  $\downarrow$  populations. Unpaired electrons in an outer  $p$  shell tend to form covalent bonds, pairing up with electrons from neighbouring atoms. The unpaired electrons in outer  $d$  and  $f$  shells, which have charge density  $\rho_0(\mathbf{r})$  find themselves subjected to electrostatic interactions with the electrons belonging to neighbouring atoms or ions. It is convenient to separate the two sets of charges, and consider the potential  $\varphi_{cf}(\mathbf{r}) = \int \{\rho(\mathbf{r}')/4\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|\} d^3r'$ , created by the neighbouring charges  $\rho(\mathbf{r}')$  around the central atom, which has the point symmetry of the site. The crystal field interaction is represented by the Hamiltonian

$$\mathcal{H}_{cf} = \int \rho_0(\mathbf{r}) \varphi_{cf}(\mathbf{r}) d^3r \quad (17)$$

Site symmetry and coordination depends on bond type. The two main classes of magnetic crystals are metals and ionic insulators. In the first case, the coordination is usually 8- or 12-fold. In the latter, the coordination of cations by anions is often 6-fold (octahedral), and sometimes 4-fold (tetrahedral) or 8-fold (cubic). Octahedral and tetrahedral sites are typical of oxides and fluorides. Both have cubic point symmetry, when undistorted. The crystal -

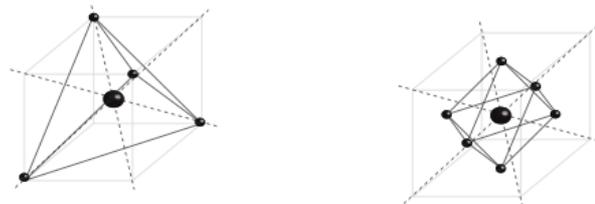


Fig 5. Tetrahedral and octahedral sites, showing how each has cubic symmetry

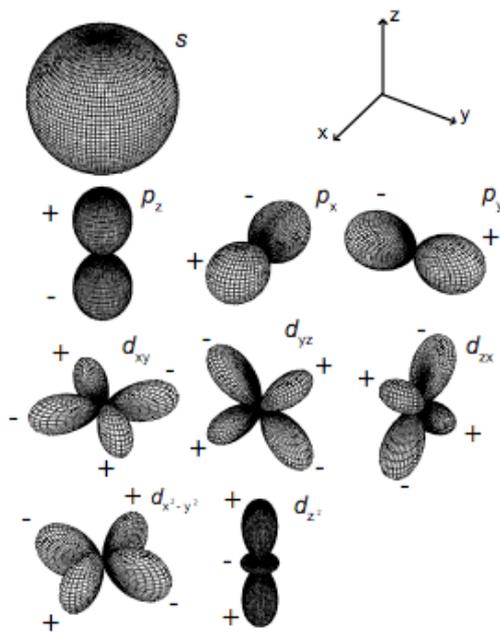
	$\mathcal{H}_0$	$\mathcal{H}_{so}$	$\mathcal{H}_{cf}$
$3d$	$1 - 5 \cdot 10^4$	$10^2 - 10^3$	$10^4 - 10^5$
$4f$	$1 - 6 \cdot 10^5$	$1 - 5 \cdot 10^3$	$\approx 3 \cdot 10^2$

Table: Interaction energies for  $3d$  and  $4f$  ions(K)

field interaction is much weaker for  $4f$  than for  $3d$  ions because the  $4f$  shell is screened by the outer  $5p$  electron shells. In  $3d$  ions, the  $3d$  shell is the outermost shell.

### Effects on $3d$ ions

Here the crystal field interaction is much stronger than the spin-orbit interaction. The one-electron eigenstates of the crystal field Hamiltonian are combinations of the free ion basis states, which reflect the symmetry of the lattice site. For  $p$  electrons, these the new orbitals are  $p_x, p_y$  and  $p_z$ , which remain degenerate in a cubic site. For  $d$  orbitals they are the  $d_{xy},$



$d_{yz}$  and  $d_{zx}$  group and the  $d_{x^2-y^2}$  and  $d_{3z^2-r^2}$  group. The former, known as  $t_{2g}$  orbitals are lower in energy on an octahedral site, whereas the latter  $e$  orbitals are lower in energy on a tetrahedral site. The crystal field splittings  $\Delta_{cf}$  are indicated in Fig 6. They are of order 1 eV. The splittings are partly ionic and partly covalent in nature, because of the different overlaps of the two groups with the ligand orbitals.

The main consequences are:

- the orbital angular momentum is quenched. The  $3d$  ions behave as if they were *spin-only ions*, which greatly simplifies matters
- Magnetocrystalline anisotropy arises as a consequence of perturbations due to  $\mathcal{H}_{so}$ .

Fig 6. One-electron orbitals in the crystal field

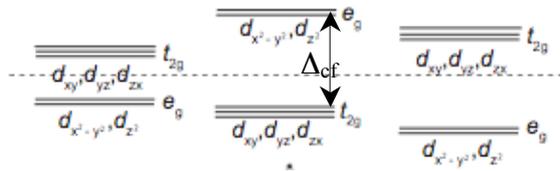


Fig. 7 Splitting of one-electron energy levels in tetrahedral, octahedral and cubic sites

The one-electron picture allows us to deal with D terms, the  $d^1$  ions, but also  $d^4$  and  $d^6$  (hole or electron in a half-filled shell) and  $d^9$  (hole in a filled shell). For the F terms, the strong interelectronic correlations must be considered, and the ground state and excited states are shown on the Tanabe-Sugano diagrams. The one-electron picture still has merit if a set of  $\uparrow$  levels like those in Fig 7 is separated from a similar set of  $\downarrow$  levels by the on-site exchange energy  $U_{ex}$ , which is the interaction responsible for Hund's first rule. The high-spin/low-spin crossover occurs when  $U_{ex}$  exceeds  $\Delta_{cf}$

### Effects on $4f$ ions.

Here  $J$  remains the good quantum number, and the effect of perturbation of the  $J$  states by the crystal field is introduction of magnetocrystalline anisotropy. For practical calculations, the method of operator equivalents  $\mathbf{O}_n^m$ , which are combinations of the angular momentum operators is recommended. The crystal field Hamiltonian is then

$$\mathcal{H}_{cf} = B_n^m \mathbf{O}_n^m \quad (18)$$

where the coefficients  $B_n^m$  depend on the crystal site and the rare earth ion occupying it.

### Further Reading

*A note on units.*

Magnetism is an experimental science, intimately connected with electricity. There are compelling reasons to adopt the same unit system, SI, that is used in other branches of science. These include:

- consistency with education in high school and university
- relation to quantities measured by laboratory instruments (volts, amps, seconds ..)
- ability to check the dimensions of any expression by inspection.

Yet, for historical reasons, much of the research literature is written using the obsolete cgs system, or a confusing mixture of SI and cgs units. In order to translate them into SI, a brief guide to the main conversions is given below.

	$M$	$M$	$\sigma$	$B$	$H$	$\chi$	$\mu$	$q_m$	$A$	$\phi_m$
	moment	Magnetization	Specific magnetization	B-field	H-field	Susceptibility	Permeability	charge	vector potential	Scalar potential
SI unit	$\text{Am}^2$	$\text{Am}^{-1}$	$\text{Am}^2\text{kg}^{-1}$	T	$\text{Am}^{-1}$	—	$\text{TmA}^{-1}$	Am	Tm	A
cgs unit	emu	emu/cc	emu/g	G	Oe	—	G/Oe	emu/cm	G cm	Oe cm
conversion*	$10^{-3}$	1000	1	$10^{-4}$	$1000/4\pi$	$4\pi$	$4\pi 10^{-7}$	0.1	$10^{-6}$	$100/4\pi$

- Multiply the cgs quantity by this factor, to obtain the SI quantity.

The cgs version of Eq 5 is  $B = H + 4\pi M$