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CLUSTERING AND MAGNETIC COUPLING

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Abstract. - Effects of limited and extensive aggregation on magnetic coupling between \( \gamma \)-Fe\(_2\)O\(_3\) colloids have been investigated by Mössbauer spectroscopy. Various clusters in frozen-in sols have been studied. Magnetic anisotropy constant exhibits a minimum with the aggregation state.

We present an investigation of the effect of aggregation, limited and extensive, on the magnetic interparticle (MIP) interactions for \( \gamma \)-Fe\(_2\)O\(_3\) (cubic, \( a = 0.837 \) nm) colloids.

As many oxide particles, spinel iron oxide colloids undergo surface acid-base reactions in aqueous medium, with ionization of the surface hydroxyl groups. The resulting surface electric charge raises electrostatic interparticle repulsions which compete with Van der Waals and magnetic attractions. Surface phenomena on \( \gamma \)-Fe\(_2\)O\(_3\) colloids can be sufficiently enhanced to stabilize dispersions (sols) in acidic or basic medium, giving aqueous ferrofluids [1, 2]. The particle charge is positive or negative respectively. Electroneutrality is kept by counterions in solution. The charge magnitude controls the repulsions and, hence, the agglomeration state. The isolation of distinct particle clusters in sols has been reported previously [3].

Surface charge cancelling by acid-base reactions provokes extensive agglomeration. That can also be induced by screening the surface charge with electrolyte in excess. Then, the particle remains charged and the counterions adsorbed.

Investigated materials were [3, 4]: i) aqueous sols, cationic and anionic, ii) organosols in toluene prepared from aqueous sols by adsorbing oleous species on the particles, iii) aqueous cationic sols flocculated by an excess of electrolyte. Elementary particles were ca. 9 nm (\( \sigma \approx 2.5 \) nm) in size.

Limited aggregation was characterized by electron microscopy and magnetic features were investigated by Mössbauer spectroscopy. Dispersed samples were observed as sols frozen-in in a polymer, the colloid dispersion was the same in both samplings. Flocculated sols were dispersed in an acrylic resin.

Various configurations were isolated (Fig. 1): small chains (ca. 3-5 to 15 particles on average, \( \bar{n} \)), much longer chains (\( \bar{n} \approx 50 \) branched and coiled, and large compact aggregates. They led to three types of Mössbauer spectrum at 300 K (Figs. 2A, B, C).

Compact agglomerates (Fig. 1C) gave the spectrum C (Fig. 2), typical of \( \gamma \)-Fe\(_2\)O\(_3\) particles with blocked superparamagnetic relaxation. Hyperfine field (hf) distributions lead to values \( h(T) = \bar{H}(T)/H_0(T) \) (\( \bar{H} \) is the average field, \( H_0 \) the field in the bulk), showing a linear temperature dependence (Fig. 3). Using the relation \( h(T) = 1 - kT/2K V \) [5] (\( V \) is the particle volume, \( K \) the effective anisotropy constant), we obtain \( K = 3.5 \times 10^4 \) Jm\(^{-3}\).

Linear clusters (Figs. 1A, B) gave the spectrum A or B (Fig. 2) depending on the chain length, roughly \( \bar{n} < 10 \) or \( \bar{n} \geq 10 \) respectively, and apparently not on...
the particle surface characteristics (sign of the surface charge, adsorbed species). Type B persisted at $n \simeq 50$ as long as the configuration remained somewhat linear, increased compactness led to a spectrum of type C. By concentrating small chains, the pattern changed from A to B. As increasing chaining always proceeds with branching and coiling, the good parameter, in both cases, seems to be the average number of first near-neighbours ($n_1$) for a particle in the system. The turning point is at around $n_1 = 3$.

No paramagnetic component was resolved up to 300 K, for both A and B series, except that of a Fe-adsorbate complex (temperature independent contribution, less than 5 %). Above 150 K roughly, hf distributions (Figs. 4A, B) exhibit a plateau (5 T-30 T) which results from non lorentzian lineshapes due to relaxation times ($\tau$) in the range $10^{-9}$ s–$10^{-8}$ s, and not to reduced fields. In spite of relaxation effects, the plot $h(T)$ vs. $T$ (Fig. 3) remains a straight line up to 275 K roughly, leading to $K = 1.7 \times 10^4$ Jm$^{-3}$ and $1.4 \times 10^4$ Jm$^{-3}$ for type A and B respectively. Magnetic dipole interaction variation with increasing $n_1$ lowers the $\tau$ values, that seems related to $K$ decreasing, it may also result from a shift of the pre-exponential factor $\tau_0$ in the Arrhenius law [6].

Cationic sols flocculated by electrolyte effect exhibited distinct features, very sensitive to the counterion [4]. Strong affinity for iron (PO$_4$, Cit.) led to interactions similar to those in the concentrated sols (Figs. 2, 3). Decreasing affinity (SO$_4$, ClO$_4$, NO$_3$) progressively led to pattern D (Fig. 2). The hf distribution (Fig. 4D), distinct from types A and B, suggests that reduced fields do exist. This is typical of systems with strong interaction energy [4, 5]. The increase in $K$, from $1.4 \times 10^4$ Jm$^{-3}$ (B) to $2.0 \times 10^4$ Jm$^{-3}$ (D) is attributed to increasing interactions. The physicochemical characteristics are similar for the various samples, hence, the topology is probably the same. Decreasing complexation effect is therefore attributed to a coupling rising between spins at the surface of neighbouring particles.

Interactions remain weaker than in the compact agglomerates (Figs. 1C, 2C) formed near the point of zero charge. This is due to counterions adsorbed on the particles. Thermal degradation of adsorbed species led to pattern C in every case (except PO$_4$, remarkably stable), thus restoring the particle coupling at maximum. Obtained data agree very well with our previous interpretation of the room temperature spectra, based on a local field model to account for interactions, and using least-squares fits [4].

The set of $K$ values is consistent with data reported for various ferrofluids [7, 8] assuming independent particles. Clustering seems the rule in the sols. We find that the effective anisotropy constant varies by more than a factor 2, and goes through a minimum with increasing aggregation, so that similar data may correspond to quite distinct situations.

![Fig. 4. – Hyperfine field distributions for frozen-in sols (A, B), and a flocculate (D). Relaxation effects (A, B).](image-url)