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MAGNETISM AND NANOMATERIALS : AN INTRODUCTION AND REVIEW

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ABSTRACT:
Brief introductions to basic magnetism and nanomaterials have been discussed. Nanomaterials have found various technological applications. The structural, magnetic and superparamagnetic properties are discussed. To prepare nanomaterials, different techniques are used depending upon the technological requirements.
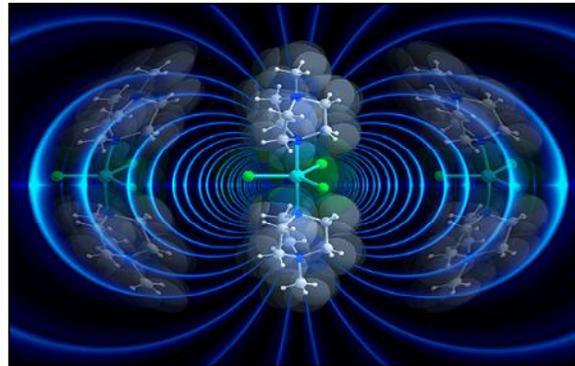
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1. INTRODUCTION AND REVIEW

. DIFFERENT TYPES OF MAGNETISM IN MATERIALS:

1.1.1 Diamagnetism & Paramagnetism:

The magnetic moment of a free atom has three principal sources: the intrinsic spin which the electrons possess; the orbital angular momentum of electrons about the nucleus; and the change in orbital angular momentum induced by an applied magnetic field. The first two effects show paramagnetic contributions to the magnetization, and the third one gives a diamagnetic contribution. The magnetization M is defined as the magnetic moment per unit volume. The magnetic susceptibility per unit volume is defined as

$$\chi = \frac{\mu_0 M}{B}$$

$$1.1$$

where μ_0 is the free space permeability, B is the macroscopic magnetic field intensity.
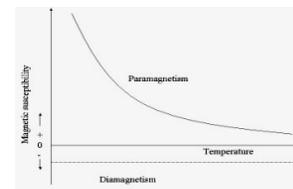

Fig.1.1 Characteristic magnetic susceptibilities of diamagnetic and paramagnetic substances. Substances with a negative magnetic susceptibility are called diamagnetic and that with a positive magnetic susceptibility are called paramagnetic and their variation with temperature are as shown in Fig. 1.1 [1].

1.1.2 Ferromagnetism:

A ferromagnet has a spontaneous magnetization even in absence of an applied field. All the magnetic moments lie along a single unique direction. This effect is generally due to exchange interactions between spin states. Above a critical temperature T_f, called the ferromagnetic Curie temperature, the spontaneous magnetization vanishes. The material is then paramagnetic with a susceptibility given approximately by the Curie-Weiss law

$$\chi = \frac{C}{T - T_f}$$

$$1.2$$

where C is Curie's constant, T is the absolute temperature and T_f is the Curie temperature. It is well known that in spite of the spontaneous magnetization property a ferromagnetic specimen may exhibit no magnetic moment when the applied field is zero. However, the application of a even a small field usually produces a magnetic moment which is many order of magnitude larger than that

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produced in a paramagnetic substance. The application of a relatively small field changes the domain arrangement, and hence leads to an appreciable net magnetization [2].

In general, a specimen consists of many domains, with a domain configuration that is a function of the applied field. Since the magnetic moment of the specimen is a vector sum of the magnetic moments of each domain, the magnetization, or the average magnetic moment per unit volume, may take on any value between zero and the saturation. The variation of M_H with the applied field depends, of course, on the material, but frequently the curves have the general appearance shown in the Fig. 1.2. It is assumed that the material is initially in a demagnetized state, indicated by the point O. When a field is applied, the magnetization M_H increases until the saturation value is reached. This behavior in indicated by the curve OABC. This part of the plot of M_H versus H is known as the magnetization curve. By performing the sequence of operations reducing the field to zero, increasing it in reverse direction, decreasing it to zero and then increasing it to the original value, the curve CDEFGC, known as a hysteresis curve or loop, is obtained.
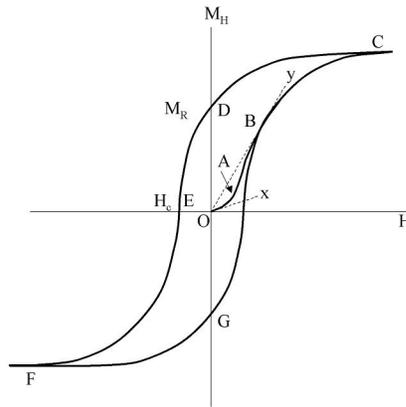

Fig. 1.2 Magnetization curve (OABC) and the hysteresis loop (CDEFGC) of a typical ferromagnetic material.

Certain numerical quantities are employed to describe the salient features of magnetization curve and the hysteresis loop. Since the susceptibility $\chi(=\frac{M_H}{H})$ of a ferromagnetic material depends both on the applied field and on the previous magnetic history, several susceptibilities may be defined. The initial susceptibility χ_0 is the slope of the tangent of the magnetization curve at the origin O (the slope ox). The maximum susceptibility χ_m normally occurs near the knee of the magnetization curve at the point B, the slope oy in Fig. 1.2. The differential susceptibility is the slope of the M_H versus H curve, dM_H/dH. On the hysteresis loop, the value of the magnetization for H=0 is called the residual magnetization or the remanence, M_r (point D in Fig. 1.2). The value of the filed for which M_H=0 is called the coercive filed H_c (point E in Fig. 1.2). The magnetization at the point C is the saturation value of magnetization.

As has been stated already, a ferromagnetic specimen in general consists of many domains. Under certain circumstances, the specimen may consist of a single domain. The specimen becomes a single domain when it is magnetized to saturation by application of a sufficiently large field or when the specimen is a very small particle. For a very small particle the exchange forces may dominate in such a way that in spite of the presence of the demagnetization energy and in the absence of any applied field, the particle is uniformly magnetized i.e. it is a single domain.

1.1.3 *Antiferromagnetism*:

An antiferromagnetic material has been defined as one in which an antiparallel arrangement of the strongly coupled atomic dipoles is favored. Néel [3] originally imagined an antiferromagnetic substance as compound of two sublattices, one of whose spins tend to be antiparallel to those of the other. He assumed

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the magnetic moment of the two sublattices to be equal, so that the net moment of the materials was zero. The term antiferromagnetism has been extended to include materials with more than two sublattices and those with triangular, spiral or canted spin arrangements; where the latter may have a small nonzero magnetic moment.

The Curie temperature T_f of ferromagnetism has its counterpart, the Néel temperature T_N, in antiferromagnetism; i.e., T_N is the temperature above which the ordered antiparallel arrangement of the dipoles disappears. The subject of antiferromagnetism may be said to be similar to that of ferromagnetism with certain important differences. Use of this similarity is made in the development of theories of antiferromagnetism. The predictions of the molecular field theory [4-7] of antiferromagnetism for a two sublattices system are in accord with the main features of the experimental results. The molecular field theory has its origin in an exchange interaction, as in ferromagnetism, there is the following difference; most antiferromagnetic materials are compound in which the cations are separated by much larger distances from those in ferromagnetic materials. Thus it is concluded that the exchange interaction must occur indirectly via nonmagnetic anions such as O^{2-}.

1.1.4 *Ferrimagnetism*:

A ferrimagnetic material may be defined as one, which below a certain temperature possesses a spontaneous magnetization that arises from a nonparallel arrangement of the strongly coupled atomic dipoles. The example originally considered [8] was that of a substance composed of two sublattices with the magnetic moments of one sublattice tending to be antiparallel to those of the other. When the sublattice magnetizations are not equal there will be a net magnetic moment. Just as for antiferromagnetism, the concept of ferrimagnetism has been broadened to include materials with more than two sublattices and with other spin configurations, such as triangular or spiral arrangements.

For a two-sublattice system, there are several schemes that can lead to ferrimagnetism. As for the antiferromagnetism, the two sublattices are denoted by A and B. Suppose that all the magnetic ions, N ions per unit volume, have identical moments, regardless of whether they are situated on A or B sites. If a fraction λ and $\mu (=1-\lambda)$ occupy A and B sites, respectively, the material will possess a net moment if $\lambda \neq \mu$ as shown in the Fig. 1.3 a.
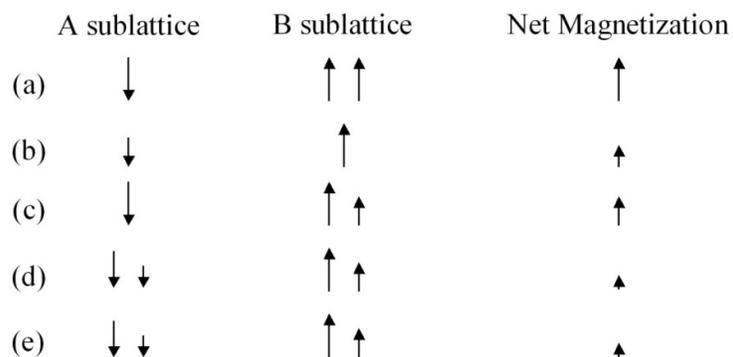

Fig. 1.3 Various possible ferrimagnetic arrangements for two sublattices. The magnitudes of the vectors may represent either the magnetic moments of the individual ions or the moment per chemical formula unit for each type of ion.

Even when $\lambda = \mu$ there will be ferrimagnetism if the magnetic moments of the ions on the A and B sites are unequal (Fig. 1.3 b). The inequality may develop (a) from elements in different ionic states, e.g., Fe^{2+}

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and Fe^{3+}, (b) from different elements in the same or different ionic states, e.g., Fe^{3+} and Co^{2+} or (c) from different crystalline fields acting at the two sites. Frequently there is a combination of two different numbers of ions with dissimilar moments on the sublattices (Fig. 1.3 c). Here there are two types of ion, with all the ions in one type on B sites and those of the other type equally divided between the A and B sites. Other examples of a more general nature in which there are different types of ions in both sites as are shown in the Figs. 1.3 d & 1.3 e.

1.2 *Nanomaterials:*

Nanostructured materials may be defined as those materials whose structure elements mainly composed of crystallites having dimensions in the range of 1 nm to 100 nm. As many properties of solids depend on the atomic nearest neighbor configuration, e.g., inter atomic potential or the exchange energy. This new type of solid-state structure has been suggested to exist in nanocrystalline materials [9]. They are usually polycrystals in which the size of the individual crystallite is of the order of several (1-10) nanometers. Nanosrtuctured materials or nanomaterials (NM) consist of the following two components; a crystalline component formed by all atoms located in the lattice of the crystallites (grains) and an interfacial component comprising all atoms, which are situated in the grain (or interface) boundaries between the crystallites. The atomic structure of such an interface is known to depend on the orientation relationship between adjacent crystals and boundary inclination [10]. A nanocrystalline material with a crystallite size of 5 nm contains typically about 10^{19} interfaces per cm^3. The interfacial component is the sum of 10^{19} interfacial structures. As the inter atomic spacing in all boundaries are different, the average of 10^{19} different boundaries results in no preferred inter atomic spacing except for one prevented by inter atomic penetration. Hence, the interfacial component is proposed to represent the solid-state structure with a new atomic arrangement. Depending on the chemical composition, these NM may be grouped into four families. In the first family, all crystallites and the interfacial regions have the same chemical composition. The second family consists of crystallites with different chemical compositions. The compositional variation between crystallites and the interfacial regions refers to the third family of the NM. The fourth family of NM is formed by nano-sized crystallites dispersed in a matrix of different chemical compositions. To prepare NM, different techniques such as standard co-precipitation method, sol-gel method, planetary ball mill technique, spray pyrolysis, sputtering method, inert gas condensation, and decomposition from precursor compounds etc. are used. All of these applications are based on crystal size effects [11].

1.2.1 *Superparamagnetism*:

It has been assumed that when the applied field is zero, the magnetization is stable, i.e. the direction of magnetization remains unchanged with time. To be specific, considering a single domain particle with uniaxial anisotropy, the total free energy is given by the following expression,

$$F_T = \frac{1}{2} CV \sin^2 \alpha \qquad\qquad 1.3$$

where V is the volume of the particle, α is the angle between the magnetization $\vec{M}$ and the easy direction and C depends on the anisotropy present in the particle but is a constant for a given particle. The dependence of the energy F_T on α is shown graphically in Fig. 1.4.

It is clear from Fig. 1.4 that the energy is minimum for $\alpha = 0$ or $\alpha = \pi$, and these directions are separated by an energy barrier of height $\frac{1}{2} CV$.
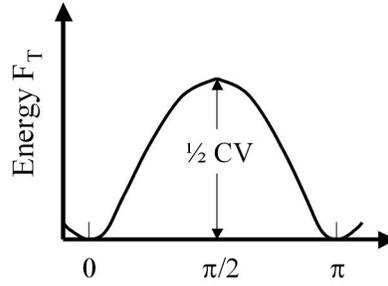
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Fig. 1.4 The energy of a single domain particle with uniaxial anisotropy as a function of the angle alpha between the magnetization and the easy direction. The height of the energy barrier is ½CV and H=0.

The magnetization will remain stable and lie along the direction defined by $\alpha = 0$ or by $\alpha = \pi$ unless some perturbing force exists that can take the magnetization over the energy barrier. Thermal agitation may provide such a perturbation. This process is most likely to occur if the volume V of the particle is small, so that the height of the energy barrier is lowered, or if the temperature T is high. If the process does occur, the time average of the remanence will be zero. This process is presumably the reason for the decrease in the coercive force for the small particle. Particles, whose magnetization changes spontaneously are analogous to paramagnetic atoms, except that their magnetic moments are much larger than that of paramagnetic atoms, are superparamagnetic. Such particles are said to exhibit superparamagnetism [12-13]. The superparamagnetism may be characterized by a relaxation time τ . Consider a powder with uniaxial particles having easy directions all lying along the z-axis and a field is applied along the positive z-axis so that the powder is magnetized to saturation M. After the field is removed, the magnetization will decay according to the equation

$$\mathrm{M_H} = \mathrm{M}e^{-t/\tau} \qquad\qquad 1.4$$

A new and interesting application of superparamagnetic particles is in materials for magnetic refrigeration well above the liquid helium temperature [14-16].

The superparamagnetic relaxation time is normally expressed by

$$\tau = \tau_0 \exp(\Delta E / kT) \qquad\qquad 1.5$$

where τ_0 is of the order of 10^{-10} -10^{-13} s [17-20] and depends only weakly on temperature. ΔE is the energy barrier between two easy directions of magnetization, k is the Boltzmann's constant, and T is the temperature. For uniaxial particles the magnetic anisotropy energy may be written as $E(\alpha) = KV \sin^2 \alpha$, where K is the magnetic anisotropy energy constant, V is the particle volume, and α is the angle between the magnetization vector and an easy direction of magnetization.

1.3 SUMMARY OF REVIEWS AND CONCLUSION:
The above review briefly discussed the basics of magnetism of naturally available magnetic materials and some basics of nanomaterials. Nanostructured materials have been widely studied because of their novel electric, magnetic and optical properties, which are different from their bulk counterparts.

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