

ER210005E

Magnetic nanoparticles and superparamagnetic resonance (1)

"Size effects"

Product used : Electron Spin Resonance spectrometer (ESR)

Bulk crystals (> 100 nm) of metal and semiconductors have electrical conductivity that is derived from free electrons, which belong to the continuous energy levels called "band structure". When these crystals are downsized to the mesoscopic region (Fig.1 : 1 - 100 nm), the space of energy levels is no longer regarded as "continuous", but discrete. Consequently, it shows new physical properties that are different from the bulk, atoms and molecules. This is called quantum size effect^[1].

Triiron tetraoxide (Fe₃O₄), which is ferrimagnet as well as half metal (or semiconductor), is well known as "magnetite", and is a historically familiar compound. Fine particles of magnetite, as well as other metals, show characteristic physical properties based on the quantum effect. Magnetic particles of mesoscopic size have a single magnetic domain, and behave as "*superparamagnets*" no longer the ferrimagnets by the effects of Brownian motion and Neel relaxation. Different from ferromagnets/ferrimagnets, superparamagnets do not have hysteresis and its magnetic anisotropy is small. Nevertheless, it has large magnetic moments similar to a ferrimagnet. Magnetic nanoparticles like magnetite are applied to the fields of Hyperthermia^{[2][3]}, Magnetic Particle Imaging^[4] and as contrast agents^[5] of Magnetic Resonance Imaging.



Fig. 1 A diagram that expresses the size and energy structure of conductive matter.

Variation of FMR/SPR spectra that depend on particle size

Figure 2 shows ferromagnetic resonance (FMR) spectrum of Fe_3O_4 powder with a diameter of 50 – 100 nm and superparamagnetic resonance (SPR) spectra of Fe_3O_4 magnetic nanoparticles dispersion in toluene. Large size magnetic powder has electrical conductivity as well as magnetic anisotropy. Therefore, its spectrum is observed as a broad Dysonian shape. On the contrary, magnetic anisotropy of nanoparticles becomes smaller and smaller according to downsizing, and additionally a new narrow isotropic signal appears. These spectral patterns are completely different from the large size powder and paramagnetic iron ions. This is a unique electron state dependent on the size.



Fig. 2 ESR spectra of magnetite (Fe₃O₄) particles with different diameters. (a) FMR spectrum of Fe₃O₄ powder with diameter of 50 – 100 nm. (b) SPR spectra of Fe₃O₄ magnetic nanoparticles dispersion in toluene (0.625 mg/mL).

Reference: [1] R. Kubo, J. Phys. Soc. Jpn., 17, 975 (1962).

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3-1-2 Musashino Akishima Tokyo 196-8558 Japan Sales Division Tel. +81-3-6262-3560 Fax. +81-3-6262-3577 www.jeol.com ISO 9001 • ISO 14001 Certified

