

Chapter 2

Magnetic Properties

Abstract The magnetic properties of a material are the basis of their applications. Specifically, the contrast agents that will be developed in Chaps. 4 and 5 use their magnetic properties to play their role in magnetic resonance imaging. It is thus important to describe briefly the different magnetisms.

The magnetic properties of a material are characterized by its magnetic susceptibility χ , which describes the ability of the material or substance to be magnetized by an external magnetic field H .

$$M = \chi H$$

The magnetization, M , represents the net magnetic moment per unit volume that is aligned parallel to the external magnetic field. The magnetism of the material comes from either electrons (electronic magnetism) or atomic nuclei (nuclear magnetism). However, the magnetization created by one electron being 657 higher than that created by one proton, electronic magnetism masks the nuclear one. According to the behavior exhibited in the presence of a magnetic field, several classes of substances can be distinguished.

2.1 Diamagnetic Substances

The majority of atoms constituting tissues of the body are diamagnetic because they do not have unpaired electrons. The global electronic magnetic moment of each atom is zero. However, an external magnetic field B_0 may slightly alter the orbital paths of the electrons in motion and low magnetization can then be detected in a direction opposite to the external field direction B_0 . Diamagnetic agents are not used as contrast agents for their effects on T_1 and T_2 relaxation time. The consequence of diamagnetism is a very weak and negative susceptibility.

2.2 Paramagnetic Substances

Ions or molecules possessing unpaired electrons tend to move in the direction of the magnetic field and increase its effect, these compounds are called paramagnetic substances. The more unpaired electrons, the greater is the electron magnetic moment and the more important will be the paramagnetic properties. All transition metals (Cr^{2+} , Cr^{3+} , Mn^{2+} , Mn^{3+} , Fe^{2+} , Fe^{3+}) and lanthanides (Gd^{3+} , Dy^{3+}) have a significant number of unpaired electrons. The gadolinium ion, with seven free electrons, has a large magnetic moment. It was first chosen as the base of paramagnetic MRI contrast agents.

2.3 Ferromagnetic Substances

While paramagnetism is a property from the isolated ion, ferromagnetism is a property based on the cooperation of thousands of atoms in a paramagnetic crystal structure. Ferromagnetic compounds have regions or domains where there is an overall magnetization. Before being subjected to an external field, a ferromagnetic compound has no spontaneous magnetization: the different magnetic domains are oriented randomly. After application of an external field, the magnetic fields are oriented along the axis of the field and have a bulk magnetization describing a hysteresis curve (Fig. 2.1a). When the magnetic field B reaches a certain value, the saturation magnetization M_s is obtained and the magnetization stays constant. When B is stopped, the magnetization is maintained at M_s and then slowly decreases to the isothermal remanent magnetization. The coercive force (or coercivity) is the intensity of the applied magnetic field required to reduce the magnetization to zero after reaching the M_s .

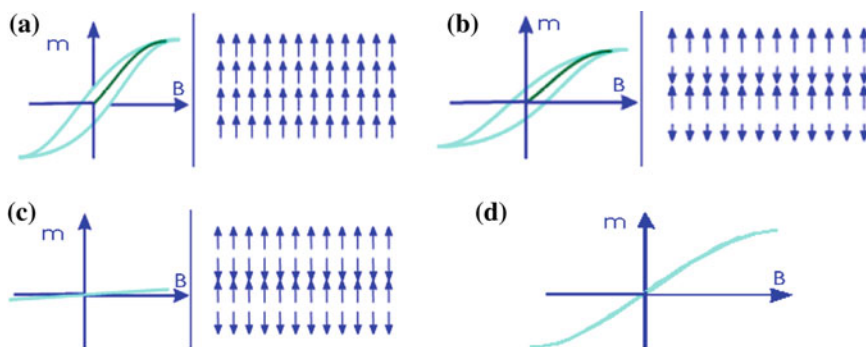


Fig. 2.1 Different kinds of magnetisms: magnetisation curves of **a** ferromagnetic **b** ferrimagnetic **c** antiferromagnetic **d** superparamagnetic material

2.4 Ferrimagnetic Substances

Ferrimagnetism is characterized by two sub-networks in which the spins are antiparallel. However, their magnetic moments are not equal and do not compensate completely (Fig. 2.1b).

2.5 Antiferromagnetic Substances

Antiferromagnetic materials are composed of ferromagnetic sub-networks whose magnetic moments are identical and of opposite directions (Fig. 2.1c). Therefore, in the absence of an external field, the resulting magnetization is zero. By heating above a characteristic temperature of the material (Neel temperature), the material becomes paramagnetic.

2.6 Superparamagnetic Substances

The concept of superparamagnetism is very close to that of ferromagnetism, the difference being the coherent strength of the magnetic domains. When the external magnetic field is stopped, different magnetic domains found a random orientation and their resultant is zero (Fig. 2.1d). The superparamagnetism appears when the crystal size becomes sufficiently small. The crystal becomes a single domain when the size is below a critical value. A single domain magnetic crystal has no hysteresis loop. A crystal is superparamagnetic when it demagnetizes completely when the field is removed. Suspensions of iron oxide nanoparticles smaller than 20 nm display superparamagnetic behavior at room temperature. The degree of alignment of magnetic moments depends of the temperature. The alignment decreases when the temperature increases and beyond a critical temperature, the magnetization becomes zero.

For magnetite and maghemite, this critical temperature is called Curie temperature T_c . For example, magnetite has a Curie temperature of 850 K [1]. At room temperature, magnetite particles smaller than 6 nm are superparamagnetic [2]. Their magnetic properties depend on their synthesis method and crystal morphology [3–6].

The bulk magnetite is a natural material in which the magnetic domains are divided in **Weiss domains** separated thanks to walls called **Bloch walls** [7]. Inside each domain, the magnetic moments possess uniform directions whereas the surrounding magnetic domains exhibit a different direction of magnetic moments (Fig. 2.2a). The disposition in magnetic domains optimizes the system energy [8].

If an external magnetic field (H) is applied, the Bloch walls move and induce an increase of the magnetic domains oriented in the same direction as the external magnetic field. Depending on the strength of the external magnetic field, the

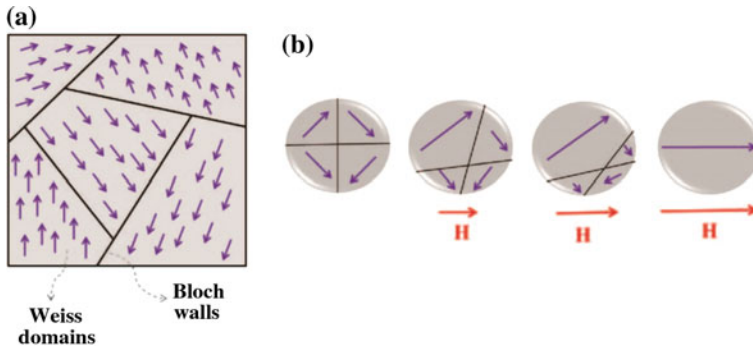


Fig. 2.2 **a** Organization of magnetic domains for ferromagnetic materials and **b** arrangement of Weiss domains as a function of applied magnetic field (H) with different intensities

predominant magnetic domains expanded much more compared to the other domains. A high magnetic field is required to completely remove the Bloch walls as shown in Fig. 2.2b. This phenomenon is at the origin of the remanent magnetization (M_r) and of the hysteresis observed [9, 10] during the measurement of magnetic moments as a function of applied magnetic field (Fig. 2.3).

Initially, the material is not magnetized (**a**) and the magnetic moment increases while an external magnetic field (H) is applied. The red curve (**b**) represents the first magnetization curve in which the Bloch walls move to promote the dominant direction of the magnetic domains present in ferromagnetic compounds as previously shown in Fig. 2.2b. The magnetic moment increases until reaching the

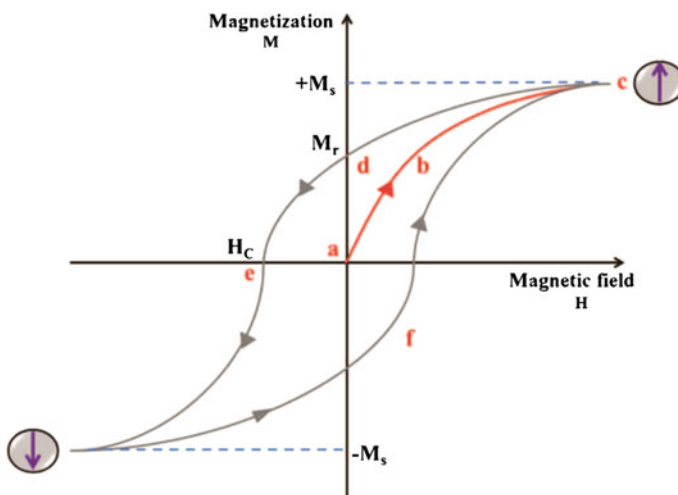


Fig. 2.3 Hysteresis curve of a ferromagnetic compound with the representation of the saturation magnetization (M_s), the coercive field (H_c) and the remanent magnetization (M_r)

saturation magnetization (M_s), corresponding to the state where all the magnetic moments are aligned with the external magnetic field (c). If the intensity of magnetic field is then reduced, the magnetic moment will decrease (d). At zero magnetic field, the magnetic moment is equal to a value corresponding to the remanent magnetization (M_r). This resulting magnetization is a fundamental characteristic of the ferromagnetic substances and it is due to the presence of domain structure [11]. To demagnetize the materials (e), it is necessary to apply an opposite magnetic field called coercive field (H_c). By a continuous increase of the magnetic field in opposite direction, the magnetic moment decreases to a minimum value ($-M_s$). At this point, an increase of H induces an enhancement of magnetization to the saturation magnetization; however, a larger value of H will be needed to reach a zero magnetization. The final curve describes the hysteresis cycle that is an important characteristic of the ferromagnetic compounds. It is important to determine the remanent magnetization and the coercive field. Both parameters depend on the nature and the size of the materials. On the contrary, the saturation magnetization does not depend on the material size and it is only influenced by chemical composition.

If the material size is small enough, the coercive field will become equal to zero and the remanent magnetization will disappear. Consequently, these materials react as a paramagnetic compound. However, the size of these magnetic substances must be small enough to form a single crystal domain in which these materials acquire uniform high magnetization with all the spins aligned in the same direction (Fig. 2.4). This phenomenon is called **superparamagnetism** and differs from paramagnetism. Indeed, the magnetic moments of these compounds are much larger than those of electrons responsible of paramagnetic behavior. To have superparamagnetic materials, the size must be less than a Weiss domain of the corresponding material bulk.

The magnetization curve of superparamagnetic materials is not defined by a hysteresis curve as observed for the ferromagnetic compounds. The curve is reversible with no remanence and no coercive field (Fig. 2.5).

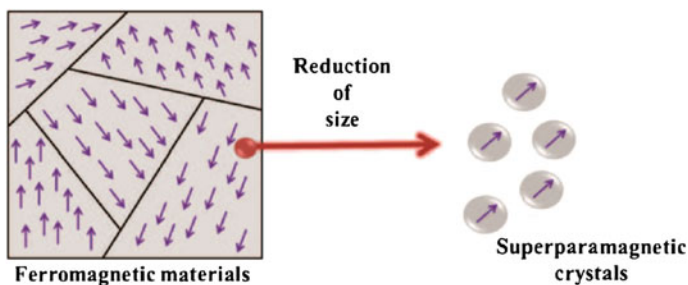


Fig. 2.4 Comparison between the multidomain structure of ferromagnetic materials and the singledomain of superparamagnetic crystals

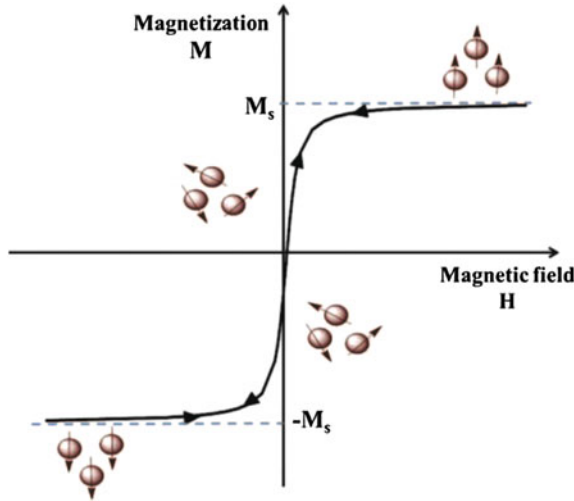


Fig. 2.5 Magnetization curve of superparamagnetic materials

The appearance of the magnetization curve of superparamagnetic materials can be defined as a Langevin function ($L(\alpha)$) as follows:

$$L(\alpha) = \cosh\left(1 - \frac{1}{\alpha}\right) \quad \text{with } \alpha = \frac{\mu H}{k_b T}$$

Where μ is the particle magnetic moment, H is the external magnetic field, k_b is the Boltzmann constant and T is the temperature.

The net magnetization (M) is described as the saturation magnetization (M_s) multiplied by Langevin function ($L(\alpha)$):

$$M = M_s L(\alpha)$$

The size and the saturation magnetization of superparamagnetic particles can be determined from the measurements of magnetization curve thanks to their fitting by Langevin function [12, 13]. For this, the assumptions are that all particles exhibit the same volume and that the saturation magnetization is considered as an average value. The superparamagnetism is a particular magnetic property widely exploited in the field of relaxometry and relaxing agents.

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MRI Contrast Agents

From Molecules to Particles

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