

Diffraction Results in Oriented Ferrofluids

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Ferroparticles from ionic ferrofluids were studied by X-ray diffraction. Particles of $\gamma\text{-Fe}_2\text{O}_3$, MnFe_2O_4 and CoFe_2O_4 extracted from the ferrofluid were investigated in powder form. Effects of orientation and aggregation of particles of CoFe_2O_4 were investigated by preparing samples from the ferrofluid, in presence and absence of an external magnetic field, in different conditions: ferroparticles trapped in a fastly solidifying gel (in order to preserve the spatial structure of the magnetic colloid) and ferroparticles obtained by natural drying of the solution. Diffractograms of the spinel structure of the magnetic particles give information on the particle diameter (peak width) and orientation (relative peak intensities). No marked differences in line width were detected (precision 10%), what gives an upper limit of 10% to shape anisometry of the particles. But marked differences in relative intensities occur, showing orientation in the absence of gel and stable preservation of spatial structure in the "gelated" system.

I. Introduction

Ferrofluids are magnetic colloids consisting of magnetic particles (nanometer sized) in suspension in a fluid^[1]. In the traditional type, each spherical magnetic particles is coated with a non-magnetic molecular surfactant layer and stabilized in a hydrocarbon solvent. Such materials are well known for their industrial applications in several optical devices. The dynamic magnetic birefringence properties of these particles are of particular interest for the physicists. It is possible, for example, to measure visco-elastic constants in the medium in which they are suspended^[2].

In 1980 an easy and convenient chemical synthesis of ionic ferrofluids in aqueous solutions (without the need of a coating surfactant layer) was first carried out by Massart on colloidal magnetite^[3] (Fe_3O_4). The procedure was improved by Massart and Cabuil on maghemite^[4] ($\gamma\text{-Fe}_2\text{O}_3$) and further improved by Tourinho, Franck and Massan^[5] on cobalt and manganese ferrites (CoFe_2O_4 and MnFe_2O_4).

Magnetic particles with spherical symmetry have

a magnetization that may be represented by a permanent dipole moment situated at the centre of each particle. In the absence of a magnetic field the fluid is isotropic. In the presence of a constant field the medium becomes optically birefringent^[6-13]. The origin of such birefringence has been much discussed and remains controversial^[7,8]. The usual hypothesis are shape anisotropy of the particles and crystalline anisotropy^[9].

Since the usual structure of these magnetic particles is of spinel-type^[14], which has cubic symmetry, the crystalline anisotropy becomes noticeable if a tetragonal order of vacancies occurs. In the case of $\gamma\text{-Fe}_2\text{O}_3$ such tetragonal symmetry has been inferred from observation^[15] of additional superstructure reflections. However it has been shown^[16,17] that this effect depends on crystallite size and the superstructure reflections disappear for mean particle sizes $< 200 \text{ \AA}$. Therefore this effect is not to be expected in the small magnetic particles of ferrofluids. In a study of iron-oxide colloids^[18] no superstructure lines were ever de-

tected, although weak diffuse scattering appeared at their places.

It has been experimentally shown^[7] that the birefringence is size independent in the case of CoFe_2O_4 but size dependent in the case of $\gamma\text{-Fe}_2\text{O}_3$ (increases with particle diameter). This shows that, even if crystalline anisotropy may play a role in the case of $\gamma\text{-Fe}_2\text{O}_3$, it is not the dominant cause for the birefringence of CoFe_2O_4 (that presents a very high magnetocrystalline anisotropy^[19]).

Electron micrographs^[5,6] show that ferrofluid samples are never monodisperse, but rather polydisperse, and roughly spherical. These results do not support any strong individual shape anisotropy as being a probable origin for the birefringence.

In this paper we investigate by X-ray diffraction ferroparticles obtained from ionic ferrofluids, focusing on the line broadening, that gives information on particle size, and also the relative peak intensities, related to orientational effects. Besides analysing samples with different magnetic particles, we investigate samples oriented in magnetic fields, trying to detect some shape anisotropy of the particles.

In order to achieve our goal we compare results obtained with particles in powder form ($\gamma\text{-Fe}_2\text{O}_3$, MnFe_2O_4 and CoFe_2O_4 , extracted from ionic ferrofluids) and results obtained with CoFe_2O_4 particles in samples prepared in several different conditions.

In particular, we used trapping of the ferroparticles in a fastly solidifying gel as:

- an opportunity to inhibit external (mechanical) degrees of freedom of the particles, simultaneously preserving the initial spatial structure of the magnetic colloid^[20]
- an opportunity to do the same in the presence of an external magnetic field, but permitting only the orientation, not aggregation, of the particles.

On the other hand, results on ferroparticles ob-

tained by natural drying of the solution evidence both orientation and aggregation effects. Our results are still preliminary, not yet conclusive, but indicate directions for further exploration.

II. Experimental

Ionic water based ferrofluids with particles of $\gamma\text{-Fe}_2\text{O}_3$, MnFe_2O_4 and CoFe_2O_4 were prepared according to Massart's method^[3-5] as dilute frozen solutions ($\phi \leq 1\%$). In a first series of measurements the magnetic particles were extracted from the ferrofluid with acetone, forming a concentrated powder that was deposited in a metal support convenient for powder diffraction. In another series of measurements, CoFe_2O_4 ferrofluid films were deposited in glass plates (used in microscopes) and oriented in a magnetic field of 3 KGauss in different conditions:

1. - Samples trapped in a gelatin array (5% gelatin) of mesh size smaller than the magnetic particle size^[19] formed a film in the plate, in three different conditions: without magnetic field \vec{H} , with \vec{H} perpendicular to the plate and with \vec{H} parallel to the plate (samples 1, 2, 3 respectively).

If ferrofluid particles are frozen in the gel, they are mechanically trapped in the matrix, and the particle distribution remains as it was in the liquid ferrofluid^[20]. The gel takes about 20 minutes to get hard, and during this time the particles can orient in the film.

2. - A film of ferrofluid (without gel) in the plate was let to dry in the same three conditions (samples 1a, 2a, 3a). The result was a quite inhomogeneous distribution of material due to the high dilution, specially in the sample dried without magnetic field. For \vec{H} parallel to the plate the dried material showed some preferred orientation perpendicular to \vec{H} .

X-ray diffraction patterns of the particles in the

supports were obtained with an automatized powder diffractometer, using $\text{CuK}\alpha$ radiation (wavelength $\lambda = 1.54 \text{ \AA}$) in reflection geometry. The condition \vec{H} perpendicular to the plate corresponds to \vec{H} parallel to \vec{q} (scattering vector, $q = 2\sin\theta/\lambda$).

III. Results

Figs. 1 and 2 show partial diffractograms obtained for the three types of magnetic particles in powder form. The peaks corresponding to the interplanar spacings (220), (311) and (400) of the spinel structure are seen. A (100) peak of a Si standard crystal is also shown, just to evidence that the broadening is due essentially to the particle diameter D , according to:

$$D = 0.9\lambda/\Delta\cos\theta$$

where θ is the Bragg angle and A is the width at half-height (in radians).

The particle size associated with the broadening of the dominant (311) peak is shown in Table I. The differences between the particles are due to differences in the preparation of the ferrofluids. Results show the sensibility of the method, that can easily detect changes of 10% and more in particle size. The widths of the other several peaks lead to same particle sizes within 10%, what means that deviations from sphericity are not larger than 10%. The relative intensities of the peaks agree with the powder ASTM values, as seen in Table II. It is noted in Figs. 1 and 2 that the weak (222) reflection can be seen for MnFe_2O_4 and CoFe_2O_4 as a small bump. For $\gamma\text{-Fe}_2\text{O}_3$ a tetragonal assignment cannot be ruled out, due to the high intensity of the (440) peak that could also be due to some textural effect.

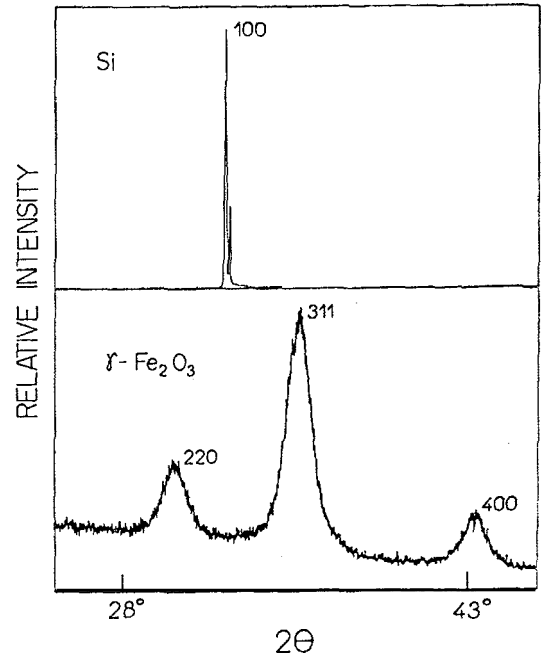


Figure 1: X-ray diffractograms for particles of $\gamma\text{-Fe}_2\text{O}_3$ in powder form. It is also shown the (100) peak of a Si single crystal (2θ scale shifted) to evidence the very small broadening due to experimental resolution.

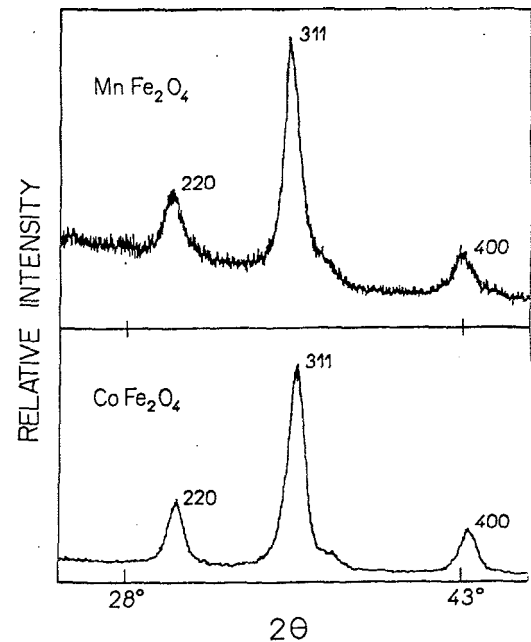


Figure 2: X-ray diffractograms for particles of CoFe_2O_4 and MnFe_2O_4 in powder form. The line broadenings are due essentially to the small particle size.

Another sample of CoFe_2O_4 ferrofluid has been more carefully investigated, allowing to be oriented in a magnetic field, with gel and without gel as described in the previous section.

Table I - Particle diameter estimated from the width of the (311) diffraction for the first serie of saniples, in powder form.

diameter Å	
CoFe ₂ O ₄	93
MnFe ₂ O ₄	111
γ-Fe ₂ O ₃	74

For the sample dried without gel in presence of \vec{H} parallel to the film (and therefore \vec{H} perpendicular to \vec{q}), two conditions have been measured: \vec{H} in the scattering plane and \vec{H} perpendicular to the scattering plane. In such a drying process particles may eventually aggregate, and such aggregation process could correlate with small particle shape anisometry.

The samples dried without gel showed a noticeable difference in relation to samples dried in gel: the intensity of the diffractions decreased with increasing q more strongly for samples without gel than for samples in gel. Results are shown in Table III.

Analysis of samples 1, 2, 3 (respectively no \vec{H} , \vec{H} perpendicular to film and \vec{H} parallel to film) indicate a small textural effect for particles trapped in gel, with enhancement of 5% of the (400) reflection in relation to powder ASTM results (see Table II). Changes in line width were less than 10%. No effect of the magnetic field could be detected, neither on peak width nor on peak intensities.

This may mean that the particle brownian rotation may have been inhibited by the gel, preventing orientation of the particles, or alternatively that orientation of the magnetic dipole moment is not directly correlated with crystallographic orientation.

Analysis of results from samples dried from the dilute ferrofluid without gel evidenced large textural effects in sample 1a (no \vec{H}), with a considerable de-

crease of the dominant (311) peak and therefore increase of the relative intensities of the other peaks. The dried material was quite inhomogeneous in this sample, and measurements in different parts of the sample resulted in different degrees of depletion of the (311) peak, and enhancement of the other peaks. Particularly the (440) peak was largely enhanced in some diffractograms, reaching intensities even higher than the (311) peak. Such textural effects must be connected with interactions of the still ionized magnetic particles with the glass plate during the drying process. There is thus indication that, even if deviations from sphericity are less than 10%, anisometry may be playing a role in the way the magnetic particles adhere to the glass plate; alternatively, the interaction may be via the magnetic moment, if it is coupled to the crystallographic orientation.

A marked difference occurs in the sample dried from the dilute ferrofluid without gel in presence of the magnetic field (samples 2a and 3a). In such case the opposite trend is verified, with strong decay in intensity of the peaks at higher scattering angles, and particularly decrease of the (440) peak in front of the dominant (311) peak (see Table III). The effect is very strong for \vec{H} perpendicular to the plate (\vec{H} parallel to \vec{q}) (sample 2a) and one of the directions for sample 3a, with \vec{H} parallel to the plate (\vec{H} perpendicular to \vec{q} but in the scattering plane), and intermediate for the condition \vec{H} perpendicular to the scattering plane (sample 3a rotated 90°).

The line width of the stronger (311) line remained the same within 5% (indicating particles of about 132Å).

Macroscopically, the dried sample with \vec{H} parallel to the plate showed two regions with material, and both in form of an arc perpendicular to the \vec{H} direction. Measurements in these two regions gave reproducible re-

Table II - Intensities of diffraction peaks measured in this paper for samples in powder form compared with standard ASTM values.

cubic assignment	MnFe ₂ O ₄		CoFe ₂ O ₄		γ-Fe ₂ O ₃			tetragonal assignment
	this work	ASTM FCC	this work	ASTM FCC	this work	ASTM cubic	ASTM tetragonal	
111	11	20	10	10	6	4	6	113
220	29	35	31	30	30	35	30	206
311	100	100	100	100	100	100	100	100
(222)								
400	18	25	21	20	22	16	15	00 12
422	9	20	7.5	10	11	10	9	22 12
511	29	35	29	30	33	24	20	11 15
440	36	40	37.5	40	48	34	40	40 12

Table III - Intensities of peaks in relation to intensity of dominant (311) peak. Samples, 1, 2, 3 trapped in gel and 1a, 2a, 3a dried from dilute solution. 1: no magnetic field. 2: magnetic field perpendicular to glass plate (\vec{H} parallel to \vec{q}). 3: magnetic field parallel to glass plate.

Sample	I ₂₂₀	I ₄₀₀	I ₅₁₁	I ₄₄₀
1	26%	26%	28%	38%
2	29%	27%	32%	38%
3	29%	26%	29%	38%
1a	28%	31%	38%	66%
2a	26%	20%	18%	23%
3a				
\vec{H}_\perp line beam 3a	32%	22%	18%	22%
\vec{H}_\parallel line beam	32%	26%	26%	32%

sults.

Analysis of Table III allow some conclusions to be drawn:

- The magnetic orientation opposes to and cancels the textural effects observed in sample 2a without field.
- Results in sample dried in presence of \vec{H} can be understood in terms of enhancement of particle oscillations in the direction perpendicular to the glass plate (larger Debye-Waller factor, decreasing intensities of peaks at larger angles).
- The meaning of the differences in results of the two condition for \vec{H} parallel to the plate is still un-

clear, but it might be connected to the anisotropic aggregation of particles in the glass plate, with preferred orientation perpendicular to \vec{H} .

The existence of aligned strings of magnetic particles has been proposed by de Gennes and Pincus^[21] in 1970, and anisotropy of the small angle diffraction pattern in presence of magnetic fields has been observed for conventional ferrofluids^[22,23] and also recently for ionic ferrofluids^[24].

The evidence for field induced anisotropy reported in this paper is not conclusive, but points directions for future work. We intend to proceed the investigation focusing the production of films of particles dried in presence of fields in more controlled conditions, and measuring diffraction with a better precision in both peak widths and relative intensities.

We emphasize that our results give a qualitative proof of an intense poor-controllable aggregation and orientation in the absence of gel and stable preservation of spatial structure in the "gelated" system. The method of trapping of the ferroparticles in a fastly solidifying gel looks promising for X-ray as well as other probing techniques.

Also, full analysis of X-ray diffractograms, including line widths for several peaks, give an estimation of the particle non-sphericity in the studied colloids and a

method to assess the same in any new ferrofluids.

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References

1. For a bibliography on ferrofluids see V. Cabuil, S. Neveu and R. E. Rosensweig, *J. Magn. & Magn. Mat.* **122**, 437 (1993).
2. *Complex Fluids*, edited by J. C. Bacri and R. Perzynski in L. Garrido, (Springer-Verlag, Berlin, 1993), p.85.
3. R. Massart, *C. R. Acad. Sci.* **291 C**, 1 (1980).
4. R. Massart and V. Cabuil, *J. Chim. Phys.* **89**, 967 (1987).
5. F. A. Tourinho, R. Franck and R. Massart, *J. Mater. Sci.* **25**, 3249 (1990).
6. J. C. Bacri, V. Cabuil, R. Massart, R. Perzynski and D. Salin, *J. Magn. Mater.* **65**, 285 (1987).
7. F. A. Tourinho, S. Neveu-Prin, J. C. Bacri, R. Perzynski and R. Rajaharison, *ICMF 6*, Paris 92, p.94.
8. S. Neveu-Prin, F. A. Tourinho, J. C. Bacri and R. Perzynski, *Colloids and Surfaces A: Physico-Chemical and Engineering Aspects* **80**, 1 (1993).
9. P. C. Sholten, *IEEE Trans. Magn. Mag* **16**, 221 (1980).
10. M. M. Maiorov and A. O. Cebers, *Kolloidn Zh.* **39**, 949 (1977).
11. H. W. Davies and J. P. Llewellyn, *J. Phys. D* **12**, 1357 (1979).
12. P. J. Llewellyn, *Appl. Phys.* **16**, 95 (1983).
13. S. Taketomi, H. Takahashi, N. Inaba, H. Miyajima and S. Chikazumi, *J. Phys. Soc. Jpn.* **59**, 2500 (1990).
14. S. Krupicka and P. Novak, in *Ferromagnetic Material*—edited by E. P. Wohlfarth, (North Holland, Amsterdam, 1982) vol.3, p.189.
15. C. Greaves, *J. Sol.-State Chemistry* **49**, 325 (1983).
16. K. Haneda and A. H. Morrish, *Sol. State Commun.* **22**, 779 (1977).
17. B. Gillot and F. Bouton, *J. Solid State Chem.* **32**, 303 (1980).
18. E. Tronc, J. P. Jolivet and R. Massart, *Mat. Res. Bull.* **17**, 1365 (1982).
19. H. R. Rechenberg and F. A. Tourinho, *Hyperfine Int.* **67**, 627 (1991).
20. F. A. Tourinho, R. Franck, R. Massart and R. Perzynski, *Progr. Colloid Polym. Sci.* **79**, 128 (1989).
21. P. G. de Gennes and P. A. Pincus, *Phys. Kondens. Mater.* **11**, 189 (1970).
22. D. J. Cebulla, S. W. Charles, J. Popplewell, *Colloid Polym. Sci.* **259**, 395 (1981).
23. R. Pynn, J. B. Hayter and S. W. Charles, *Phys. Rev. Lett.* **51**, 710 (1983).
24. M. F. da Silva and A. M. Figueiredo Neto, *Phys. Rev. E* **48**, (1993).