New approach to understand the NMR relaxivity properties of cobalt ferrite nanoparticles - Electronic Supplementary information†

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The synthesis of ferrite cobalt nanoparticles for each set of samples is detailed. The influence of several parameters (the anisotropy constant, the damping factor, the dead layer and the $\tau_0$) used in the model are detailed here. The linear dependences of the relaxation rate versus the volume fraction of MNPs are shown for several temperatures. The Arrhenius plot of the relaxivities at 20MHz is presented and from the linear regression an activation energy is obtained.

1 Ferrite Cobalt nanoparticles samples

The protocol used for each sample is detailed in table 1. The TEM images and the size distribution for all the samples used in this study are also provided figure 1. The distribution is fitted using a log-normal law:

$$f(d, d_0, \sigma) = \frac{1}{d_0 \sigma \sqrt{2\pi}} \exp\left(-\frac{(\ln d - \ln d_0)^2}{2\sigma^2}\right)$$

(1)

with $\sigma$ the standard deviation of the distribution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Synthesis</th>
<th>$D_{TEM}$ (nm)</th>
<th>$\sigma_{TEM}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>coprecipitation and size-sorting</td>
<td>4.7</td>
<td>0.47</td>
</tr>
<tr>
<td>S2</td>
<td>coprecipitation and size-sorting</td>
<td>5.8</td>
<td>0.53</td>
</tr>
<tr>
<td>S3</td>
<td>coprecipitation with complexing species</td>
<td>5.9</td>
<td>0.41</td>
</tr>
<tr>
<td>S4</td>
<td>coprecipitation with complexing species</td>
<td>6.8</td>
<td>0.43</td>
</tr>
<tr>
<td>S5</td>
<td>coprecipitation and size-sorting</td>
<td>7.9</td>
<td>0.44</td>
</tr>
<tr>
<td>S6</td>
<td>coprecipitation process</td>
<td>8.5</td>
<td>0.4</td>
</tr>
<tr>
<td>S7</td>
<td>coprecipitation process</td>
<td>10.1</td>
<td>0.62</td>
</tr>
<tr>
<td>S8</td>
<td>coprecipitation process</td>
<td>10.6</td>
<td>0.44</td>
</tr>
<tr>
<td>S9</td>
<td>coprecipitation process</td>
<td>10.6</td>
<td>0.42</td>
</tr>
<tr>
<td>S10</td>
<td>coprecipitation and size-sorting</td>
<td>10.7</td>
<td>0.45</td>
</tr>
<tr>
<td>S11</td>
<td>hydrothermal process</td>
<td>12.7</td>
<td>0.28</td>
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<td>S12</td>
<td>hydrothermal process</td>
<td>16.2</td>
<td>0.28</td>
</tr>
<tr>
<td>S13</td>
<td>hydrothermal process</td>
<td>18.7</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Table 1 Samples used in this study.

1.1 Coprecipitation process

CoFe$_2$O$_4$ nanoparticles are obtained by precipitating Co(II) and Fe(III) hydroxydes followed by a heating at boiling temperature. For a typical synthesis, sodium hydroxide (160 mL, 10 mol.L$^{-1}$) was abruptly added under vigorous stirring to a solution of cobalt and ferric nitrate (350 mL, [M] = [Fe] + [Co] = 0.44 mol.L$^{-1}$, [Co] / [Fe] = 0.4). After stirring 30 minutes, a nonmagnetic amorphous suspension was obtained and heated at 100°C for 2 hours. The mixture became magnetic was washed three times with distilled water. The second step to obtain a cobalt ferrite ionic magnetic fluid is the dispersion of the magnetic nanoparticles. In order to stabilize the nanoparticles in neutral aqueous solution, the particles were coated by citrate species. After stirring 30 minutes in citrate solution, citrated magnetic nanoparticles were dispersed in water and the final product was a stable ionic magnetic fluid with a pH around 7. The size of the nanoparticles thus obtained was around 10 nm. We obtained by this process an aqueous magnetic fluid at pH = 7 (samples S6, S7, S8 and S9).

1.2 Coprecipitation and size-sorting

In order to obtain monodisperse magnetic fluid, we used the size sorting process described in ref$^1$. This size sorting process is based on the thermodynamical properties of aqueous dispersion of cobalt ferrite synthesized by the coprecipitation process described above. This process allows to fractionate the particle size distribution and to obtain samples S1, S2, S5 and S10.

1.3 Coprecipitation in the presence of complexing species

In order to obtain smaller particles, the coprecipitation process was realized in the presence of complexing species such as tartrate ions as described in reference$^2$. The size of the nanoparticles

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thus obtained was around 5 nm (samples S3 and S4).

1.4 Hydrothermal process
In order to obtain bigger particles, instead of heating at boiling two hours, the hydroxides were heated in an autoclave at 200°C, during 24 hours as described in reference 3. The size of the nanoparticles thus obtained was around 20 nm (samples S11, S12 and S13).

2 Theoretical Model
Here we present the effect of some parameters used in the model. As underlined in the main text, no fit was performed on the experimental data. We have used the values found in the literature. However, we must stress that some parameters being difficult to measure, they may be a matter of debate. Hence, we show here the influence of these parameters on the different contributions of $R_1$ (transverse, Curie, and Curie fluctuation), idem for $R_2$ as well as the total $r_1$ and $r_2$. These parameters are: the anisotropy constant, the damping factor, the dead layer, and tau0. We have performed these calculations for a dispersion of 8 nm MNPs in water.

2.1 effect of anisotropy constant
The anisotropy constant appears in $\tau_{//}$ and $\tau_{\perp}$. Hence, both the first and the third terms, named transversal and Curie fluctuation terms respectively, of $R_1$ equation will be influenced. The second term, the Curie term is not affected. When the anisotropy increases, we see in Figure 2, that $r_1$ and $r_2$ at low frequency is increased and the bump around 10 MHz disappears. In the expression of $R_2$, it appears in the first and third terms of the C component and in the first term of the V($\alpha_0$) component. The first terms are also named transversal term and the third terms are named the Curie fluctuation terms.

2.2 effect of the damping factor
The damping factor appears in the time $\tau_{\perp}$. Hence, it must have influence only on the first term, named transversal term, of the $R_1$ equation. In the expression of $R_2$, it appears in the first term of the C component and in the first term of the V($\alpha_0$) component. In the text, we have also referred these two terms as transversal term. With no surprised, we see that only the transversal term is influenced by the damping factor. It tends to decreases $R_1_{\text{-trans}}$ and $R_2_{\text{-trans}}$ especially at high frequency.

3 NMR relaxation measurement
3.1 $R_1$ and $R_2$ dependence in concentration
The relaxivities $r_1 = (R_1/\text{[Fe+Co]})^{-1}$ and $r_2 = (R_2/\text{[Fe+Co]})^{-1}$ were determined using five MNPs dispersions with the iron and cobalt concentration [Fe+Co] ranging from 0.5 to 20 mM, approximately. In this range, $R_1 = 1/T_1$ and $R_2 = 1/T_2$ varies linearly with [Fe+Co], and the $R_1$ and $R_2$ values are obtained with a linear regression. Figure S 6 presents the variation of $R_1$ and $R_2$ as a function of the volume fraction $\phi$ in %. The slope gives a relaxivity in s$^{-1}$%$^{-1}$ and the conversion factor $\alpha$, to s$^{-1}$ mM$^{-1}$ is $\alpha = (d n)/(100000 M) = 1.476 \times 10^{-1}$ with $d$ the density of cobalt ferrite (5300 kg/m$^3$), $n$ the number of metal mole (cobalt + iron) in the cobalt ferrite compound and $M$ the molar mass (234.619 g/mol).

3.2 $R_1$ and $R_2$ dependence in temperature
The evolution of $R_1$ and $R_2$ versus the MNPs volume fraction $\phi$ is presented for five temperatures (10, 17, 25, 33 and 40°C). The linear evolution versus $\phi$ is observed for all the temperatures. This is a good indicator that the dispersion is stable and no aggregation of MNPs occurs. The temperature dependence of $R_1$ and $R_2$ for a medium size sample is presented in figures S 7 and S 8, respectively. The Neperian logarithms of $R_1$ and $R_2$ vary linearly with $1/RT$. A linear regression is performed in order to get the corresponding activation energy. The variations shown here for a 10.6 nm typify those observed for all samples.

References
**Fig. 1** TEM images and the size distribution for all the samples used in this study (for the name, see table 1).
Fig. 2 Effect of the anisotropy constant on the relaxivity $r_1$ on the left (top) and on the relaxivity $r_2$ on the right (top), as well as its effect on the three components (transversal term, Curie term and Curie fluctuation term).
Fig. 3 Effect of the damping factor on the relaxivity $r_1$ on the left (top) and on the relaxivity $r_2$ on the right (top), as well as its effect on the three components (transversal term, Curie term and Curie fluctuation term).
Fig. 4 Effect of the dead layer on the relaxivity $r_1$ on the left (top) and on the relaxivity $r_2$ on the right (top), as well as its effect on the three components (transversal term, Curie term and Curie fluctuation term).
Fig. 5 Effect of $\tau_0$ on the relaxivity $r_1$ on the left (top) and on the relaxivity $r_2$ on the right (top), as well as its effect on the three components (transversal term, Curie term and Curie fluctuation term).
Fig. 6 Variation of the relaxation rates $R_1$ and $R_2$ as a function of the volume fraction $\phi$ in % at 60 MHz for two temperatures ($25^\circ$C and $40^\circ$C). The lines represent the linear regression on the experimental data.

Fig. 7 Top: variations of the relaxation rates $R_1$ as a function of the volume fraction $\phi$ in % at 20 MHz for five temperatures ($10$, $17$, $25$, $33$ and $40$ $^\circ$C); the lines represent the linear regression on the experimental data. Bottom: variation of the neperian logarithm of $R_1$ versus $1/RT$; the line represents the linear regression on the experimental data.

Fig. 8 Top: variations of the relaxation rates $R_2$ as a function of the volume fraction $\phi$ in % at 20 MHz for five temperatures ($10$, $17$, $25$, $33$ and $40$ $^\circ$C); the lines represent the linear regression on the experimental data. Bottom: variation of the neperian logarithm of $R_2$ versus $1/RT$; the line represents the linear regression on the experimental data.