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Résumé. — La réduction progressive du composé d'intercalation du graphite de premier stade C₁₄FeCl₃.₀₄ par une solution de n-butyl lithium dans l'hexane à 60 °C conduit à la formation des composés C₁₄FeCl₃₋ₓ(LiCl)x avec x = 0, 1, 2, 3. On observe une diminution de la valence du fer de 3 à 0 avec x. Le composé final est ferromagnétique à la température ordinaire. Il est constitué de plans contenant essentiellement du Fe⁰ formant un composé de premier stade, en présence de Fe³⁺ et de Fe²⁺. Un comportement de verre de spin ferromagnétique est observé entre 4,2 et 300 K pour x = 2 et x = 3.

Abstract. — Progressive reduction of the stage-1 graphite intercalation compound, (GIC), C₁₄FeCl₃.₀₄ using a solution of n-butyllithium into hexane at 60 °C leads to the formation of zero valent iron layers of stage 1 containing small amounts of Fe³⁺ and Fe²⁺. The reduced compounds have the average formula : C₁₄FeCl₃₋ₓ(LiCl)x with x = 0, 1, 2, 3. For x = 2 and 3 the compounds behave as ferro-spin glasses with a freezing temperature around 300 K.

Introduction.

Graphite easily forms intercalation compounds with most alkali or alkali earth metals and with some rare earth metals by a direct reaction using the vapor transport technique [1]. However, this method cannot be applied to transition metals because of their very low volatility. Only indirect syntheses have been tempted involving a chemical [2-7] or an electrochemical [7, 8] reduction : the transition metal cation is preliminarily intercalated into
graphite (as chloride [2-5, 7] or oxide [6]) and then reduced to lower valency states including the zero one.

The main difficulties arising from the indirect methods are first of all the incompleteness of the reaction due to the inhomogeneous reactive diffusion within the graphite layers and/or secondly the difficulty of maintaining the two dimensional (2D) character of the structure. When one uses gas as a reductive reagent at high temperatures, (vapor phase with alkali metals [7] or hydrogen [2]), the strong tendency to form three dimensional (3D) clusters rather than layered domains results from the increasing metastability of the 2D state with the reaction temperature. With liquids at low temperature the solvent is generally polar and partially dissolves the transition cation. The reduction reaction tends to occur at the graphite surface. Thus, the resulting compounds contain high amounts of 3D clusters. They are regarded as inclusion compounds rather than intercalation ones.

We recently suggested a new route to achieve the in situ reduction of transition metal chlorides GIC's by using n-butyl lithium dissolved in hexane at room temperature [9]. In the case of FeCl₃-GIC, X-ray diffraction and Mössbauer experiments demonstrated the efficiency of this method in producing zero valent state metal forming 2D domains regularly stacked along the c-axis. However, the Mössbauer experiments evidenced the presence of Fe³⁺ ions even after using an excess of n-butyl lithium solution [10]. In addition, reduction occurs in two steps: Fe³⁺ → Fe²⁺ → Fe⁰ by increasing the amount of n-butyl lithium. We suggested a simple model in which the reduction reaction begins at the border of the domains and propagates towards the core. Thus, each domain is made of 3⁺ ions surrounded by 2⁺ and zero valent ones.

An improvement of the reduction method can be expected if the reaction temperature and duration are increased.

This paper deals with the observation of the progressive reduction of a stage-1 FeCl₃-GIC, (FeCl₃/graphite/FeCl₃/graphite... stacking sequence along the c-axis), by a titrated solution of n-butyl lithium at 60 °C during more than two months. The Mössbauer experiments, the magnetic properties and the structure changes induced by the reduction are analysed within the same model.

Results and discussion.

1. PREPARATION AND STRUCTURE. — Details of the preparation conditions have been given elsewhere [9]. They can be summarized as follows: 100 mg of fine powder (= 10 μm) of stage-1 FeCl₃-GIC (average formula, C₄ₓFeCl₃) were treated with n-butyl lithium in solution in hexane [9]. A well defined amount of intercalated lithium, x = 1, 2 or 3, is obtained. The ideal formula is C₁₄LiₓFeCl₃. The reaction tube is sealed under high purity water free argon atmosphere and maintained at 60 ± 1 °C during 10 weeks. The samples were regularly stirred in order to achieve a good homogeneity. The liquid phase was then eliminated through centrifugation and the unreacted lithium was analysed [9]. The remaining solid powder was repeatedly washed with hexane and methanol and finally dried under vacuum at 100 °C. An X-ray diffraction analysis (Debye-Scherrer) was then performed on the resulting compound.

The chemical analysis shows that the unreacted part of butyl lithium does not exceed 5 % the initial quantity introduced into the reaction tube. This indicates that within the experimental accuracy the intercalation into the FeCl₃-GIC has a very high efficiency even though the possibility of a partial oxydization of butyl lithium cannot be excluded. As we have shown in a previous study [10], the parent structure of C₁₄FeCl₃ completely disappears only for a lithium concentration x greater than 2. At this concentration a new phase appears with a smaller identity parameter along the c-axis.
Table I. — Debye-Scherrer pattern indexation of the most reduced compound with \( x = 3 \). The iron atoms arrange in a hexagonal lattice incommensurate with that of graphite leading to a stage-1 GIC (G-Fe). Pristine graphite appears as a consequence of the decrease of the domain size. Three-dimensional LiCl is encapsulated between the graphene layers.

Graphite-iron \( x = 3 \) (hexagonal, \( a = 4.15 \, \text{Å}, \; c = 10.88 \, \text{Å} \))

<table>
<thead>
<tr>
<th>I</th>
<th>( d ) (Å) (obs)</th>
<th>( 1/d^2 ) (obs)</th>
<th>( 1/d^2 ) (cal)</th>
<th>G-Fe</th>
<th>Graphite</th>
<th>LiCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>w</td>
<td>3.67</td>
<td>0.07425</td>
<td>0.0774</td>
<td>0.0760</td>
<td>100</td>
<td>003 (?)</td>
</tr>
<tr>
<td>S</td>
<td>3.36</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>002</td>
</tr>
<tr>
<td>S</td>
<td>2.95</td>
<td>0.1149</td>
<td>0.1112</td>
<td></td>
<td>102</td>
<td></td>
</tr>
<tr>
<td>vw</td>
<td>2.72</td>
<td>0.1352</td>
<td>0.1352</td>
<td></td>
<td>004</td>
<td></td>
</tr>
<tr>
<td>m</td>
<td>2.54</td>
<td>0.1550</td>
<td>0.1534</td>
<td></td>
<td>103</td>
<td></td>
</tr>
<tr>
<td>w</td>
<td>2.09</td>
<td>0.2289</td>
<td>0.2322</td>
<td></td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>w</td>
<td>2.03</td>
<td>0.2426</td>
<td>0.2407</td>
<td></td>
<td>111</td>
<td>101</td>
</tr>
<tr>
<td>m</td>
<td>1.815</td>
<td>0.3036</td>
<td>0.3041</td>
<td></td>
<td>006</td>
<td>220</td>
</tr>
<tr>
<td>vw</td>
<td>1.712</td>
<td>0.3412</td>
<td>0.3434</td>
<td></td>
<td>202</td>
<td></td>
</tr>
<tr>
<td>vw</td>
<td>1.609</td>
<td>0.3867</td>
<td>0.3857</td>
<td></td>
<td>203</td>
<td></td>
</tr>
<tr>
<td>m</td>
<td>1.546</td>
<td>0.4184</td>
<td>0.4139</td>
<td></td>
<td>007 (?)</td>
<td>103</td>
</tr>
<tr>
<td>w</td>
<td>1.229</td>
<td>0.6621</td>
<td></td>
<td></td>
<td>110</td>
<td></td>
</tr>
</tbody>
</table>

S: strong; m = medium; w: weak; vw: very weak

This phase was ascribed to a stage-1 Fe\(^{0}\)-GIC in which the Fe\(^{0}\) domains have a regular crystalline structure along the \( c \)-axis and in the (ab) plane.

In table I we report the indexation of the X-ray powder diagram lines for the most reduced compound \((x = 3)\). Besides the characteristic lines of graphite and three dimensional LiCl, the major part of the lines can be attributed to the stage-1 Fe\(^{0}\)-GIC. The deduced structure is interpreted within the following model: the iron atoms arrange in a hexagonal lattice with \( a = 0.415 \, \text{nm} \) and \( c = 1.088 \, \text{nm} \). Within this model the 00\( \ell \) lines with \( \ell \) and odd number should not be present. The possibility of attributing the distances \( d = 0.367 \, \text{nm} \) and \( d = 0.1546 \, \text{nm} \) to 003 and 007 lines results from the inhomogeneous interplane Fe density and/or from the existence of stacking defects of the Fe domains. It should be emphasized that the calculated Fe-Fe distance in this hexagonal iron (0.2396 nm) with the coordination number \( n = 3 \) is smaller than that of \( \alpha \)-iron (0.2482 nm, \( n = 8 \)) and that of \( \gamma \)-iron (0.2545 nm, \( n = 12 \)) \[11\], as expected. The iron lattice is not commensurate with the graphite lattice. This is the indication of strong correlations between the iron atoms and shows that the iron layers should be stabilized through metallic-like bondings. Our model differs from the one of Vol’pin \emph{et al.} \[5\] who described the structure with a double layer of Fe\(^{0}\) coordinated with the graphene hexagones, and also from the model of Touzain \emph{et al.} \[7\] who proposed a quadratic cell.

Four different samples were prepared with \( x = 0, 1, 2 \) and 3. They were hermetically sealed under argon atmosphere in appropriate holders and used for the Mössbauer and magnetic measurements.
2. Mössbauer spectroscopy. — The driving idea was to check the Fe state at different reduction steps, that is for the different amounts of lithium \((x = \text{Li/Fe})\) intercalated into the parent stage-1 FeCl₃-GIC, with the theoretical values \(x = 0, 1, 2\) and 3. The Mössbauer spectra were measured as a function of temperature in the range 4.2-300 K with a conventional apparatus using a \(^{57}\text{Co}\) source in Rh.

Figure 1 represents the spectra obtained for the four different values of \(x\), at room temperature and 4.2 K. The analysis was done with an usual least square fit procedure, making use of lorentzian shaped line. The Mössbauer parameters of the subspectra are reported in tables III, IV, V and VI. They are:

i) the Isomer Shift \(\delta\) (information about the Fe valency), with a typical error of 0.01 mm/s,

ii) the Quadrupole Splitting \(\Delta = e^2 q Q / 2 \sqrt{1 + \eta^2 / 3}\) reflects the symmetry of the Fe site through the Electric Field Gradient (EFG) parameters: \(eq = V_{zz}\), main EFG component, \(\eta = (V_{xx} - V_{yy}) / V_{zz}\) asymmetry parameter; typical error: 0.02 mm/s,

iii) the magnetic hyperfine field \(H\), proportional to the iron magnetic moment (at least in the case of Fe³⁺ and Fe⁰); typical error: 0.1 T,

iv) the angle, \(\theta\), between \(V_{zz}\) (local symmetry axis) and \(H\) through the measured quadrupole parameter in the presence of the hyperfine field: \(2 \varepsilon = \Delta (3 \cos^2 \theta - 1) / 2\). Experimentally, we never had access to this angle because we always measured a zero mean quadrupole parameter \(2 \varepsilon = 0\) in the magnetic sextets. There are two possible reasons for that: a cubic symmetry of the Fe site (\(\Delta = 0\)) or a random angular distribution of \(H\) versus \(V_{zz}\) (\(\langle 3 \cos^2 \theta - 1 \rangle = 0\)) due to a spin glass-like freezing for instance.

The line width \(\Gamma / 2\) can reflect eventual broadenings due to disorder (distribution in \(\Delta\), \(H\) and \(\theta\)). Experimentally, hyperfine field distributions have been observed for all magnetic hyperfine structures. As an approximation, it was taken into account in the fit with three different line widths for the six-line pattern. \(H\) denotes the mean hyperfine field (typical error: 0.5 T).

Finally, the relative amount of the different Fe species present in the samples was determined with the spectral area ratios (typical error: 2 %). The final values reported in figure 9 are taken from the spectra at 4.2 K because the resolution is much better than at room temperature.

In addition, for an easier comparison, we have mentioned in table II the hyperfine parameters for several reference compounds: \(\alpha\)-Fe, FeCl₃ [12], FeCl₂ [13], FeCl₃-GIC [14] and FeCl₂-GIC [15].

\(x = 0\): The spectrum is quite in agreement with those obtained in a number of previous studies [14-16]. According to Prietsch et al. [14], the weak electronic charge transfer from the graphene layers to the intercalant (~ 0.2 electron per FeCl₃) is characterized by a thermally activated electron hopping between iron sites. This results, in the static limit, in the presence of 20 % Fe²⁺ among the Fe³⁺ sites. For the Mössbauer time window these two valency states are only observable at low temperatures (slow relaxation time limit). At higher temperatures an average spectral line is observed because of the fast electronic relaxation. Our spectra exhibit clearly this situation: the major paramagnetic line at room temperature splits at 4.2 K into two well separated subspectra, i.e. a broad Fe³⁺ line (indicating the onset of magnetic order at \(T \leq 4.2\) K) and a Fe²⁺ doublet. The Fe²⁺ amount is about 9 % of FeCl₃, less than what is obtained in reference [14]. However, the compound of these authors was a stage-2 prepared under a very low chlorine pressure while ours is a stage-1 prepared under a 2 atmosphere chlorine pressure, which should increase the Fe³⁺/Fe²⁺ in the parent compound. The hyperfine parameters of the two components are in good agreement with [14]. In our
Table II. — $^{57}$Fe Mössbauer hyperfine parameters for reference compounds: $\alpha$-Fe, FeCl$_3$, FeCl$_3$-GIC, FeCl$_2$, and FeCl$_2$-GIC. ($\delta$: isomer shift referred to $\alpha$-Fe at room temperature; $\Delta$: quadrupole splitting; $H$: hyperfine field).

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\alpha$-Fe</th>
<th>FeCl$_3$</th>
<th>FeCl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta$ (mm/s)</td>
<td>$\Delta$ (mm/s)</td>
<td>$H$ (T)</td>
</tr>
<tr>
<td>295</td>
<td>0</td>
<td>0</td>
<td>33</td>
</tr>
<tr>
<td>4.2</td>
<td>0.12</td>
<td>0</td>
<td>34</td>
</tr>
</tbody>
</table>

FeCl$_3$-GIC | FeCl$_2$-GIC

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\langle Fe^{3+} + Fe^{2+} \rangle$</th>
<th>Fe$^{3+}$ (81 %)</th>
<th>Fe$^{2+}$ (19 %)</th>
<th>Fe$_{II}^{2+}$ (33 %)</th>
<th>Fe$_{I}^{2+}$ (67 %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta$ (mm/s)</td>
<td>$\Delta$ (mm/s)</td>
<td>$H$ (T)</td>
<td>$\delta$ (mm/s)</td>
<td>$\Delta$ (mm/s)</td>
</tr>
<tr>
<td>295</td>
<td>0.42</td>
<td>0.15</td>
<td>1.1</td>
<td>1.6</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>0.45</td>
<td>0.19</td>
<td>1.08</td>
<td>1.86</td>
<td>0</td>
</tr>
<tr>
<td>4.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.6</td>
<td>0.45 ~ 0</td>
<td>48.6</td>
<td>1.09</td>
<td>2 ~ 0</td>
<td>0</td>
</tr>
</tbody>
</table>

case, however, an additional Fe$^{2+}$ quadrupole doublet is observed in the whole temperature range. This parasitic Fe$^{2+}$ may lie at the surface of the graphite. Indeed, the hyperfine parameters seem to correspond to the hydrated compound FeCl$_2$, 4 H$_2$O which is probably due to some surface water contamination. Chemical reduction eliminates this parasitic phase.

$x = 1$: The spectrum is drastically altered, as can be seen in figure 1 (295 and 4.2 K) and figure 2 which shows the more detailed temperature dependence. The fit parameters are reported in table IV. The most representative spectrum is to be considered at 30 K because the decomposition into three subspectra is rather obvious. It is the superposition of two Fe$^{2+}$ symmetrical quadrupole doublets of same isomer shift $\delta = 1.2$ mm/s with $\Delta = 1.4$ and 2.4 mm/s, and a Fe$^{3+}$ broad magnetic hyperfine pattern ($H = 48$ T).

When the temperature is lowered the Fe$^{3+}$ components undergo a magnetic transition at 12 ± 2 K which can be observed on the spectrum by the progressive broadening and asymmetry of the main Fe$^{2+}$ doublet due to the presence of a small hyperfine field ($H = 1$ T). These characteristics of the Fe$^{2+}$ spectrum correspond rather well to the two quadrupole doublets of FeCl$_2$-GIC [15] and our hyperfine parameters are quite similar to the corresponding parameters of table II at least at low temperatures.
For temperatures higher than 30 K the decomposition is not easy. The line width of the Fe$^{3+}$ magnetic component becomes larger and larger when the temperature is raised. The magnetic structure completely disappears above 60 K without showing the usual decrease of the hyperfine field magnetic transition, but rather gives rise to a curvature of the background level. Around 80 K the appearance of a corresponding Fe$^{3+}$ paramagnetic spectrum can be characterized by the occurrence of a progressive asymmetry in the Fe$^{2+}$ doublets. However, it is difficult to define a transition point for Fe$^{3+}$. Moreover the nature of this paramagnetic component is questionable.

The room temperature spectrum for instance shown in the figures has been fitted by including a Fe$^{3+}$ doublet together with a Fe$^{2+}$ one. Another way of fitting could be the use of a unique Fe$^{3+}$ line of larger isomer shift $\delta = 0.46$ mm/s (as in FeCl$_3$); in this case one should
Fig. 2. — Temperature dependence of the Mössbauer spectrum for C\textsubscript{6}Li\textsubscript{1}FeCl\textsubscript{3} (x = 1).
introduce an anisotropy effect for the Fe$^{2+}$ doublets leading to a much more pronounced inequality of the two lines for the doublet $\Delta = 2$ mm/s.

This could arise either from texture effects (no random orientation of the graphite particles in the sample) or from an anisotropic resonance absorption factor (anisotropy of the nucleus mean squared vibrational amplitudes in the lattice).

Table III. — Hyperfine parameters for $C_nLi_xFeCl_3$ ($x = 0$).

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\langle Fe^{3+} + Fe^{2+} \rangle$</th>
<th>Fe$^{3+}$</th>
<th>Fe$^{2+}$</th>
<th>Fe$^{2+}$ (FeCl$_2$, 4 H$_2$O)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta$</td>
<td>$\Gamma/2$</td>
<td>$\Delta$</td>
<td>$%$</td>
</tr>
<tr>
<td></td>
<td>mm/s</td>
<td>mm/s</td>
<td>mm/s</td>
<td></td>
</tr>
<tr>
<td>295</td>
<td>0.503</td>
<td>0.187</td>
<td>0</td>
<td>84</td>
</tr>
<tr>
<td>4.2</td>
<td>0.453</td>
<td>0.305</td>
<td>0.267</td>
<td>78.5</td>
</tr>
</tbody>
</table>

The first effect has to be rejected because the asymmetry should be maintained in the whole temperature range, while the doublets are quite symmetrical below 100 K. The second effect (Goldanskii-Karyagin effect) may exist and should decrease at lower temperatures. Vibrational anisotropy has already been observed for intercalated species [14] because of the low dimensionality, but not evidenced for powdered FeCl$_2$-GIC [15]. Consequently, we must admit that the extra component (Fe$^{3+}$) should be a doublet. However its isomer shift at room temperature is low for a trivalent iron chloride ($\delta = 0.2$ mm/s) while its value at 4.2 K ($\delta = 0.47$ mm/s) is in agreement with that of FeCl$_3$-GIC. This feature will occur for all values of x.

As a first qualitative conclusion, the parent FeCl$_3$-GIC has been mostly reduced to FeCl$_2$-GIC by n-butyl lithium. About 25% of iron remains in the trivalent unreduced state. It is not identical to FeCl$_3$ as far as the magnetic behavior is concerned.

Finally, at this step of the reduction no Fe$^0$ is detected.

$x = 2$: The first appearance of Fe$^0$ is observed. The room temperature Mössbauer spectrum exhibits a magnetic hyperfine pattern with an isomer shift very close to zero.

Table IV. — Hyperfine parameters for $C_nLi_xFeCl_3$ ($x = 1$).

(* denotes parameters which are kept constant in the fit and $\Delta = 2 \varepsilon = \langle (e^2 qQ)/2 (3 \cos^2 \theta - 1)/2 \rangle$ when $H \neq 0$).

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Fe$^{3+}$</th>
<th>Fe$^{2+}$</th>
<th>Fe$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta$</td>
<td>$\Gamma/2$</td>
<td>$\Delta$</td>
</tr>
<tr>
<td></td>
<td>mm/s</td>
<td>mm/s</td>
<td>mm/s</td>
</tr>
<tr>
<td>295</td>
<td>1.106</td>
<td>0.256</td>
<td>0.964</td>
</tr>
<tr>
<td>30</td>
<td>1.224</td>
<td>0.264</td>
<td>1.454</td>
</tr>
<tr>
<td>4.2</td>
<td>1.22*</td>
<td>0.336</td>
<td>$-1.45^*$</td>
</tr>
</tbody>
</table>
(referred to $\alpha$-Fe) and a hyperfine field of 32 T (to be compared with 33 T for $\alpha$-Fe). From the intensity ratios at low temperatures one can estimate that 35% of the iron atoms are reduced to $\text{Fe}^0$ inside the graphene layers. Since we did not observe any X-ray lines characteristic of $\alpha$-Fe, we conclude that this contribution is not due to bulk iron expelled from graphite. In addition, the temperature dependence of the hyperfine field and its saturation value ($H(O) = 38$ T) are quite different from those of bulk iron (Fig. 3). We find that 45% of the iron is in the $2^+$ valency state and 20% in the $3^+$ state, characterized by the hyperfine field of 49 T at 4.2 K. Concerning the evolution of the spectrum as a function of temperature, the same features as in the case $x = 1$ are observed, i.e. a broad «magnetic transition» starting from about 200 K due to $\text{Fe}^{3^+}$ and an ordering transition of 10 K which we attribute to $\text{Fe}^{2^+}$. Here again the nature of the $\text{Fe}^{3^+}$ doublet raises some problem, as the isomer shift at room temperature is quite low as in the case $x = 1$.

In conclusion, with $x = 2$ the quantity of unreduced $\text{Fe}^{3^+}$ has not been changed with respect to $x = 1$ but the proportion of $\text{Fe}^{2^+}$ has been considerably decreased showing that the production of zero valent iron is made at the expense of the $\text{FeCl}_2$-GIC phase. This is again in agreement with the islandic picture of the compound, the surface of the islands being first reduced while their core remains unmodified.

$x = 3$ : The $\text{Fe}^{2^+}$ component is considerably reduced in the spectrum (18% at room temperature). Besides this feature, the room temperature spectrum exhibits two major components:

i) The $\text{Fe}^0$ component, already present for $x = 2$, now accounts for 34% of total iron. This only corresponds to a slight increase with respect to the preceding compound. The thermal evolution is identical. A small decrease of $H$ with respect to the case $x = 2$ is observed: $H = 31$ T instead of 32 T.

![Fig. 3. — Hyperfine field of the different species of iron versus temperature present in the compound $C_n\text{Li}_x\text{FeCl}_3$.](image-url)
Table V. — Hyperfine parameters for C\textsubscript{n}Li\textsubscript{x}FeCl\textsubscript{3} (x = 2).

<table>
<thead>
<tr>
<th>T (K)</th>
<th>295</th>
<th>4.2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\delta) mm/s</td>
<td>(\Gamma/2) mm/s</td>
</tr>
<tr>
<td>Fe\textsuperscript{3+} \textsubscript{i}</td>
<td>1.11</td>
<td>0.284</td>
</tr>
<tr>
<td>Fe\textsuperscript{3+} \textsubscript{il}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe\textsuperscript{3+}</td>
<td>0.12</td>
<td>0.349</td>
</tr>
<tr>
<td>Fe\textsuperscript{0}</td>
<td>-0.07</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table VI. — Hyperfine parameters for C\textsubscript{n}Li\textsubscript{x}FeCl\textsubscript{3} (x = 3).

<table>
<thead>
<tr>
<th>T (K)</th>
<th>295</th>
<th>4.2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\delta) mm/s</td>
<td>(\Gamma/2) mm/s</td>
</tr>
<tr>
<td>Fe\textsuperscript{3+} \textsubscript{i}</td>
<td>0.98</td>
<td>0.351</td>
</tr>
<tr>
<td>Fe\textsuperscript{3+} \textsubscript{il}</td>
<td>0.98</td>
<td>0.351</td>
</tr>
<tr>
<td>Fe\textsuperscript{0} \textsubscript{i}</td>
<td>0.174</td>
<td>0.361</td>
</tr>
<tr>
<td>Fe\textsuperscript{0} \textsubscript{il}</td>
<td>-0.002</td>
<td>0.453</td>
</tr>
</tbody>
</table>
ii) A well defined quadrupole doublet with $\delta = 0.17 \text{ mm/s}$ and $\Delta = 0.6 \text{ mm/s}$ represents almost half of the total quantity of iron (48%). It cannot be attributed to Fe$^{3+}$ as was done for $x = 1$ and $x = 2$ because its behavior when the temperature is lowered to 4.2 K is complex: it splits into the usual Fe$^{3+}$ sextuplet with a hyperfine field of 48 T (corresponding to a concentration of 20% Fe$^{3+}$) and a new type of Fe$^0$ sextuplet with $H = 34$ T, $\delta = 0.17 \text{ mm/s}$ representing 20% the total iron. It should be noted that these parameters are quite similar to those of bulk iron. However the thermal variation of the hyperfine field is characteristic of superparamagnetic particles.

The room temperature doublet disappears progressively below 60 K and transforms into the hyperfine pattern. At 4.2 K a small part of the doublet remains unsplit (corresponding to 7% the total iron). This is due to the particles whose moment relaxes more rapidly than the Mössbauer time window ($3 \times 10^{-8}$ s).

In conclusion, 61% of the iron atoms are in the zero valent state for $x = 3$:

- 34% are included in large monolayers magnetically ordered at room temperature, with a hyperfine field at 4.2 K, 10% higher than that of bulk iron.
- 27% are included in small superparamagnetic particles with a hyperfine field at 4.2 K nearly equal to that of bulk iron.

3. MAGNETIC PROPERTIES. — We have measured the static susceptibility $\chi_{st} = M/h$ in a 10 mT field and the magnetization $M(h)$ up to 11 T at various temperatures in the range 4.2-300 K.

Figures 4 and 5 show the variation of $\chi_{st}$ for the four compounds ($x = 0, 1, 2, 3$).

Fig. 4. — Static susceptibility $M/h = \chi_{st}$ measured in a 10 mT field for $x = 0$ and $x = 1$. The arrows indicate the direction of the temperature sweep.
$x = 0$: $\chi_{st}$ decreases monotonously with the temperature (Fig. 4). The magnetization curves show no saturation effect even in the highest fields confirming the absence of ordering in this compound above 4.2 K (Fig. 6a). This is in agreement with previous results which show no ordering above 4.2 K in this compound [17].

$x = 1$: An ordered phase appears, evidenced by the thermal hysteresis between 10 K and 60 K in good agreement with the Mössbauer results (Fig. 4). The magnetization tends to saturate at 4.2 and 20 K. In high fields a linear behavior is observed and the magnetization $M$ can be written as: $M = \sigma_s + \chi_{hf} \cdot h$. A small saturation exists also at high temperatures (200 K) which is due to the presence of a small amount of a ferromagnetic phase (less than 1%) (Fig. 6b), not detected in the Mössbauer spectrum.

$x = 2$ and $x = 3$: The susceptibility is considerably increased with respect to the previous cases (Fig. 5). If the compounds are cooled down to 4.2 K in zero field and then heated up to 300 K in the measuring field one observes first a decrease of $\chi_{st}$ up to around 20 K, then an increase and a very broad maximum near 200 K above which $\chi_{st}$ again decreases. If the samples are cooled under the measuring field a very large hysteresis can be seen. The field cooled susceptibility is much higher than the zero field cooled one due to the appearence of a remanent magnetization around 250 K. In fact, a part of the samples is ordered well above room temperature. As shown in the figures the susceptibility curves $\chi_{st}(T)$ for $x = 2$ and $x = 3$ are almost parallel above 50 K indicating that the only effect of increasing the reduction from $x = 2$ to $x = 3$ is to increase the amount of Fe$^0$.

Above 50 K the magnetization saturates in low fields ($h < 1$ T), (Fig. 6c and 6d), whereas in the preceding cases the $M(h)$ curves at the same temperatures were almost linear (Fig. 6a).
Fig. 6. — Magnetization curves up to 11 T at various temperatures for the four compounds. Starting from the highest magnetization curve: a) $x = 0$; 4.2 K, 10.1 K, 20.4 K, 50.5 K, 101.3 K, 199.5 K, 300 K. b) $x = 1$; 4.2 K, 10.24 K, 19.9 K, 29.98 K, 40.2 K, 50 K, 101.5 K, 200 K. c) $x = 2$; 4.2 K, 10.35 K, 20.3 K, 50.9 K, 100.5 K, 200 K, 300 K. d) $x = 3$; 4.2 K, 101.5 K, 50.9 K, 300 K. Note that, in the last case, the magnetization does not vary monotonously with temperature.

and 6b). In addition the high field part of the curves, corresponding to the saturated moments, does not vary very much with temperature between 100 and 300 K indicating that a magnetic order appears below room temperature. We attribute it to the Fe° phase detected by Mössbauer spectroscopy and which also appears in the susceptibility (plateau around 200 K). For $x = 3$ the saturation is much easier even at 4.2 K (Fig. 5d), but the overall behavior is the same as for $x = 2$.

Finally, we see that the chemical reduction tends to produce a ferromagnetic phase in the compound, which we attribute to Fe° atoms in agreement with the Mössbauer experiments. These Fe° atoms are gathered in domains of very different sizes and form an inhomogeneous assembly of clusters exhibiting a spin-glass like behavior: the fact that the magnetization saturates more easily at 50 K than at 4.2 K and the absence of divergence of the susceptibility at a well defined temperature show that the magnetic properties are driven by strong ferromagnetic interactions at short range, still existing in the pristine FeCl₃ and FeCl₂ (in these compounds there exist a ferromagnetic interaction at short range, in the planes, between the first neighbours, and an antiferromagnetic interaction at longer range between the adjacent layers) and also in metallic iron, coexisting with antiferromagnetic interactions at long range. The Mössbauer experiments, performed in zero external field, cannot distinguish between both types of interactions since the hyperfine field is an average over the absolute value of the interactions.
The distinction can be made with the use of magnetic measurements. The antiferromagnetic interaction may be of two origins: dipolar between the supermoments of the ferromagnetic domains or of the RKKY type via the conduction electrons. The overall behavior of the susceptibility can be interpreted as a gradual freezing of the ferromagnetic domains when the temperature is decreased. For a domain containing $N$ atoms, with an internal field $H_0$, the ordering will occur at $T(N) = (N)^{1/2} \mu_0 H_0/k_B$, where $\mu_0$ is the individual moment of each atom [18]. Thus, the biggest domains order first while the smallest ones order only at low temperatures or do not order. If the domain size distribution is narrow, the susceptibility has a well pronounced peak, and the ordering process looks like a phase transition. If the distribution is broad, no well defined ordering temperature can be found. This is the case of the compounds with $x = 2$ and $x = 3$. When the temperature is decreased well below $T(N)$, the antiferromagnetic interactions at long range become important and $\chi_{st}$ tends to decrease.

The increase of $\chi_{st}$ below 10 K can be attributed to the remaining FeCl$_3$ and FeCl$_2$ into graphite and also to the domains containing a very small number of Fe$^0$ atoms which do not order (« frustrated spins » [19]). It can be shown [18] that the average number of Fe$^0$ atoms per domain is given by the equation:

$$N = 1/2 \pi (\sigma_s/\sigma_r)^2$$

where $\sigma_s$ and $\sigma_r$ are the saturation and the remanent magnetization respectively. At 200 K one has $\sigma_s = 21$ emu/g and $\sigma_r = 0.48$ emu/g which gives $N = 300$ atoms. According to the X-

![Graph](image)

Fig. 7. — Comparison of $\chi_{st}$ measured (black dots) and $\chi_{st}$ calculated (open dots) for $x = 3$. The vertical bar indicates 20% of $\chi_{st}$.
ray results \((a = 0.415\ \text{nm} \ \text{and} \ c/2 = 0.544\ \text{nm})\) we find that a hypothetical spherical cluster containing 300 atoms should have a radius of 2.6 nm. The same calculation made at 4.2 K gives an average number of 9 atoms per cluster. This confirms our simple model and shows that the Fe\(^0\) atoms are mainly included in very small domains.

The susceptibility for \(x = 3\) can be written as follows:

\[
\chi_{\text{eff}} = x_2 \cdot \chi_2 + x_3 \cdot \chi_3 + x_0 \cdot \chi_0
\]

where \(x_2\), \(x_3\) and \(x_0\) are the respective concentrations of Fe\(^{2+}\), Fe\(^{3+}\) and Fe\(^0\) deduced from Mössbauer experiments. \(\chi_2\), \(\chi_3\) and \(\chi_0\) are the corresponding susceptibilities. \(\chi_3\) is deduced from the curve for \(x = 0\), \(\chi_2\) is deduced from the curve for \(x = 1\), \(\chi_0\) is calculated by subtracting the contributions \(\chi_2\) and \(\chi_3\) from the curve for \(x = 2\). Figure 7 shows the calculated (open dots) and the measured (black dots) susceptibilities. Within our crude approximations the agreement between the two curves is fairly good (better than 25\%)

We can also apply this analysis to the saturation magnetization at 4.2 K by writing for \(x = 3\):

\[
\sigma_s = x_2 \cdot M_2 + x_3 \cdot M_3 + x_0 \cdot M_0
\]

\(M_2\), \(M_3\), the saturation magnetizations of the Fe\(^{2+}\) and Fe\(^{3+}\) phases respectively are deduced from the magnetization curves at 4.2 K for \(x = 0\) and \(1\) in the same way as described above.

We find \(M_3 = 0\), \(M_2 = 37.5\ \text{emu/g}\). Assuming a 2.2 \(\mu_B\) moment per Fe\(^0\) (as in bulk) we calculate \(M_0 = 32\ \text{emu/g}\).

Finally the calculated value of \(\sigma_3\) is 29 emu/g to be compared with the measured value 32 emu/g.

![Graph showing the relation between saturation magnetization and temperature](image)

Fig. 8. — Saturation magnetization (left scale), and high field susceptibility \(\chi_{hf}\) multiplied by \(10^5\) (right scale), \textit{versus} temperature of the compound with \(x = 3\).
In figure 8 we have plotted the thermal variation of the saturation magnetization $\sigma_s$ and of the high field susceptibility $\chi_{hf}$ between 4.2 and 300 K of the most reduced compound ($x = 3$). We find for $M_s$ the same behavior as for $\chi_{hf}$: a broad maximum around 200 K due to the Fe$^0$ and a low temperature tail due to the Fe$^{2+}$ and Fe$^{3+}$ ions (their average moments are respectively 6 and 5 $\mu_B$, higher than the Fe$^0$ moment). The susceptibility $\chi_{hf}$ exhibits a well marked peak at 50 K indicating that some phase orders at this temperature, in good agreement with the Mössbauer results ($x = 1$).

**Conclusion.**

The improvement of the chemical reduction of the stage-1 FeCl$_3$-GIC leads to a progressive and controlled reduction of the iron valency from 3 to 0. In the most reduced compound ($x = 3$), the major phase consists in a stage-1 Fe$^0$-GIC. Its crystalline structure has been described within the framework of a new model (hexagonal lattice), differing from the previous ones [5, 7]. Figure 9 summarizes the reduction process by showing the relative amounts of the different species at 4.2 K.

It should be noted that, for $x > 1$, the quantity of Fe$^{3+}$ is almost independent of the number of intercalated lithium atoms. This may be related to the island picture. In large islands the diffusion of lithium is long and the core cannot be reduced. Another explanation, not contradictory, should be the presence of defects in the parent compound, such as Daumas-Herold defects [20]. Figure 9 also shows that the reduction process begins with the reduction of the Fe$^{3+}$ ions to Fe$^{2+}$ ($x = 1$). The reduction to Fe$^0$ occurs at the expense of the Fe$^{2+}$ ions. For $x = 3$ two different kinds of Fe$^0$ exist. The first one is ordered at room temperature while the second one consists in small superparamagnetic particles.

The Mössbauer experiments and the magnetization measurements give complementary information and are in good agreement. X-ray analysis allows a determination of the $I_c$ parameter which is intermediate between pure graphite and first stage FeCl$_3$-GIC.

![Fig. 9. — Diagram summarizing the various concentrations of Fe$^{3+}$, Fe$^{2+}$ and Fe$^0$ as a function of the ratio Li/Fe = $x$ initially intercalated into the first stage FeCl$_3$-GIC. Right hatched area : Fe$^{3+}$, left hatched area : Fe$^{2+}$, dots : Fe$^{2+}$ (parasitic phase), horizontal bars : Fe$^0$, vertical bars : Fe$^0$.](image-url)
In addition neither the value of the hyperfine field measured on the Fe° sites nor its thermal variation nor the magnetic behavior look like those of bulk iron. We thus conclude that the Fe° islands are intercalated between the graphene layers. This is not in contradiction with the fact that they exhibit 3D magnetic properties.

In order to get more information about the local magnetic properties, Mössbauer experiments under an external magnetic field should be of great interest. The synthesis of a reduced Fe-GIC from HOPG (Highly Oriented Pyrolitic Graphite) should also be very useful and should give information about the anisotropy of the interactions. Some anisotropy of the Mössbauer absorption factor is expected for the intercalated species. Therefore, it should be possible to distinguish which species are really intercalated and which ones are not if they exist.

The problem of the stability of such compounds containing mixed Fe valencies remains open. The presence of Fe²⁺ and/or Fe³⁺ even though difficult to eliminate may be necessary to stabilize the Fe° layers via strong electron exchanges.

Acknowledgements.

R. Tur is thanked for having performed the magnetic measurements.

References

[1] Many references can be found in the literature concerning this point. We refer to a recent review paper: HEROLD A., Chemical Physics of Intercalation, NATO-ASI Series, M. P. Legrand and S. Flandrois Eds. (Plenum, New York) B 172 (1987) p. 3 and references therein.


