Size-dependent magnetic properties of magnetoferritin

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Ferritin is the iron storage protein of living beings from bacteria to mammals [1]. In its natural form, each ferritin molecule stores about 4500 Fe atoms in a weakly magnetic nanoparticle of ferrihydrite. In 1991, it was shown that the cavity of the apo-ferritin, i.e. the empty form of the protein, can be used as a confined reaction vessel to synthesize nanoparticles of maghemite (magnetoferritin) [2]. Since then, other oxides, like Co_3O_4 and also metals like Cu, Pd, Ni, Cr, Co, CoPt, etc, have been prepared [3]. In this contribution, we report a detailed experimental study of the structure, morphology and magnetic properties of magnetoferritin. By controlling the amount of iron added to an aqueous solution of apo-ferritin, it is possible to control the particle's average diameter D from 2 nm up to more than 6 nm (Fig. 1). Chemical analysis, X-ray diffraction, and Mössbauer spectroscopy data are compatible with the formation of maghemite γ-Fe_2O_3. TEM images (see Fig. 2), suggest that the nanoparticles grow from the protein's wall towards the centre of the cavity, and only tend to become spherical when the molecule becomes nearly full. The magnetic susceptibility shows the typical superparamagnetic behaviour (Fig. 3) with a magnetic freezing below a blocking temperature T_b that increases with the average particle's size. From the combined analysis of the susceptibility curves and the magnetization isotherms, we have extracted the distribution of magnetic moments. The comparison of these data with the distribution of sizes obtained from TEM (inset of Fig. 1) reveals the existence of a large disorder in the inner magnetic structure of the particles. This disorder, which becomes larger with decreasing size, leads to a smaller magnetic moment than what would be expected for a perfect alignment of spins. A scaling analysis of the ac susceptibility similar to that described in [4] enables us to extract the magnetic anisotropy constant K. It is found to be much larger than the anisotropy ($\approx 4.7\times10^4$ erg/cm^3) of bulk maghemite and to increase with decreasing D. These results indicate that the magnetic properties of magnetoferritin are largely influenced by the surface. This influence is probably enhanced in the present case by the special mechanism of particle growth. Indeed, for low iron contents, the nanoparticles have a very large surface to volume ratio and probably a considerable degree of structural disorder as well. The enhanced anisotropy is probably due

to the existence of low-symmetry surface atomic sites. This interpretation is confirmed by the observation of a component in the Mössbauer spectra associated with a very large quadrupolar splitting $\Delta E_Q \approx 0.96$ mm/s, whose intensity increases with decreasing size.

References:

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Figures:

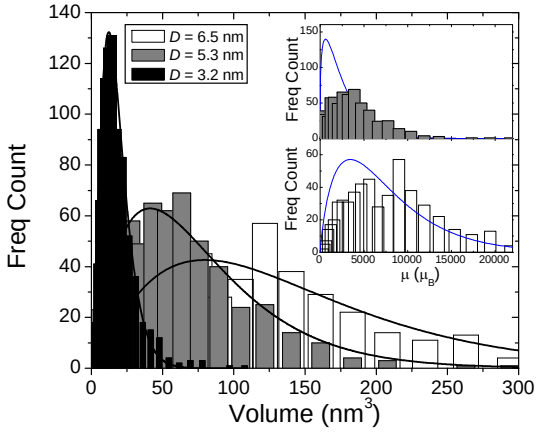

Figure 1: Distribution of particle sizes of three magnetoferritin samples. The inset compares two of these distributions with the corresponding distributions of magnetic moments obtained from the magnetic measurements (solid lines).

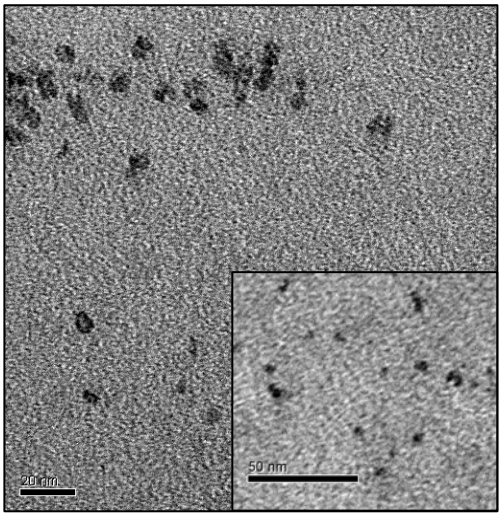

Figure 2: TEM image of a magnetoferritin sample with D = 6.5 nm. The inset shows the typical shape of the nanoparticles of the sample with D = 3.2 nm.

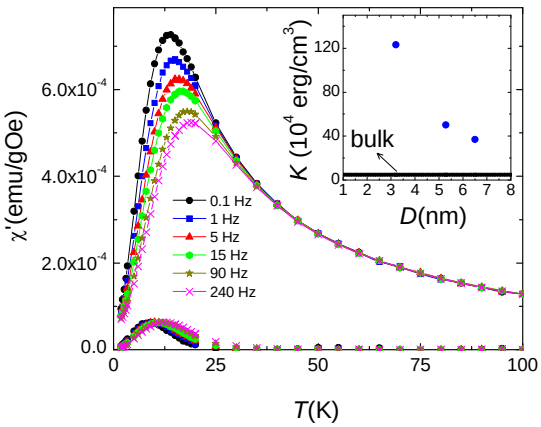

Figure 3: Ac susceptibility data of the D = 3.2 nm magnetoferritin nanoparticles. The inset shows the magnetic anisotropy constant of magnetoferritin as a function of the average particle's size