Superparamagnetic transition in nanoparticles of iron oxides

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The magnetic materials display a rich variety of physical behaviours depending on the size of their particles. When the dimensions of the particles are gradually decreased, we observe a change in the character of their magnetic properties connected to a radical change of their domain structure – the originally **multi-domain** state changes to a **single-domain** one. This change has a deep topological reason – the reduction of the particle size increases the relative share of the surface atoms with respect to the core ones. In other words the surface energies become more important than the volume energies [1]. The energy of the Bloch walls dividing individual magnetic domains belongs to the surface energies while the magnetostatic self-energy of the particle is a volume energy. We may also look on the transition between the multi-domain and single-domain state of the particle as reaching the size when the particle cannot support any more the domain walls as their energy exceeds the energy of the stray fields around the magnetically saturated particle.

The transition occurs thus at a critical size of the particle given by the equilibrium between these two contributions to the total magnetic energy. Let us slightly quantify this approach: the domain wall energy σ_w is given by another equilibrium of two energies – the exchange and anisotropy ones. As a result it is proportional to the square root of the product of the exchange constant A and the (effective) anisotropy constant K

$$\sigma_w \propto (K A)^{1/2} \quad . \qquad (1)$$

If we assume a spherical particle with relatively high uniaxial (magnetocrystalline) anisotropy we may compare the energies of the single-domain state and of two symmetrical domains divided by a Bloch wall. For the **critical radius R_c** of the transition between these two states we then obtain [1]

$$R_c \propto \sigma_w / M_s^2 = (K A)^{1/2} \ / M_s^2 \ . \qquad (2)$$

Let us mention that the critical radius is proportional to $(K)^{1/2}$ which may strongly depend on temperature and thus make also the critical size temperature dependent. The anisotropy need not be of the magnetocrystalline origin – its source may be the shape anisotropy, stress anisotropy via magnetoelastic coupling etc. The estimates along similar lines made for various materials gave values of the critical radius of the order of tens to many hundreds of nm. All the above reasoning concerns isolated particles and the situation may be dramatically changed when the interaction among particles is taken into account, usually leading to higher critical sizes for the transition to single-domain state.

The above discussion was concerned with the upper limit for the size of single-domain particles – the existence of this state is, however, also limited from below. According to Néel [2] the relaxation time τ_N of the particle moment to its equilibrium position is given by

$$\tau_N = \tau_0 \ \exp(K_{eff} V / k_B T) \ , \qquad (3)$$

where K_{eff} is the (effective) anisotropy constant, V the particle volume, k_B is the Boltzmann constant, T is temperature, and τ_0 is a constant of the order of $10^{-9} - 10^{-11}$s.

If the volume V of the particle with uniaxial anisotropy becomes sufficiently small, the thermal energy k_BT prevails over the energy barrier $K_{eff}V$ and τ_N decreases below the observation time. This leads to spontaneous fluctuations of the direction of the magnetic moment between the two orientations along the (uniaxial) easy axis and the time average of the magnetic moment vanishes. In an applied magnetic field the behaviour of a system of such particles resembles a paramagnet and the state of the system is called **superparamagnetic**. Let us remark at this point that the appearance of superparamagnetism is closely connected with the relevant time τ_m ("time window") of our measurement, observation or application of external magnetic fields.

The two limiting possibilities $\tau_N >> \tau_m$ and $\tau_N << \tau_m$ thus lead either to magnetically ordered/stable state in the former case or superparamagnetism in the latter one. They are separated by the region where $\tau_N \sim \tau_m$. This condition may be fulfilled according to (3) by changing either the particle volume or temperature, assuming that the anisotropy constant does not essentially change in the considered temperature range.

For the given particle volume V and the relevant time τ_m we can then define the so called **blocking temperature T_B** which is from (3) given by

$$T_B = \ K_{eff} V / C k \ , \qquad (4)$$

where the constant $C = ln(\tau_m / \tau_0)$ is equal to 27.6, 16.1, and 6.9 for the relevant times of observation 100 s (DC measurement), 10^{-3} s (frequency of 1 kHz), and 10^{-7} s (e.g. Mössbauer spectroscopy) assuming $\tau_0 = 10^{-10}$ s. Relation (4) illustrates the sensitivity of the blocking temperature to the relevant time window – the blocking temperature derived from the DC magnetic measurements is about four times lower than that determined from the behaviour of the Mössbauer spectra, if K_{eff} remains constant. In real situations we deal with a system of particles displaying a distribution of sizes and consequently the blocking temperatures also possess a distribution. A meaningful estimate of this distribution from DC magnetic measurement may be done from the temperature dependences of the magnetization after cooling the system in zero (ZFC) or non-zero magnetic field (FC). Lu et al. [3] have shown that the distribution p of T_B should be proportional to the derivative by T of the difference between the M_{ZFC} and M_{FC} moments:

$$p\ (T_B) = d\ (M_{ZFC} - M_{FC}\ )\ /\ dT\ . \qquad (5)$$

For the relevant value of the blocking temperature of the system we may then use the temperature at which the function p (T_B) passes through its maximum. .

On the other end of the time scale stands the Moessbauer spectroscopy with the characteristic time of $\sim 10^{-7}$ s. For the rather frequent case of alloys and compounds of iron, we may exploit the Mössbauer spectroscopy of the ^{57}Fe isotope. From the spectra acquired at various temperatures we may estimate the relative number of Fe moments that are either in the blocked or superparamagnetic state and accept for the average blocking temperature that one where these two quantities are approximately equal. In our work [4] we applied this approach to the system of particles of iron oxides predominantly consisting of γ-Fe_2O_3 (maghemite). From the two independent estimates of the “average” blocking temperatures for the two rather different observation times (DC magnetic measurements and Mössbauer spectroscopy) we had the unique possibility to derive the ranges of both relevant quantities from relation (3): the energy barrier $K_{eff}\ V$ and the constant τ_0 . For τ_0 we obtained $5\text{x}10^{-8}$ s – $2\text{x}10^{-11}$ s in good agreement with the usual estimates of this quantity. .

With the average particle size of about 5 nm which gives for the volume $\sim 10^{-25}$m^3, we obtained for the absolute value of $K_{eff} \approx 2.4\text{x}10^4 - 3.6\text{x}10^5$ J/m^3. This value compares well with the magnitude of the first constant of magnetocrystalline anisotropy of bulk cubic maghemite equal to $-2.5\text{x}10^4$ J/m^3 [5]. We may thus conclude that in this case the relevant anisotropy constituting the energy barrier for spontaneous change of the direction of particle moment is of the magnetocrystalline origin.

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