Lecture 15. Magnetic properties of nanoparticles

The purpose of the lecture: to familiarize students with magnetic properties of nanoparticles.

Expected results: students getting information about magnetic properties of nanoparticles..

Recently, there has been a considerable increase in the application of magnetic nanoparticles, possibly due to their unusual size-dependent magnetism. The properties of magnetic nanoparticles having the same material and similar size show a strong dependence on their morphology, microstructure, or the nature of the matrix. As a consequence, there is a great variety of data, often contradictory, in the literature about magnetic nanoparticles. In this section, various key aspects of the magnetic nanoparticle properties have been discussed.

Brief Overview of Magnetism

The magnetic moment of electrons and intra-atomic interactions are the fundamental sources of magnetism. In general, magnetism can be classified as weak (diamagnetic or paramagnetic) or strong (ferromagnetic, antiferromagnetic, and ferromagnetic).

Diamagnetic particles do not have magnetic moments because all of their orbitals contain paired electrons with opposite spins. Paramagnetic particles contain unpaired electrons that, in the absence of a magnetic field, exhibit random coordination. In the presence of a magnetic field, the electrons spin parallel to the applied field, resulting in the development of transient magnetism that reverses when the force is removed.

Ferromagnetic particles consist of a number of small domains, each spontaneously magnetized to saturation. The boundaries between domains are called domain walls, in which the magnetization gradually changes from the direction on one side to that on the other. In the absence of an applied force, the electrons in different domains exhibit random orientation.

In a magnetic field, all electrons spin parallel to the force. Bulk ferromagnetic particles remain magnetized even after the force has been removed (hysteresis effects). In ferromagnetic particles, domains disappear over the Curie temperature (Tc); thus, the particles exhibit paramagnetic properties. A coercive force (Hc) must be applied to reverse the magnetization to zero. The atoms in antiferromagnetic materials exhibit oppositely spinning electrons that cancel out the magnetic moments. In an applied field, the magnetic moments do not cancel out because they have different magnitudes, which result in a net spontaneous magnetic moment.

The key factors that modulate the magnetic moment are chemical composition, type and degree of defectiveness of the particle lattice, size and shape, the morphology, particle interaction with the surrounding neighboring atoms, and the environment.

Comparison of Bulk Particles and Nanoparticles: The Concept of Critical Diameter

Size reduction alters the physicochemical, electronic, and magnetic properties of particles. However, for ferromagnetic particles, a critical diameter (Dc ranging from 15 to 35 nm, but in rare cases as high as 800 nm) exists, below which a particle undergoes a multiple-domain to single-domain transition, resulting in a large increase in coercivity. Thus, below a critical diameter, many novel properties appear in magnetic nanoparticles that are not found in bulk particles.

Effects of Size Reduction on Magnetic Properties

The size-dependent effects of magnetic nanoparticles are classified as (i) the surfacemediated effects that include surface-to-volume ratio, differential electronic properties of surface and core atoms, surface oxidation, etc.; and (ii) the direct size-related effects that include thermodynamic disruption, electron confinement, and single- or multiple-domain structures.

MAGNETIC MOMENT: THE SURFACE AND CORE ATOMS

The core atoms of a particle form bonds with their nearest atoms. The paired electrons exhibit opposite spins that may cancel the magnetic moment of each electron.

The surface electrons, however, exhibit uncompensated spin. The density of unpaired electrons increases as the particle size decreases. This results in a high level of anisotropy between the surface and the core atoms in smaller nanoparticles. Therefore, the surface and core atoms may respond differently to an applied magnetic field.

Surface atoms also modulate the properties of the inner layers. In Ni nanoparticles, the second layer may be magnetically dead, while in Fe and Co nanoparticles, the second layer acquires the properties of the surface atoms.

In Fe nanoparticles, the fourth layer acquires antiferromagnetic properties. This suggests that the magnetic nanoparticles, depending on the parent metal, exhibit structural anisotropy that is amplified as the size decreases. This may result in size-dependent changes in the nanoparticles' magnetic properties. Studies have shown that magnetization (per atom) and the magnetic anisotropy is much greater for nanoparticles than for bulk particles.

Morales et al. (1999) have shown that size reduction exponentially increases the surface area/volume ratio of nanoparticles, thus, increasing electronic anisotropy of the surface and ensuing magnetic changes.

DIRECT EFFECTS OF SIZE REDUCTION

In addition to altering the surface characteristics, size reduction also results in electron confinement and ferromagnetic to superparamagnetic transitions.

The quantum confinement effect: Quantum confinement is defined as a transition fromcontinuous to discrete energy levels as the particle size becomes smaller than the electrons' wavelength, size of the magnetic domain (for ferromagnetic or paramagnetic particles), or wavelength of magnetic oscillations (for superparamagnetic properties).

In general, a decrease in dimension results in a widening of the band gap, ferromagnetism to paramagnetism transition, and/or superparamagnetic to sub-superparamagnetic (electron freezing) transition in nanoparticles. Because of the confinement, many metals may acquire semiconductor properties.

• The spin states of electrons: Electrons, in addition to having negative charge, also exhibit magnetic moments with measurable north and south poles. The electronic magnetic moments possibly arise due to their angular moment around the nucleus and spin around its axis, although, in a quantum sense, electrons may not have an axis.

In general, the electrons can have two spins called up (ю) and down (_). The spins are given half integer values, either 1/2 (for up spin) or _1/2 (for down spin). When a magnetic field is applied, electrons spin either parallel to or antiparallel to the direction of the applied force. If the direction is parallel, the spin of the electron is termed spin-down or _1/2. If the direction is antiparallel, the spin of the electron is negative spin or spin-up or ю1/2. According to the quantum theory, atomic orbitals have an angular momentum (designated I). The s-orbital has I j 0, p-orbital has I j 1, and so on. In a lowstrength magnetic field, the electrons' energy states are separated into the magnetic quantum numbers that represents how much of the orbital momentum (ML) can be projected along the z axis: for ML j 1, the projection will be юh (h is Planck's constant); for ML j_1, the projection will be _h; for ML j 0, the projection j 0, etc.. At relatively high strength of the magnetic field, the ML splits into two states: ms ю 1/2 or ms _ 1/2.

Therefore, if ms j 1/2, the angular momentum along the z-axis (designated sz) will be юh/2; if ms is _1/2, the sz will be _h/2. The electronic magnetic moment can be defined as m j gmB=2, where g is 2.00232 and mB is the Bohr magneton.

In the absence of a magnetic field, spin-up and the spindown electrons are in equal proportion. At a lower magnetic field, spin-up electrons are greater than the spindown electrons that may oppose the magnetic field (diamagnetic properties). At a high magnetic field, spin-up electrons are less than the spin-down electrons, which increases the magnetic moment. High temperatures neutralize the magnetic field by suppressing the spin-down electrons.

• The Curie law: The law states that the magnetic susceptibilities (M) of most paramagnetic substances are inversely proportional to the absolute temperatures in K.

• Pauli's paramagnetism law: Unlike Curie's law, Pauli's paramagnetism, however, is applicable to metals with free conduction electrons. Pauli's law states that free electrons spin up and down according to the applied magnetic field, yet the Fermi energies remain the same. Some spinup electrons (antiparallel to the applied field) are converted into spin-down electrons (parallel to the applied force).